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Modulation of liquid holdup along a trickle bed reactor with periodic operation

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Abstract

Temporal variations of the liquid holdup in a mini-pilot scale trickle bed reactor cold-mockup, induced by an ON–OFF liquid flow modulation strategy of operation, are explored at different axial positions. The reactor is packed with porous beads of γ-Al_2O_3 and the liquid holdup is approximately estimated with a conductimetric technique, using probes that mimic the packing. The effects of the liquid and gas superficial velocities, the bed depth and the cycling parameters, cycle period and split, on the liquid holdup modulation are examined for a wide range of conditions. For slow and intermediate cycle periods, the liquid holdup time dependence observed during the dry period is represented by an exponential function. The characteristic value of the decay is correlated to the examined variables. The correlation allows reconstruction of the liquid holdup time dependence along the column.

Keywords: Trickle-bed reactors; Liquid flow modulation; Liquid holdup profiles; Periodic operation; Hydrodynamics

1. Introduction

In the last decade, the improvements in terms of production capacity and/or conversion that can be attained in trickle-bed reactor (TBR) performance by modulating the fluid flow rates have been highlighted, particularly for processes limited by the gas reactant mass transfer. Significant enhancements have been achieved employing relatively long cycle periods (Lange et al., 1994; Castellari and Haure, 1995; Khadilkar et al., 1999), in which the whole reactor works for some time in the wet cycle and some time in the dry cycle. In addition, successful results have also been obtained when working with intermediate to short cycle periods (Banchero et al., 2004; Muzen et al., 2005).

A thorough understanding of the underlying hydrodynamics plays an important role in the possibility of properly describing the phenomena taking place in a TBR under liquid flow modulation. Since many key design parameters are strongly affected by the liquid holdup and the liquid distribution over the particles, the impact of liquid flow modulation needs to be addressed in detail. So far, only a few contributions accounting for the influence of liquid flow modulation on the hydrodynamics of a TBR have been reported. Furthermore, the effect of non-steady state operation on liquid hold up, mass transfer coefficients and wetting efficiency has been scarcely investigated (Boelhouwer, 2001; Borremans et al., 2004; Giakoumakis et al., 2005). Only very recently, Trivizadakis et al. (2006) studied the imposed pulse characteristics employing porous spherical and cylindrical extrudates. These authors found that spherical packings hold significant advantages over cylindrical extrudates of comparable size. Besides, Aydin et al. (2006) assessed the effect of temperature and pressure on the slow-mode induced pulsing characteristics.

Results presented in the literature for liquid holdup time variations under periodic operation are still limited and mostly carried out for non-porous packings. Besides, the influence of the cycling parameters has been examined only within a narrow range. To further understand the hydrodynamic behavior of TBRs under liquid flow modulation, experiments in a broader range of conditions using porous packings are still required

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in order to select assumptions and design parameters for appropriately simulating reactor performance when a cycling strategy is used (Lange et al., 2004).

In the present contribution, a conductimetric technique is employed to obtain the time evolution of the liquid holdup in cycling experiments with a non-reacting system, consisting of a packed bed of inert γ-Al_2O_3 spherical particles, through which air and water flow cocurrently downwards. Instantaneous liquid holdups at several column depths are estimated without affecting the flow, by using probes that mimic the packing. Steady-state liquid holdups are also measured by residence time distribution experiments to calibrate the probes response. Then, the influences of gas and liquid velocities, bed depth and cycling parameters on the liquid holdup temporal modulation are addressed. For slow and intermediate cycle periods, the liquid holdup time dependence during the dry period is fitted to an exponential function. The characteristic value of the exponential decay is correlated to the examined operating variables, to reconstruct the liquid holdup time variation along the column under periodic operation.

2. Experimental

A schematic diagram of the experimental installation is shown in Fig. 1. The setup basically consists in an acrylic column of 7 cm inner diameter and a total height of 220 cm, provided with appropriate fluid feeding and regulating systems. The actual packed bed length is 150 cm. Some characteristics of the packing are given in Table 1. The tube to particle ratio is 22.6, well above the limit suggested in the literature to avoid wall effects; thus, channeling can be assumed negligible.

The packing is supported, at the bottom of the column, by a rigid stainless steel screen. Beneath the screen, there is a gas–liquid separator that vents the gas and returns the liquid to a reservoir. The liquid enters the column at the top, through a liquid distributor made in acrylic. The distributor has 18 holes of 1 mm diameter. Gas is provided from a compressor and goes into the column at the top, above the liquid distributor.

The liquid is fed from a reservoir with a peristaltic pump controlled by a rotor velocity regulator, which is commanded by a programmable logic controller (PLC). Gas flow rate is

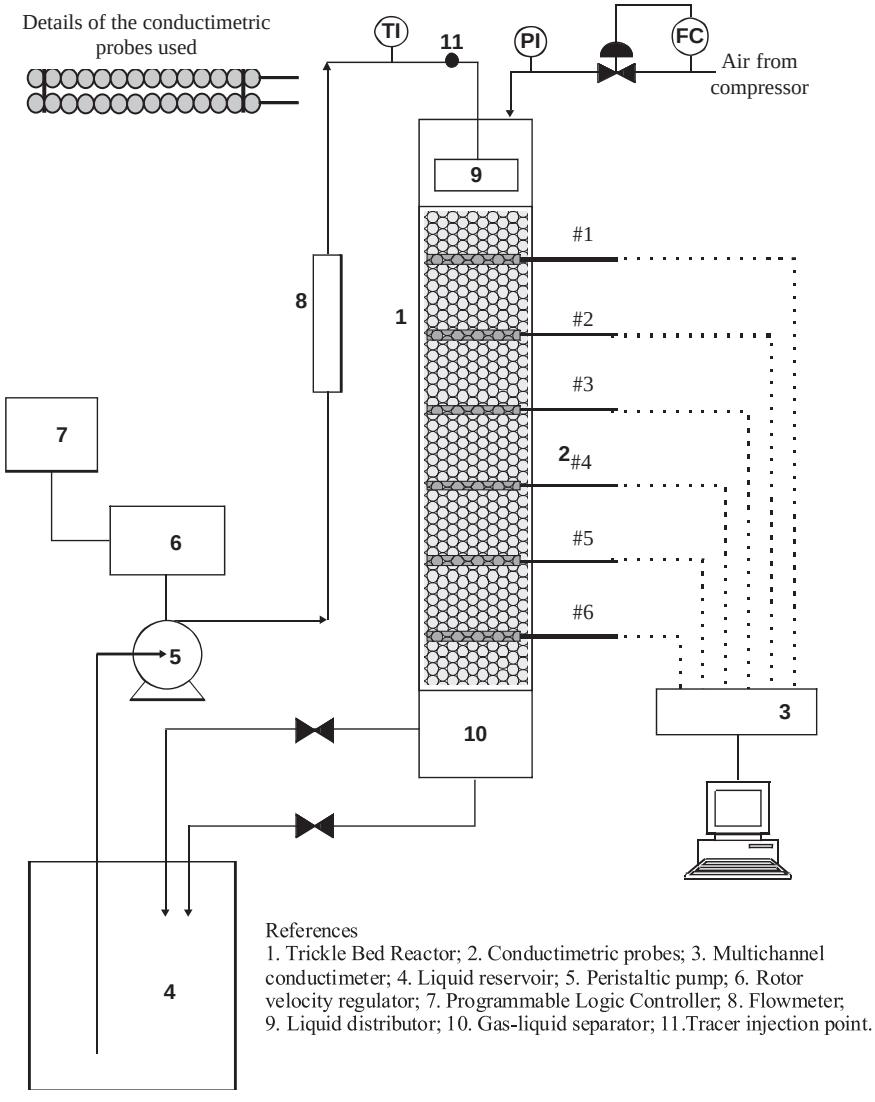

Fig. 1. Schematic diagram of the experimental setup.

