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Solid – liquid mass transfer in a fixed – bed reactor operating in induced pulsing flow regime.

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Abstract

The aim of the present study was to determine the values of the hydrodynamic parameters (liquid holdup, gas pressure drop in bed) and liquid/solid mass transfer coefficients in a reactor operating in the forced pulsing flow. The experiments were carried out for SLOW mode of base-impulse periodic liquid feeding using liquids differing in physicochemical properties. The operational parameters were chosen in such a way so as to induce natural pulsations in the impulse of the liquid. The analysis of the local and averaging values of the determined parameters (ε_{Ld}, k_{Ls}) shows that such a way of conducting the process may be favorable for the operation of the reactor. Correlations enabling to calculate the values of the hydrodynamic parameters and liquid/solid mass transfer coefficients of the reactor operating in liquid induced pulsing flow (LIPF) regime were worked out.

Keywords: trickle-bed, induced pulsing flow, hydrodynamic, liquid-solid mass transfer.

1. Introduction

Trickle bed reactors (TBRs) with fixed bed are commonly used in petroleum and petrochemical industry, mainly in the processes of treating various fractions of crude oil with hydrogen. If the aim of the process is a high conversion of the component present in the liquid phase in a low concentration then mass transfer rate of that component to the surface of the catalyst is the limiting step of the overall rate of reaction. As research showed (Bartelmus (1989)) the operation of the reactor is favourable in the pulse flow regime in which liquid/solid mass transfer coefficients are much higher than in the trickling flow. The operation of the reactor in this hydrodynamic regime requires supplying the apparatus with relatively big streams of gas and liquid, the result of which is short residence time of the reacting substances in bed and which has an impact on their conversion. One of the ways to improve the efficiency of the TBRs operation was the idea of their operation at periodically changing supply with liquid phase. It can be carried out using the method of

temporary stoppage of the liquid flow through the reactor (the ON-OFF method) or the BASE-IMPULSE method where liquid velocity is changed between low but no equal to zero (base) and high value (impulse).

As the latest literature data show (Trivizadakis and Karabelas (2006b)), one does not obtain significant increase in the liquid/solid mass transfer coefficients while carrying out the process using the ON-OFF method. Thus, the presented in this work research was done using the BASE-IMPULS method. Moreover, the velocities of both phases were chosen in such a way so as to induce natural pulsations in the liquid impulse. This is a relatively narrow range of changes in velocity of gas and liquid situated between two lines dividing (on the map) GCF/LIPF and GCF/PF regimes. The aim of research was to determine the basic hydrodynamic parameters (liquid holdup, gas pressure drop) and liquid/solid mass transfer coefficients. The determined parameters will make it possible to assess the benefits resulting from such a way of conducting the process.

2. Experiments

Our intention was to conduct measurements for both FAST – and SLOW modes of BASE-IMPULSE periodic liquid feeding. Unfortunately, as the experiments showed, the used in the research solutions foamed in contact with gas on the packing. It made it impossible to work in the LIPF FAST regime as, in case of these liquids, the region in which induced pulsing flow occurs was practically the same as for the self-induced pulsing flow (lines GCF/LIPF and GCF/PF coincided on the flow map). Therefore, measurements were done only under SLOW mode conditions. The flow map with marked ranges of changes in velocity of both phases in carried out experiments was presented in Fig.1.
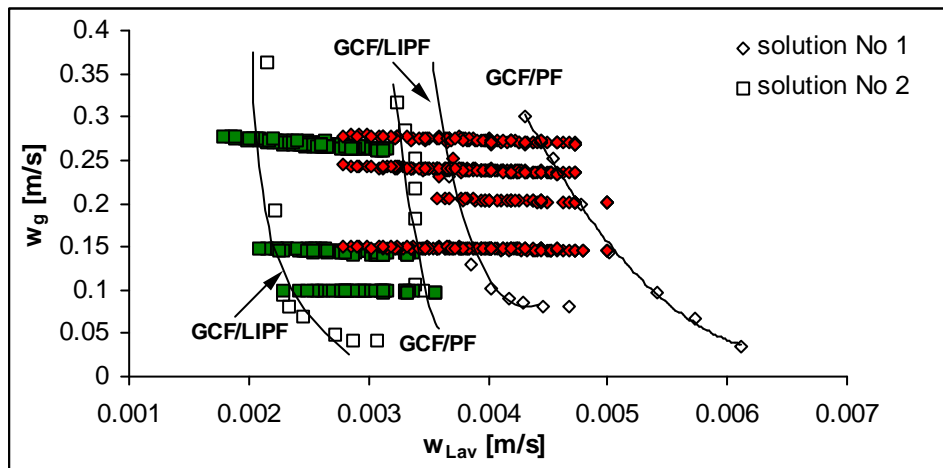

Fig. 1. Range of liquid and gas velocities covered by measurements.