Table 1
Characteristic of the packing used in the experiments

Particle	γ-Al_2O_3 spheres (A 2-5 Rhone Poulenc)
Mean particle diameter	3.1 mm
Bed void fraction	0.39
Apparent density	1400 kg/m^3
Specific area	250 m^2/g

Table 2
Examined operating conditions

Variable	Range
Temperature	$T = 20\,^{\circ}\mathrm{C}$ ($\pm 2\,^{\circ}\mathrm{C}$)
Pressure	Atmospheric
Liquid density	$\zeta_l = 997\,\mathrm{kg/m^3}$
Gas density	$\zeta_g = 1.2\,\mathrm{kg/m^3}$
Liquid viscosity	$\mu_l = 8.9 \times 10^{-4}\,\mathrm{Pa\,s}$
Gas viscosity	$\mu_g = 1.8 \times 10^{-5}\,\mathrm{Pa\,s}$
Surface tension	$\sigma_l = 0.073\,\mathrm{kg/s^2}$
Split	$0.17 < s < 1$
Cycle period	$5\,\mathrm{s} < P < 900\,\mathrm{s}$
Gas velocity	$u_g = 1.4\,\mathrm{cm\,s^{-1}}$ or $3.0\,\mathrm{cm\,s^{-1}}$
Liquid velocity	$0.15\,\mathrm{cm\,s^{-1}} < u_l < 0.89\,\mathrm{cm\,s^{-1}}$

measured by a flowmeter and regulated by means of a needle valve. Experiments are performed at atmospheric conditions. Air is used as the gas phase and distilled water or a 0.01 M KCl aqueous solution, as the liquid phase. The liquid temperature is continuously recorded.

The column is equipped with six conductimetric probes distributed at different heights (see #1 to #6 in Fig. 1). The first probe is located 22.5 cm from the top of the bed; the others are placed downstream, separated 23.5 cm in between. Each probe consists of two *lines* of 14 copper spheres, 4.6 mm diameter. The beads have been pierced across their diameter and strung onto a copper wire (see details in Fig. 1). Since the conductimetric probes are not too rigid, they have been manually located in the column as it was mounted and progressively filled.

All the experiments are performed under the trickle flow regime. Different gas and liquid velocities are examined, varying the split and the cycle period but always using an ON–OFF liquid flow modulation strategy. Explored operating conditions are listed in Table 2.

Before starting the experiments, the column was always flooded with liquid to ensure complete internal wetting of the particles and to achieve reproducible observations. Then, the selected gas flow rate was set, after adjusting the liquid flow rate to the one corresponding to the wet period considering the desired mean liquid velocity, $u_{l,\mathrm{mean}}$, and the cycling parameters. Afterwards, liquid flow modulation was imposed.

The liquid flow rate at the top of the column can be described almost as a square wave, since no dead time was noticed. The system was left at the desired cycling strategy during 10–20 min to reach an invariant cycling state before acquiring the signals. However, the invariant state was also checked directly from the measurements.

2.1. Conductance technique

The responses of the six probes are acquired simultaneously with a sampling frequency of 200 Hz using a multi-channel conductimeter. The excitation frequency of the conductimeter is 10 kHz, which allows assuming that the signal has negligible capacitance components. The acquisition is prolonged for periods long enough to get at least two complete invariant cycles. For short cycle periods, several complete cycles are recorded.

The response measured by each probe depends on the conductivity of the media contained within the two lines of tied copper spheres. That conductivity is strongly related to the amount of liquid contained and would therefore provide an approximate way of estimating the liquid holdup of the flowing liquid. Even though the conductance measured would not correspond to the one induced by a cross sectional average of the liquid at a given height, it results from the average of a significantly long portion, since the total length of each probe is almost the column diameter.

Measured conductances are normalized to the ones obtained for the flooded bed. When the column is flooded, the space between electrodes is filled with the liquid electrolyte used, and the instantaneous conductance measured follows an expression given by (Tsochatzidis et al., 1992):

$$\psi_{i,f} = \gamma_l A/L, \tag{1}$$

where γ_l is the conductivity of the liquid and A/L, the effective cell constant for a given electrode. When the gas and the liquid are flowing through the bed, the conductance measured by the probes would be given by

$$\psi_i = \gamma_l \kappa A/L, \tag{2}$$

where κ is closely related to the liquid saturation; i.e., the ratio between the liquid holdup and the bed porosity. κ would approximately represent a factor of the fraction of the cell area effectively wetted by the liquid and forming a gate between electrodes. It is experimentally obtained as the measured conductance normalized by the conductance of the flooded electrode.

To calibrate the normalized conductance, κ, against liquid holdup measurements, residence time distribution (RTD) experiments are carried out to evaluate the liquid holdups. Air and distilled water are used as model fluids for these experiments. A tracer pulse (0.05 M KCl solution) is injected into the distilled water flow that enters the bed. Downstream, the tracer concentration is continuously recorded employing the conductance probes inserted in the bed, to get RTD curves at different axial positions. Representative RTD signals for each electrode are shown in Fig. 2. Assuming that the tracer concentration is already well distributed all over the column section for the probes selected for the calculations, the mean liquid residence time is evaluated from the first moment of the RTD curves. Since the injection of a perfect pulse is hardly achievable, the tracer concentration is monitored at two points within the test section, provided the injection point is placed upstream. One of the probes close to the column entrance is considered as

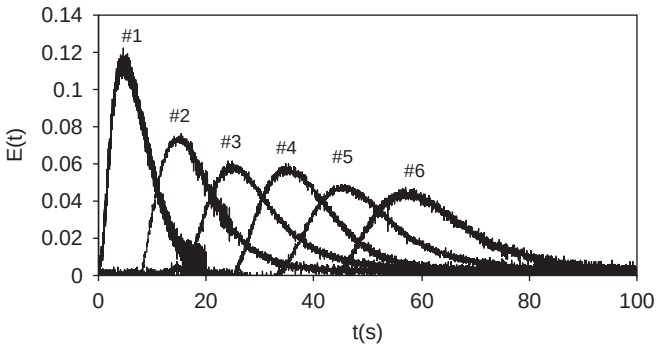

Fig. 2. Residence time distribution (RTD) curves obtained by each electrode. Operating conditions: $u_l = 0.38\,\mathrm{cm/s}$; $u_g = 3.0\,\mathrm{cm/s}$.

the input and one close to the outlet as the output, defining an open–open vessel. From the mean liquid residence time, the liquid holdup is calculated for given gas and liquid velocities and contrasted to the normalized conductance measured by each probe.

Liquid holdups are evaluated from the RTDs for different reactor lengths. Electrode #1 is always considered as the input, while electrodes #4, #5 and #6 are used as outputs to have reasonable long test sections. Each value is determined at least three times; reproducibility is within ±2%. Since the calculated liquid holdup does not vary significantly along the bed, within the range of operating conditions tested, liquid holdups calculated using the longest test section, between electrodes #1 and #6, are considered.

Further details on the experimental installation and the procedures used can be found in Ayude (2006).

3. Results

3.1. Liquid holdup in steady state experiments

Measured liquid holdups under steady-state operation are represented in Fig. 3 as a function of the superficial liquid velocity, at different superficial gas velocities. As expected, liquid holdup increases with increasing liquid flow rate and decreases with increasing gas flow rate. These results fit the following relationship with respect to Re_l and Re_g:

$$\varepsilon_l = \varepsilon_{ls} + 0.046.Re_l^{0.49}.Re_g^{-0.10}, \tag{3}$$

where ε_{ls} is the static holdup (0.047) calculated using the correlation of Sáez and Carbonell (1985).

Results are compared to correlations reported in the literature. The general correlation of Iliuta et al. (1999) based on an extensive database of liquid holdup measurements in TBRs taken from the literature and using a combination of artificial neural network and dimensional analysis, satisfactorily predicts the obtained results. Taking into account the good fit of the experimental results to the correlation of Iliuta et al. (1999) and that this correlation was developed based on an extensive database, its ability to extrapolate results for conditions different from those used for the steady-state experiments is expected to be satisfactory. Then, this general functionality is considered to establish calibration relationships for estimating liquid holdup values from results obtained with liquid flow modulation.

3.2. Conductance probes calibration

With the purpose of estimating the instantaneous liquid holdup for periodic operation at different column heights, the liquid holdups measured through the RTD experiments are related to the normalized conductance, κ, to determine appropriate calibration relationships.

The time variation of κ tends to asymptotic values for prolonged wet and dry periods. Fig. 4 compares those asymptotic values, computed as an average of the values measured for all the electrodes, to the ones obtained for steady-state operation. Asymptotic normalized conductances are quite similar to those measured under steady-state conditions at a liquid velocity equal to the one during the wet cycle. For low liquid velocities, small differences are apparent, likely due to the partial wetting of the solid and the higher probability for the liquid films to take new routes during periodic operation. The average asymptotic normalized conductance measured during prolonged dry cycles always oscillates around the same value for different splits, indicating that it could be related to the static liquid holdup. As a whole, these results suggest that, if periods are long enough, the asymptotic averageconductance measured for experiments with liquid flow modulation approach those of the corresponding steady-state condition.

Fig. 5 illustrates, as an example, the relationship between the experimental liquid holdups measured using RTD and the normalized conductance measured under steady-state conditions for one of the electrodes. Liquid holdups predicted by the correlation of Iliuta et al. (1999) are also shown in the figure.

It is important in this case to be able to extrapolate outside the range for which the liquid holdup under steady-state conditions was experimentally obtained, since holdup values even as low as the static holdup are likely to characterize the dry period during experiments with ON–OFF liquid flow modulation. Then, the static liquid holdup calculated from the correlation of Sáez and Carbonell (1985) is also included in the calibration and it is related to the average asymptotic values of κ obtained for prolonged dry periods (see Fig. 4, $\kappa_{\mathrm{av},nw}$). Fig. 5 shows that a linear dependence is found between κ and the liquid holdups for electrode #6 and $u_g = 3.0\,\mathrm{cm/s}$. A similar trend is found for the six electrodes within the examined range of fluids velocities (Ayude, 2006). Even though the liquid holdups determined with the RTD experiments correspond to a mean value for the whole testing section, and therefore should be contrasted to a value of κ averaged along the column, different linear relationships have been found for each probe likely due to small local variations in liquid holdups. Hence, a different calibration equation is considered for eachelectrode instead of a single expression for all. The fitting to a straight line is good for all the electrodes, indicating that a linear relationship between the normalized conductance and the liquid holdup exists in the

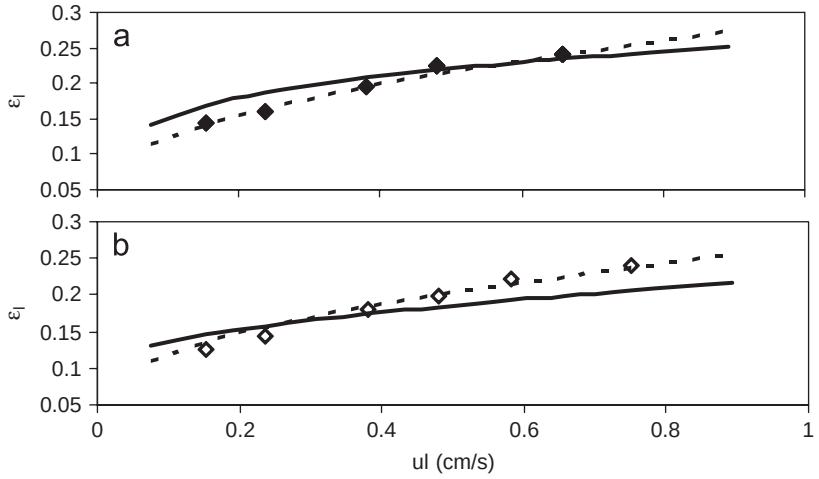

Fig. 3. Comparison of the liquid holdups obtained from the tracer experiments with those predicted by Eq. (3) (- - -) and by the correlation of Iliuta et al. (1999) (—). (a) $u_g = 1.4\,\mathrm{cm/s}$; (b) $u_g = 3.0\,\mathrm{cm/s}$.

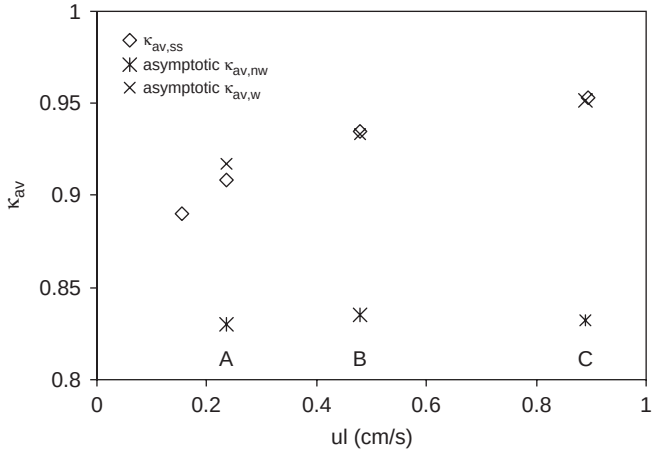

Fig. 4. Influence of the liquid superficial velocity on the average conductance, κ_{av}, measured for steady-state conditions and the average of the asymptotic values attained during cycling conditions. $u_g = 3.0\,\mathrm{cm/s}$, $P = 360\,\mathrm{s}$, $u_{l,\mathrm{mean}} = 0.15\,\mathrm{cm/s}$. (A) $s = 0.65$, (B) $s = 0.32$, (C) $s = 0.17$.

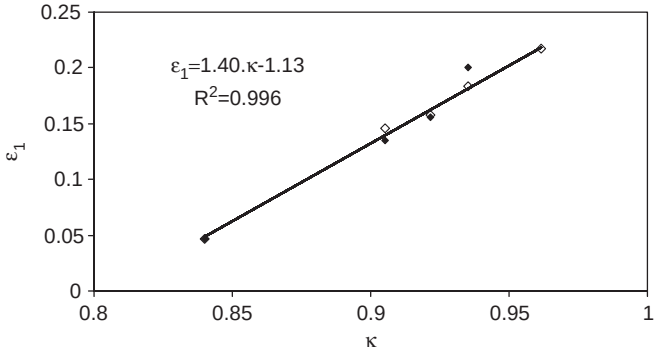

Fig. 5. Comparison of the developed calibration trend (—) with liquid holdups predicted by the correlation of Iliuta et al. (1999) (♦) and with the experimental data (♦). Experimental normalized conductance corresponding to the static liquid holdup is calculated as the average of those shown in Fig. 3 for prolonged dry periods of the cycle. Electrode #6, $u_g = 3.0\,\mathrm{cm/s}$.

whole range. Then, the instantaneous normalized conductances can be converted into liquid holdups to within a reasonable error.

3.3. Instantaneous liquid holdup under cycling

ON–OFF cycling experiments were performed. Two characteristic parameters define ON–OFF liquid flow modulation: the cycle period (P) and the split (s). The cycle period is the total time required to complete one wet and one dry period; i.e., is the time elapsed between two identical instants in the feeding dynamic. The split is defined as the ratio between the time spent during the wet period, to the whole cycle period. Representative instantaneous liquid holdup traces of the six conductimetric probes are presented in Figs. 6 and 7 for experiments under periodic operation. The liquid flow modulation is reflected in the shape of the curves, which is significantly distorted along the column and strongly depends on the cycling parameters.

For very short cycle periods (Fig. 6a), the liquid flow modulation is reflected only in the top of the column. For the electrodes inserted downstream, the measured normalized conductance is almost constant, leading to a constant value for the liquid holdup. As the cycle period is increased, modulation starts to be reflected all over the column bed. However, for a cycle period of 30 s, the amplitude is still strongly attenuated along the column and the differences between the shape in the top and the bottom depend on the split (see Figs. 6b and 7a). For these conditions a large influence of the bed depth is observed.