2.1. Experimental set-up and conditions.

The experimental set-up was shown in Fig.2. A column of 0.057m in diameter made of transparent polyvinyl chloride was filled with glass spheres of 3mm in diameter ($a=1240m^{-1}$, $\varepsilon=0.38$) up to the height of 1.4m. Nitrogen was used as the gas phase and

water solutions were the liquid phase. Their composition and properties are set together in Table 1. The column was supplied with liquid by means of two separate ways of feeding one of which ensured low (base) and the other high (impulse) liquid flow rate. Both ways were equipped with a system of electromagnetic valves controlled by timer. Moreover, the set-up was equipped with electronic temperature meters (T) and a system of electromagnetic valves making it possible to simultaneously cut off the inflow and outflow of both phases. Gas pressure drops in bed were measured by means of differential pressure transducer (DPT). During the measurements, besides velocity of gas phase and liquid velocities in base and impulse, their duration was also changed; the base duration was t_b = 20s, 15s and 10s whereas impulse duration was t_{ip} = 20s, 15s, 10s, 7s, 5s and 3s.
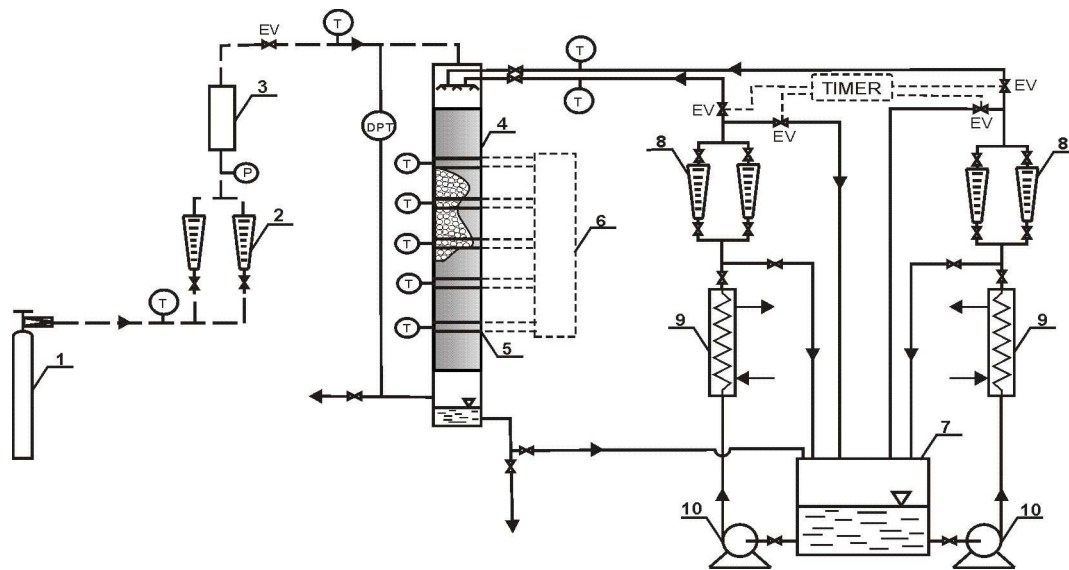

Fig. 2. Scheme of experimental set-up: 1- nitrogen cylinder, 2 – gas flow meters, 3 – dampener, 4 – packed column, 5 – conductivity cells, 6 – data acquisition, 7 – liquid tank, 8 – liquid flow meters, 9 – thermostat, 10 – liquid pumps, EV – electromagnetic valve.

Solutions number	Compositions of the solutions	Density ρ [kg/m^3]	Viscosity $\mu \cdot 10^3$ [Pas]	Surface tension $\sigma \cdot 10^3$ [N/m]
1	0.01 mol/dm^3 K$_3$Fe(CN)$_6$ 0.05 mol/dm^3 K$_4$Fe(CN)$_6$ 1 mol/dm^3 KCl	1055.85	1.091	49.1
2	0.01 mol/dm^3 K$_3$Fe(CN)$_6$ 0.05 mol/dm^3 K$_4$Fe(CN)$_6$ 1 mol/dm^3 KCl glycerol (~30% weight)	1122.7	2.468	56.6
3*	methanol (~24% weight)	960.1	1.64	45.8
4*	water	999.8	1.04	72.4

* - only for study of the hydrodynamic

Table 1. Physicochemical properties of the tested system (t = 21°C).