For long and intermediate cycle periods (Figs. 6c–d and 7b), a liquid front is normally established very fast as the wet period starts. On the contrary, when the liquid flow is interrupted, the liquid holdup decreases slowly and progressively. The liquid holdups tend to asymptotic values both for the wet and dry cycles and the possibility of attaining these asymptotic values depends on the split (compare Figs. 6d and 7b). The duration of the plateau attained during the wet period

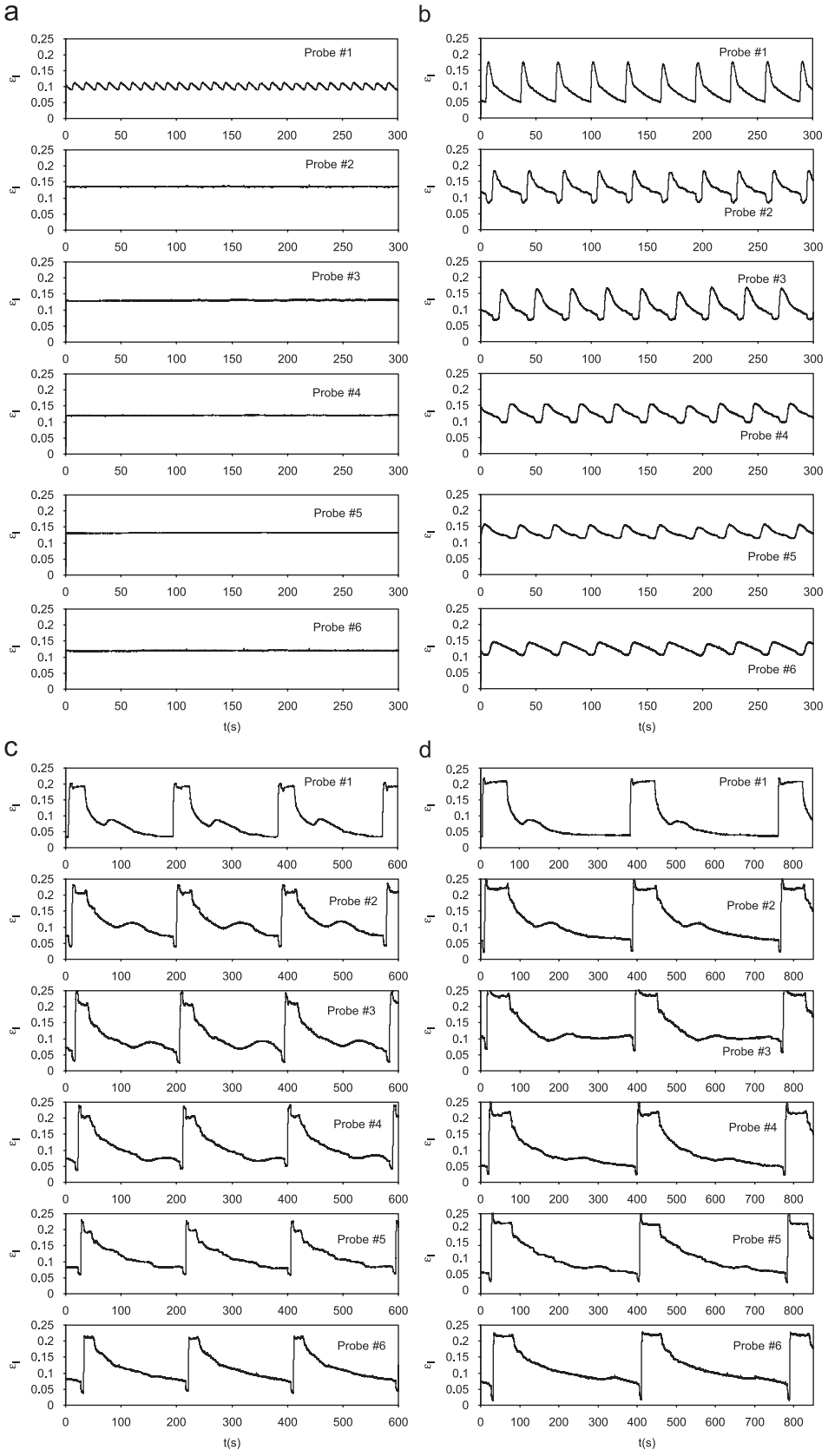

Fig. 6. Estimated instantaneous liquid holdup vs. time at different column heights. Cycling conditions: $s = 0.17$; $u_{l,\text{mean}} = 0.15\,\text{cm/s}$; $u_g = 3.0\,\text{cm/s}$; $\varepsilon_{L,\text{mean}} = 0.146$. (a) $P = 10\,\text{s}$; (b) $P = 30\,\text{s}$; (c) $P = 180\,\text{s}$; (d) $P = 360\,\text{s}$.

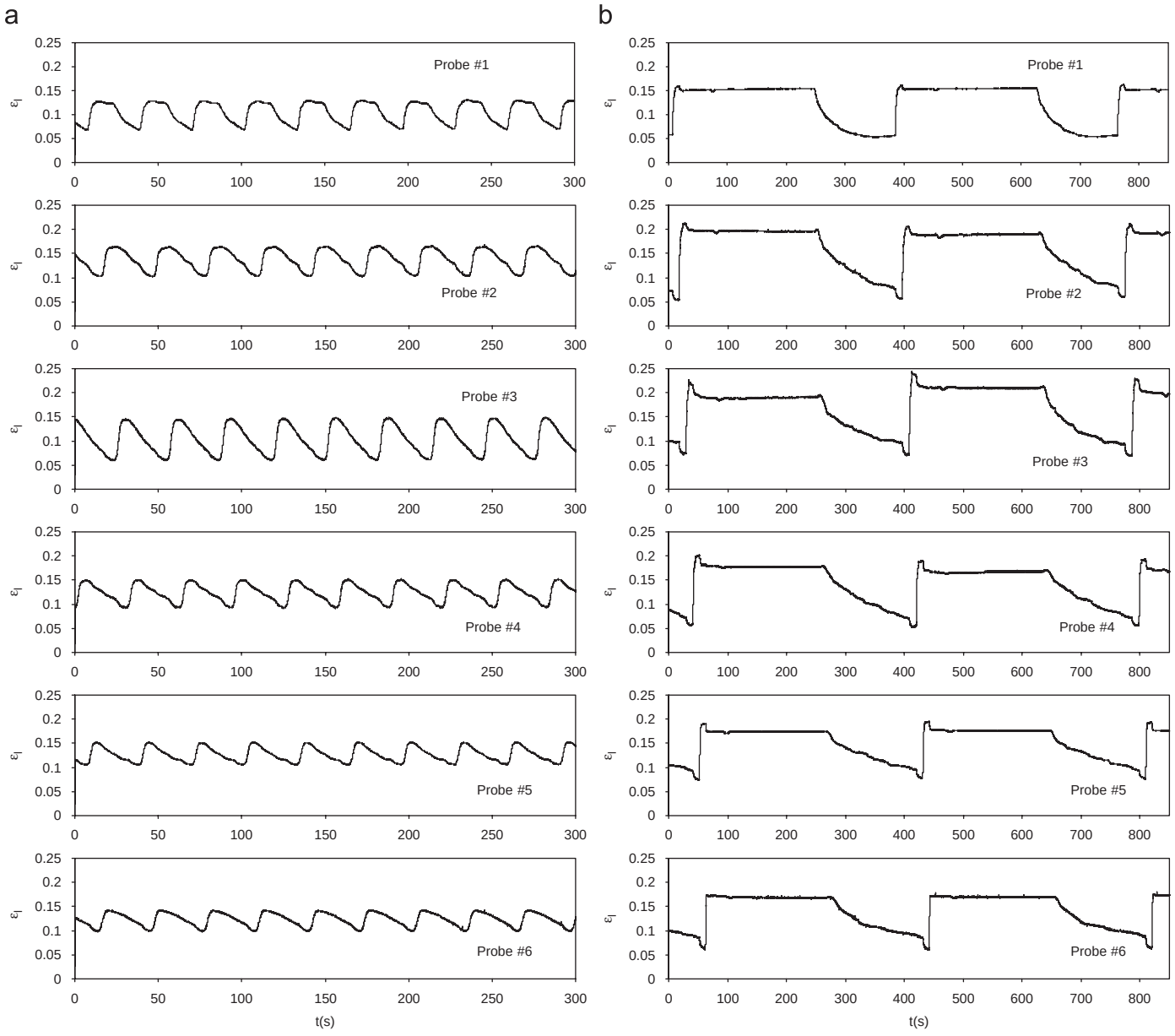

Fig. 7. Estimated instantaneous liquid holdup vs. time at different column heights. Cycling conditions: $s = 0.65$; $u_{l,\text{mean}} = 0.15\,\text{cm/s}$; $u_g = 3.0\,\text{cm/s}$; $\varepsilon_{L,\text{mean}} = 0.146$. (a) $P = 30\,\text{s}$; (b) $P = 360\,\text{s}$.

slightly decreases along the bed, in agreement with observations reported by Boelhouwer (2001). Also, the time dependence of the liquid holdup during the dry period suggests that the liquid waves decay by leaving liquid behind them. The modulation is observed in the six probes with almost the same frequency and the distortion induced by bed depth is less evident.

It is worthy to note that, for a given set of parameters, i.e., bed depth, gas velocity and mean liquid velocity, the time average liquid holdup ($\varepsilon_{l,av}$) remains almost constant independent of the cycling parameters (Ayude, 2006). In all cases, the mean liquid holdup under ON–OFF liquid flow modulation is slightly lower than the one obtained at steady state at the corresponding mean liquid velocity. For higher mean liquid velocities, higher liquid holdups are attained during the wet cycle. Therefore, the liquid holdup during the dry cycle is also higher and longer dry cycle periods are required to reach the static liquid holdup.

The time at which the probe gets in contact to a new wet period of the cycle is displaced along the column. Since the conductance change observed is very sharp, the delay time required for the perturbation to move between two different electrodes can be easily determined from the experiments. The pulse velocity (u_p), as defined by Boelhouwer (2001), can be evaluated dividing the distance between probes (23.5 cm) by the corresponding time delay evaluated in this way. Pulse velocities along the bed are calculated considering consecutive electrodes for different superficial gas and liquid velocities. They are apparently independent of the cycling parameters. Results shown in Fig. 8 indicate that the pulse velocity remains almost

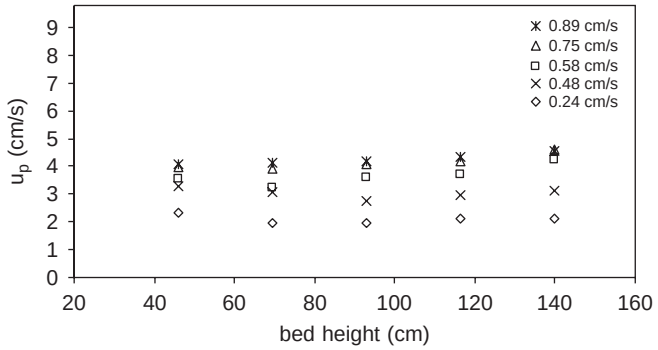

Fig. 8. Pulse velocity as a function of the reactor bed length for different superficial liquid velocities during the wet period. $u_g = 3.0\,\mathrm{cm/s}$.

constant along the column. Pulse velocities increase with superficial liquid and gas velocities (not shown in the figure) and the influence of the liquid velocity is more intense, in agreement with trends reported by Giakoumakis et al. (2005).

3.4. Effect of cycle period and split

The influence of the cycle period and split on characteristic values that the liquid holdup attains during each period of the cycle is analyzed in Fig. 9. For cycle periods in which asymptotic values of the liquid holdup are attained within the cycle, such value is computed. On the other hand, for the cycle periods where no plateau is clearly identified, the maximum and the minimum liquid holdups attained during a whole cycle period are assessed. The ratios between the characteristic values of liquid holdup for the wet ($\varepsilon_{l,w}$) and the dry ($\varepsilon_{l,nw}$) periods of the cycle to the one for steady state at the mean liquid velocity ($\varepsilon_{l,\mathrm{mean}}$) are calculated and represented as a function of the cycle period in the figures. The liquid holdup measured for the corresponding steady state at the liquid velocity for the wet cycle and the static liquid holdup, are also shown on the same basis.

Generally, the evaluated characteristic liquid holdup for each period of the cycle does not change strongly among the different electrodes distributed along the column. This is particularly true for the wet period of the cycle; for the dry period, the liquid holdup attained is higher as the bed depth increases. For the majority of the experimental conditions examined, there is an excess liquid holdup over the static liquid holdup, mainly in the lower part of the column.

Giakoumakis et al. (2005) suggested that the transition between slow and fast modulation could be estimated considering the reactor length, the cycle period and the pulse velocity. If the cycle period is less than the ratio of the reactor length over the pulse velocity, the modulation would be fast. Hence, for the present bed length of 150 cm, the cycle period that would provide a limit between slow and fast modulation depends on the split for a given mean liquid velocity, as the pulse velocity depends on the split. Transition limits are shown in Fig. 9.

For intermediate and short cycle periods, the liquid holdup during cycling departs from the steady state liquid holdup both during the dry and the wet period. The limit liquid holdup during the dry cycle tends to increase as the cycle period decreases, while the one during the wet cycle tends to decrease. The transient behavior is relatively more important and a "quasi steady state" liquid holdup is hardly accomplished for any combination of cycling parameters.

For very short cycle periods, the liquid holdups during the wet and dry cycle approach each other, particularly as the bed depth increases. In the lower part of the column, liquid pulses are not clearly distinguished in the traces, not even after magnifying the scale. According to Boelhouwer (2001), the pulses are not stable and disappear.

The previous analysis suggests different qualitative limits between slow and fast cycling. Slow cycling can be defined as the one that leads to asymptotic values of the liquid holdup comparable to those of the steady state at similar velocities. In contrast, fast modulation can be defined as the one that leads to similar limit liquid holdups for the wet and dry periods of the cycle, as in the case of cycle periods of 10 s and less in this system. A new "pseudo steady-state" condition is apparently reached, with a characteristic average liquid holdup generally lower than the one measured at steady state with the mean liquid velocity.

For intermediate cycle periods, differences between the liquid holdups during each period of the cycle are still significant. In addition, the asymptotic values are not reached. The behavior of the liquid holdup is eminently transient and approximations to pseudo steady-state behaviors may probably not describe properly the situation to within a negligible degree of error.

Results suggest that limits between the different types of liquid flow modulation depend on the different factors examined, split, gas and mean liquid velocity. The transition region between slow and fast modulation, i.e., the intermediate cycle periods, can then be broad.

3.5. Pulse intensity

To quantify the variations between peaks and troughs, Giakoumakis et al. (2005) defined the liquid pulse intensity as the ratio between the standard deviation of liquid holdup and the time average liquid holdup:

$$I_p = \frac{\varepsilon_{l,sd}}{\varepsilon_{l,av}}. \tag{4}$$

The pulse intensity characterizes pulse attenuations along the bed. In general, it increases with cycle period, as shown in Fig. 10. For long cycle periods, pulses remain quite stable along the bed, especially for higher splits. For smaller splits, the influence of bed depth is strong, the pulse intensity decreases along the bed but the values are always high.

As long as the cycle period decreases, the pulse intensity diminishes and pulse relaxation along the bed is evidenced. The influence seems to be more marked as the split decreases. For very short periods, pulse intensity tends to zero and thus, pulses fade away in the lower part of the column whatever is the split (note the magnification of the scale in Fig. 10d). This is in agreement with observations of Boelhouwer (2001)

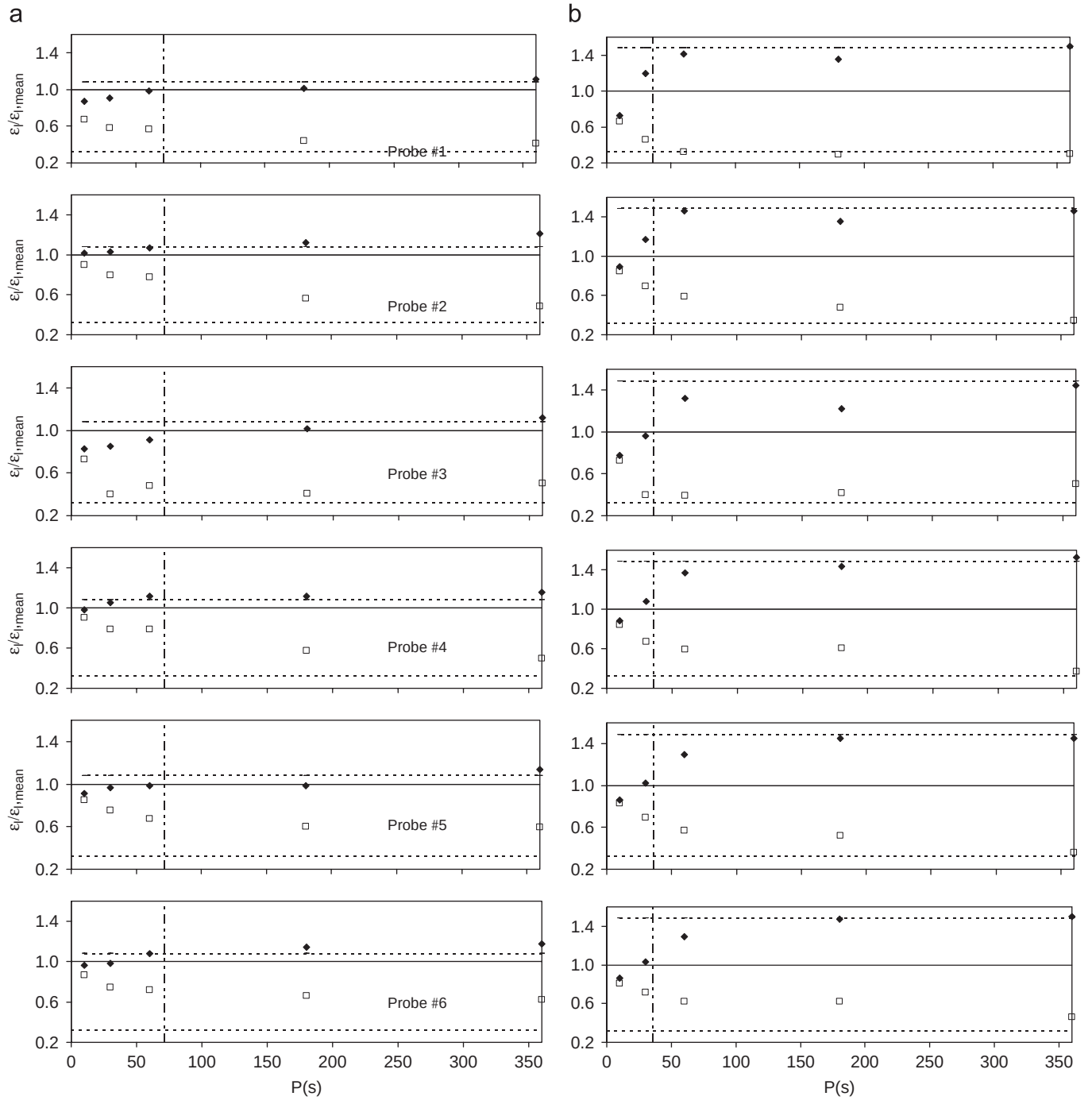

Fig. 9. Effect of cycle period on asymptotic liquid holdups for both cycles at different column heights. (⧫) wet period of the cycle (□) dry period of the cycle. $u_{l,\mathrm{mean}} = 0.15\,\mathrm{cm/s}$; $u_g = 3.0\,\mathrm{cm/s}$. (a) $s = 0.65$; (b) $s = 0.17$. (- - -) values measured at steady state; (—-·-—) limit between slow and fast modulation defined by Giakoumakis et al. (2005).

for non-porous packings. Even if the pulse intensity tends to zero and the holdup traces do not show a waving behavior, the instabilities in the liquid films may still have influence from the liquid feed perturbations, which are not reflected visually in the holdup traces.

As it was already mentioned, liquid holdup decreases with superficial gas velocity. Additionally, pulse intensity increases when the superficial gas velocity decreases, the highest possible being the one attained at $u_g = 0$ (not shown in the figures). For cycle periods greater than 180 s, this trend is noticeable, particularly for the split $s = 0.17$. As the cycle period decreases, the influence disappears.

Fig. 11 points out that the mean liquid velocity has a negligible effect on the pulse intensity for almost all the examined operating conditions, except for the lowest cycle period shown. This trend is attributed to the low interaction between liquid and gas within the examined experimental conditions.

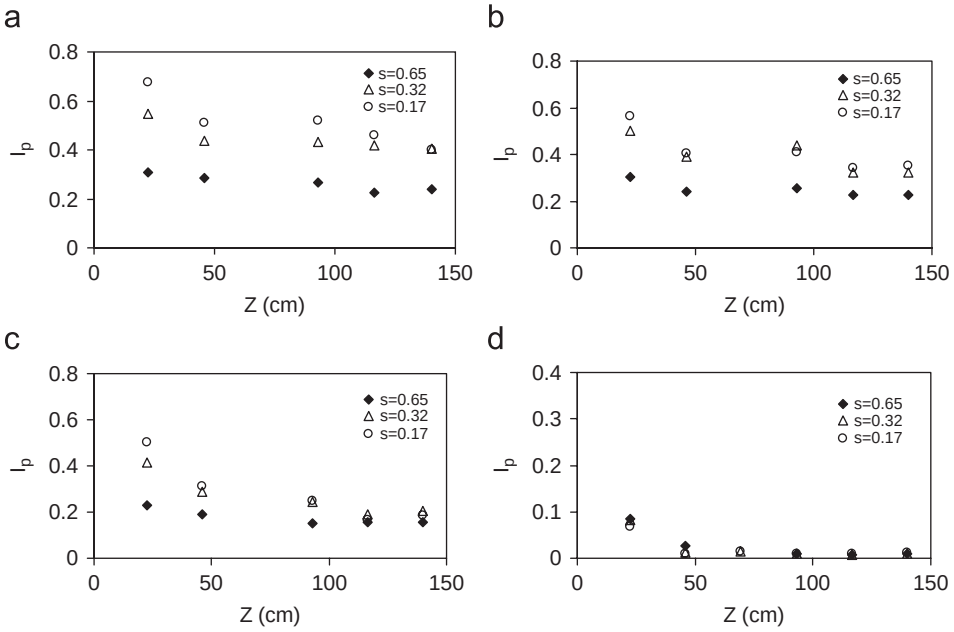

Fig. 10. Pulse intensity as a function of bed length for different splits. $u_{l,\text{mean}} = 0.15\,\text{cm/s}$; $u_g = 3\,\text{cm/s}$ (a) $P = 360\,\text{s}$; (b) $P = 180\,\text{s}$; (c) $P = 60\,\text{s}$; (d) $P = 10\,\text{s}$.

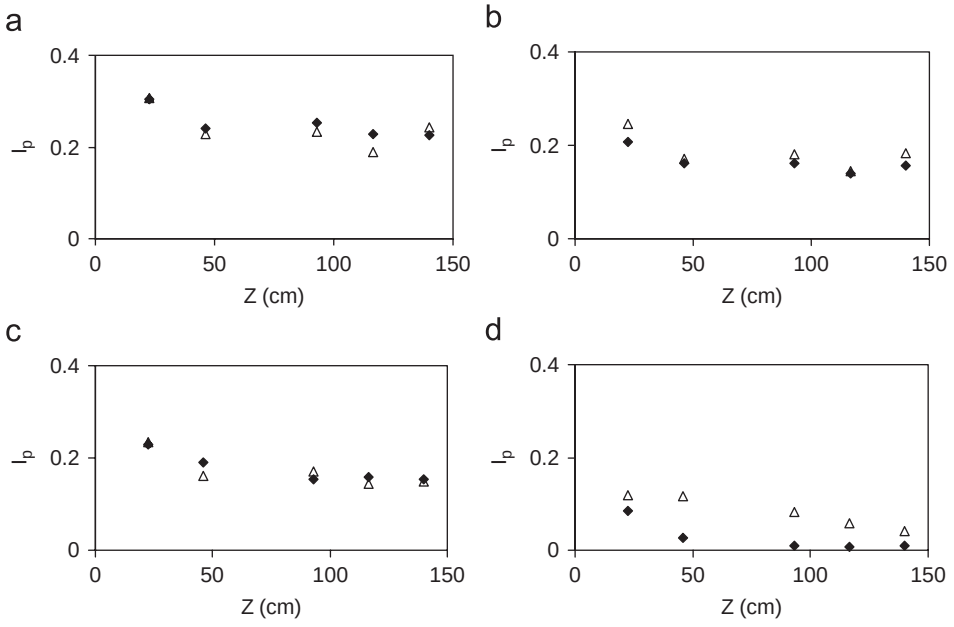

Fig. 11. Pulse intensity as a function of bed length for different splits and mean superficial liquid velocities, $u_g = 3.0\,\text{cm/s}$, $s = 0.65$. (a) $P = 180\,\text{s}$; (b) $P = 100\,\text{s}$; (c) $P = 60\,\text{s}$; (d) $P = 10\,\text{s}$. (♦) $u_{l,\text{mean}} = 0.15\,\text{cm/s}$; ($\Delta$) $u_{l,\text{mean}} = 0.38\,\text{cm/s}$.

At very short cycle periods and for a split of 0.65, a higher mean liquid velocity improves the stability of the liquid waves along the column. This effect has also been observed for non porous packings by Giakoumakis et al. (2005) for cycle periods in the range of 4–8 s and at higher gas flow rates than those considered in the present work. These authors related this fact to a relatively higher interstitial gas velocity, which tends to homogenize liquid holdup variations along the column. The conditions examined in this work are far from pulsing flow. Hence, the effect in this case should not be related to the interstitial gas velocity. Moreover, larger pulse intensities are found for the lower gas velocity at the same mean liquid velocity (not included in the figure). For conditions shown in Fig. 11d, the increase in pulse intensity due to a higher mean liquid velocity in the γ-Al_2O_3 bed may likely arise from an increased liquid-solid interaction and liquid film waving behavior due to inertia, which is more important for thicker liquid films.

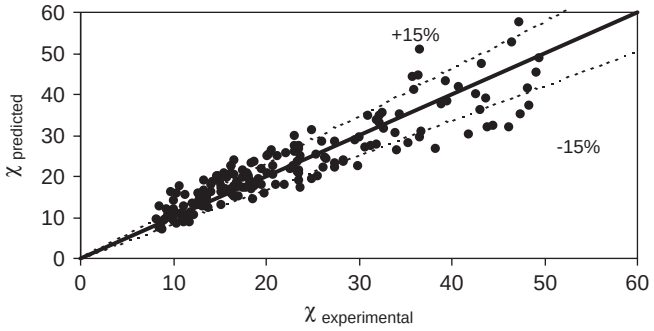

Fig. 12. Comparison among the values of the parameter χ that characterizes the liquid holdup decay during the dry period of the cycle estimated by fitting the experimental data and by using Eq. (5).

3.6. Reconstruction of the liquid holdup time evolution for intermediate and long cycle periods

To develop a methodology for estimating the time variation of the liquid holdup along the column during slow and intermediate ON–OFF liquid flow modulation, so as to use this information for modeling the behavior of a trickle bed reactor, a simple approach is presented. The approach is focused to represent the liquid holdup time profile during the time lag subsequent to the liquid flow interruption, since the transient behavior of the liquid holdup is mainly during the dry period of the cycle; the increase in liquid holdup during the wet cycle is almost instantaneous. When the liquid flow is halted, the signal decays in an almost exponential way. Hence, the time variation of ε_l during the dry cycle was fitted to the following first order exponential decay expression:

$$\varepsilon_{l,nw} = \upsilon_0.\mathrm{e}^{(-t/\chi)} + \upsilon_1, \tag{5}$$

where t is the time during the dry cycle. υ_1 is the asymptotic liquid holdup value attained for very long dry periods and $(\upsilon_0+\upsilon_1)$ corresponds to the liquid holdup value achieved during the wet cycle. The characteristic parameter χ is related to the rate of decay of the liquid holdup after liquid flow interruption. The lower is χ, the more abrupt is the drop of ε_l with time.

Considering that the liquid holdup decay during the dry period of the cycle depends on the mean liquid velocity, the superficial gas velocity, the cycle period, the split, and the bed length, the characteristic parameter χ is correlated by

$$\chi = 545\left(\frac{z}{L}\right)^{0.49}\left(\frac{P u_{l,\mathrm{mean}}}{L}\right)^{0.39} s^{0.18} Re_{l,\mathrm{mean}}^{-0.92} Re_g^{-0.21}, \tag{6}$$

where L is the total bed length; $Re_{l,\mathrm{mean}}$ is based on the mean liquid velocity (see the notation) and χ is expressed in seconds. This correlation is valid for cycle periods between 60 and 900 s, since asymptotic values during both periods of the cycle were attained for these conditions with the three tested splits. Fig. 12 compares values of χ estimated with Eq. (6) to the experimental ones. The mean relative error is 15%.

Developed correlation is used to analyze the influence of the different factors examined on the decay rate of the liquid holdup during the dry period of the cycle, as it is shown in Fig. 13.

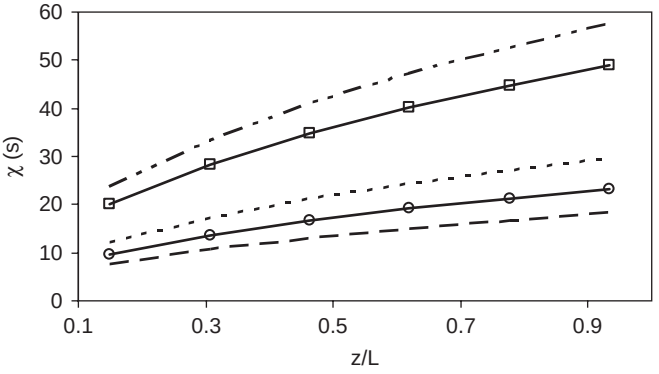

Fig. 13. Characteristic parameter χ as a function of bed length. (—□—) $P = 360$ s, $s = 0.65$, $u_g = 3.0$ cm/s, $u_{l,\mathrm{mean}} = 0.15$ cm/s; (- - -) $P = 100$ s, $s = 0.65$, $u_g = 3.0$ cm/s, $u_{l,\mathrm{mean}} = 0.15$ cm/s; (—Θ—) $P = 100$ s, $s = 0.17$, $u_g = 3.0$ cm/s, $u_{l,\mathrm{mean}} = 0.15$ cm/s; (— — —) $P = 360$ s, $s = 0.65$, $u_g = 1.4$ cm/s, $u_{l,\mathrm{mean}} = 0.15$ cm/s; (– –) $P = 100$ s, $s = 0.65$, $u_g = 3.0$ cm/s, $u_{l,\mathrm{mean}} = 0.38$ cm/s.

Liquid drainage rate tends to decrease along the bed, especially for long cycle periods and low gas and liquid mean velocities. This is related to the decrease in pulse intensity along the bed for intermediate to long cycle periods.

At a given cycle period, liquid holdup during the dry cycle decreases faster for lower splits (that is, for a higher $u_{l,w}$). For cycling experiments performed with higher superficial gas velocities, remarkably higher decay rates are found. This is probably due to an increased gas–liquid interaction; i.e., a more intense effect of the gas-drag on the liquid draining from the column.

The liquid holdup decreases faster when working with a higher mean liquid velocity. Larger mean liquid velocities imply larger velocities during the wet period, with the associated inertial effects that are reflected in a sharper draining velocity when the liquid feed is interrupted. All the effects are more evident for longer cycle periods.

The liquid holdup decay during the dry period of the cycle, for intermediate and long cycle periods, can be approximately reconstructed using χ estimated from Eq. (6) as

$$\frac{\varepsilon_{l,nw}}{\varepsilon_{l,w}} = \frac{\varepsilon_{ls}}{\varepsilon_{l,w}} + \left(1 - \frac{\varepsilon_{ls}}{\varepsilon_{l,w}}\right)\mathrm{e}^{(-t/\chi)}. \tag{7}$$

Liquid holdup during the wet period, $\varepsilon_{l,w}$, can be taken as the liquid holdup characteristic of steady state operation at a liquid velocity equal to $u_{l,w}=u_{l,\mathrm{mean}}/s$. This value has been estimated using the correlation of Iliuta et al. (1999). The same $\varepsilon_{l,w}$ can be used for the whole bed length. The static liquid holdup has been estimated by the correlation of Sáez and Carbonell (1985).

4. Conclusions

Liquid holdup time variations induced by ON–OFF liquid flow modulation vary significantly along the column. The waving character of the liquid holdup measured close to the column top is attenuated along the bed. The degree of attenuation

depends on the gas and liquid velocities and the cycling parameters, cycle period and split.

From the analysis of characteristic liquid holdups attained during the wet and dry periods of the cycle from a square wave input, three different regions can be distinguished for the ON–OFF liquid flow modulation strategy of operation:

Slow modulation: The holdup traces could be roughly assimilated to a deformed square wave and remain similar along the column, except for differences in the liquid holdup decay during the dry period of the cycle and for a slight decrease in the width of the plateau attained during the wet period.

Intermediate modulation: The decrease in pulse intensities along the bed is significant. The holdup traces never look like a square wave, except for the closest position to the column entrance and for the highest split tested ($s = 0.65$). The holdup traces resemble a saw-teeth wave or a triangular wave and the amplitude markedly decrease along the column. The transition limit suggested by Giakoumakis et al. (2005) falls always within this region, although it is closer to the zone defined as slow liquid flow modulation for high splits, and to the zone defined as fast liquid flow modulation for low splits.

Fast modulation: Cycle periods of 10 s or less in this system, characterized by similar limit values of liquid holdups attained for both the wet and dry period of the cycle. The waving trace of the liquid holdup is appreciated only in the upper part of the column, and the amplitude of the waves tends to zero in the lowest part, resembling a new "pseudo steady-state". The pulse intensity depends particularly on the mean liquid velocity. For a low mean liquid velocity, the pulse intensities fall to zero everywhere in the column except close to the entrance. For a higher mean liquid velocity, the pulse intensities are significantly different from zero and decrease more progressively along the column.

To incorporate the measured hydrodynamic information into models aimed at representing TBRs behavior under ON–OFF liquid flow slow modulation, the transient behavior of the liquid holdup, which is found to be restricted mostly to the dry period of the cycle, is fitted to a first-order exponential decay function. The characteristic parameter, χ, that describes the holdup decay is correlated with the variables that affect the decay, the gas and the liquid velocities, the cycle period, the split and the bed depth. A procedure to reconstruct the liquid holdup time variation during the dry period is proposed.

Notation

A/L	effective cell constant, m
d_p	particle diameter, m
I_p	pulse intensity
L	total bed length, m
P	dimensional cycle period, s
Re	Reynolds number ($=\zeta.u.d_p/\mu$)
s	split
t	time, s
u	velocity, m s^{-1}
u_p	pulse velocity, m s^{-1}
z	bed length, m

Greek letters

γ_l	liquid conductivity, S cm^{-1}
ε_l	total liquid holdup
ε_{ls}	static liquidholdup
ζ	density, kg m^{-3}
κ	normalized conductivity
μ	viscosity, Pa s
χ	parameter that characterizes the liquid holdup decay, s
ψ_i	instantaneous conductance, S

Subscripts

av	average
f	flooded electrode
g	gas
l	liquid
mean	referred to the mean liquid velocity
nw	dry (non-wet) cycle
w	wet cycle

Acronyms

RTD	residence time distribution
TBR	trickle bed reactor
PLC	programmable logic controller

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References

Aydin, B., Fries, D., Lange, R., Larachi, F., 2006. Slow-mode induced pulsing in trickle-bed reactors at elevated temperature. A.I.Ch.E. 52, 3891–3901.

Ayude, M.A., 2006. Periodic operation of trickle-bed reactors: effect on catalytic wet oxidation of organic pollutants. Tesis de Doctorado, Universidad Nacional de Buenos Aires, Argentina.

Banchero, M., Manna, L., Sicardi, S., Ferri, A., 2004. Experimental investigation of fast-mode liquid modulation in a trickle-bed reactor. Chemical Engineering Science 59, 4149–4154.

Boelhouwer, J.G., 2001. Nonsteady operation of trickle-bed reactors: hydrodynamics, mass and heat transfer. Ph.D. Thesis, Technische Universiteit Eindhoven, The Netherlands.

Borremans, D., Rode, S., Wild, G., 2004. Liquid flow distribution and particle-fluid heat transfer in trickle bed reactors: the influence of periodic operation. Chemical Engineering Process 43, 1403–1410.

Castellari, A.T., Haure, P.M., 1995. Experimental study of the periodic operation of a trickle-bed reactor. A.I.Ch.E. Journal 41, 1593–1597.

Giakoumakis, D., Kostoglou, M., Karabelas, A.J., 2005. Induced pulsing in trickle beds-characteristics an attenuation pulses. Chemical Engineering Science 60, 5185–5199.

Iliuta, I., Ortiz-Arroyo, A., Larachi, F., Grandjean, B., Wild, G., 1999. Hydrodynamics and mass transfer in trickle-bed reactors: an overview. Chemical Engineering Science 54, 5329–5337 The neural network based correlation, developed using NNFit software is available at the web site address: ⟨http://www.gch.ulaval.ca/∼nnfit⟩.

Khadilkar, M., Al-Dahhan, M.H., Dudukovic, M.P., 1999. Parametric study of unsteady-state flow modulation in trickle-bed reactors. Chemical Engineering Science 54, 2585–2595.

Lange, R., Hanika, J., Stradiotto, D., Hudgins, R.R., Silveston, P.L., 1994. Investigations of periodically operated trickle-bed reactors. Chemical Engineering Science 49, 5615–5622.

Lange, R., Schubert, M., Dietrich, W., Grunewald, M., 2004. Unsteady-state operation of trickle-bed reactors. Chemical Engineering Science 59, 5355–5361.

Muzen, A., Fraguío, M.S., Cassanello, M.C., Ayude, M.A., Haure, P.M., Martínez, O.M., 2005. Clean oxidation of alcohols in a trickle-bed reactor with liquid flow modulation. Industrial Engineering & Chemistry Research 44, 5275–5284.

Sáez, A., Carbonell, R., 1985. Hydrodynamic parameters for gas–liquid cocurrent flow in packed beds. A.I.Ch.E. Journal 31, 52–62.

Trivizadakis, M.E., Giakoumakis, D., Karabelas, A.J., 2006. Induced pulsing in trickle beds—particle shape and size effects on pulse characteristics. Chemical Engineering Science 61, 7448–7462.

Tsochatzidis, N., Karapantsios, T., Kostoglou, M., Karabelas, A., 1992. A conductance probe for measuring liquid fraction in pipes and packed beds. International Journal of Multiphase Flow 18, 653–667.