3. Hydrodynamic parameters of the reactor.

Liquid holdup was determined by measuring the variation in conductivity of the two-phase gas-liquid mixture flowing through the bed. In the column, 5 conductometric cells were placed at the distance of 0.225m each other. Each of them consisted of two platinum wire gauzes of diameter equal to that of the column. Measuring procedure described in earlier papers of authors (Bartelmus and Janecki (2003)) was used. One can notice the fluctuation of liquid holdup values on individual electrodes while conducting the process in the conditions of periodically changing supply of the reactor with liquid phase. Their values are shown in Fig.3 in the form of the ratio of ε_{Ld} value on a given height of bed to the arithmetic mean of the liquid holdup value in bed. The greatest differences were obtained in case of methanol solution, however they did not exceed a dozen or so percent. In view of the above fact, the averaged along the bed values of ε_{Ld} were taken into account in the next considerations.
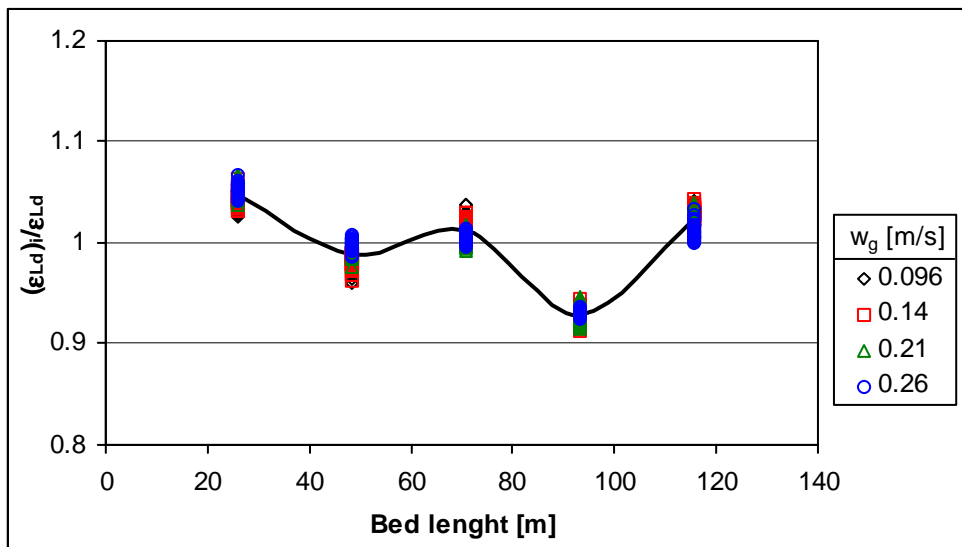

Fig.3. Relative liquid holdup distribution along the bed for solution No 4.

In LIPF SLOW regime liquid holdup decrease with the increase in gas velocity like in the GCF regime. However, the increase in mean liquid velocity causes in increase of ε_{Ld} value, which was illustrated in Fig.4 for every base and impulse duration. These parameters are taken into consideration in the mean liquid velocity defined as:

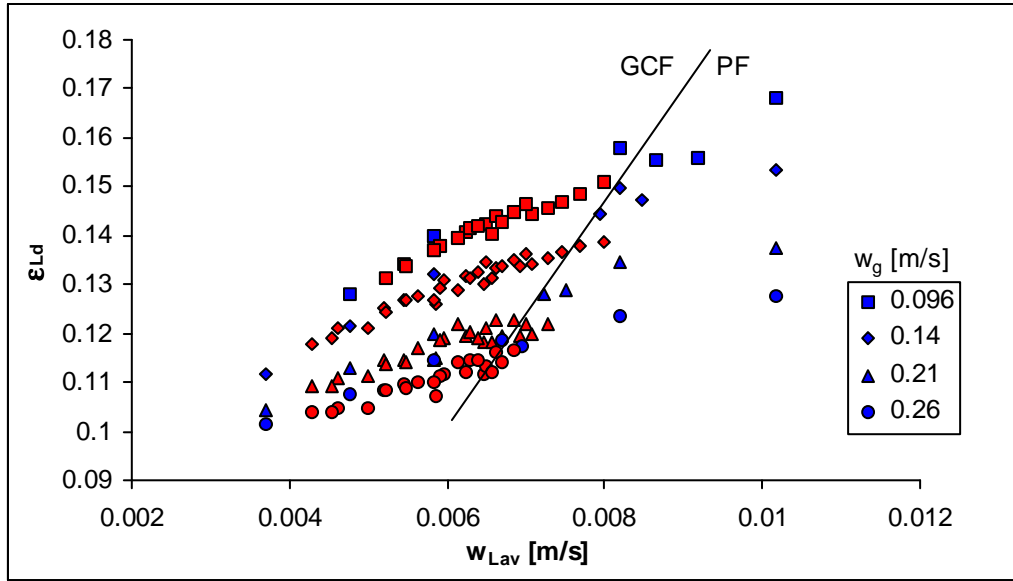$$w_{Lav} = \frac{t_b w_{Lb} + t_{ip} w_{Lip}}{t_b + t_{ip}} \tag{1}$$

Fig.4. The comparison of ε_{Ld} values obtained for GCF and PF regimes (blue points) and LIPF SLOW (red points) regime for solution No 4.

Correlations available in literature were analyzed in order to find the most favorable form of the equation correlating the measured ε_{Ld} values. Giakoumakis et al. (2005) and Trivizadakis et al. (2006a) suggested the modified Larachi et al. (1991) equation as the correlation which describes the measured ε_{Ld} values with good accuracy and which were obtained at FAST mode of liquid modulation in the ON-OFF method. The carried out computational simulations showed that for determined in the present work ε_{Ld} values the most appropriate is the form of equation suggested by Specchia and Baldi (1977). Thus, that form of the equation was used to correlate our own data base obtaining:

$$\varepsilon_{Ld} = 3.48 \cdot \left(Re_{Lav}\right)^{0.416} \left(Ga'_{Lav}\right)^{-0.351} \tag{2}$$

The equation (2), with the mean relative error of $e_y = 1.93\,\%$ and standard deviation of $\sigma_{st} = 1.88\,\%$, correlates 578 experimental data obtained for the LIPF SLOW regime (Fig.5).
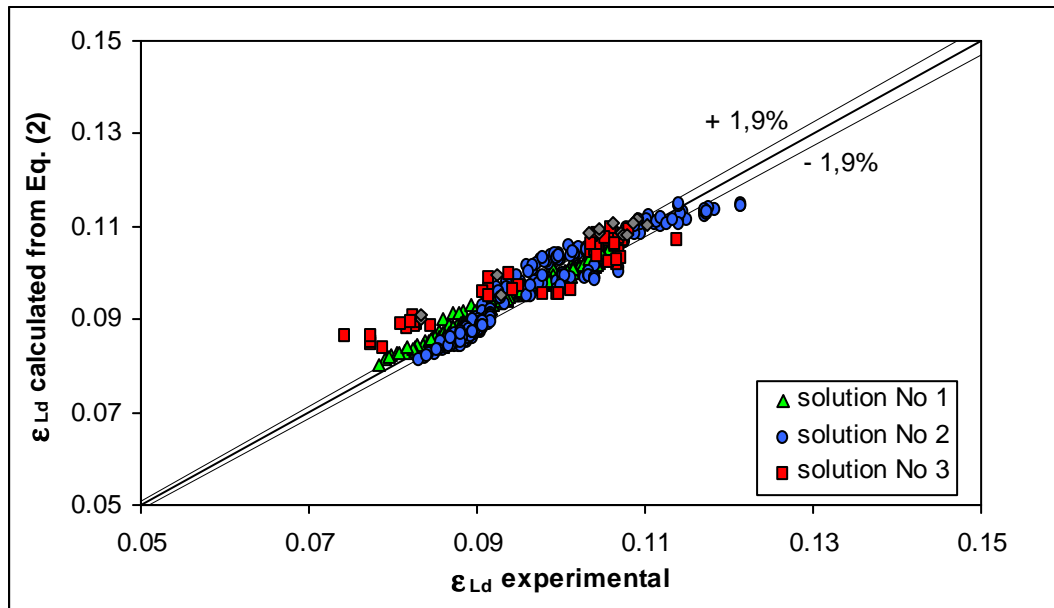
Fig.5. The comparison of ε_{Ld} values experimentally determined and calculated from equation (2).

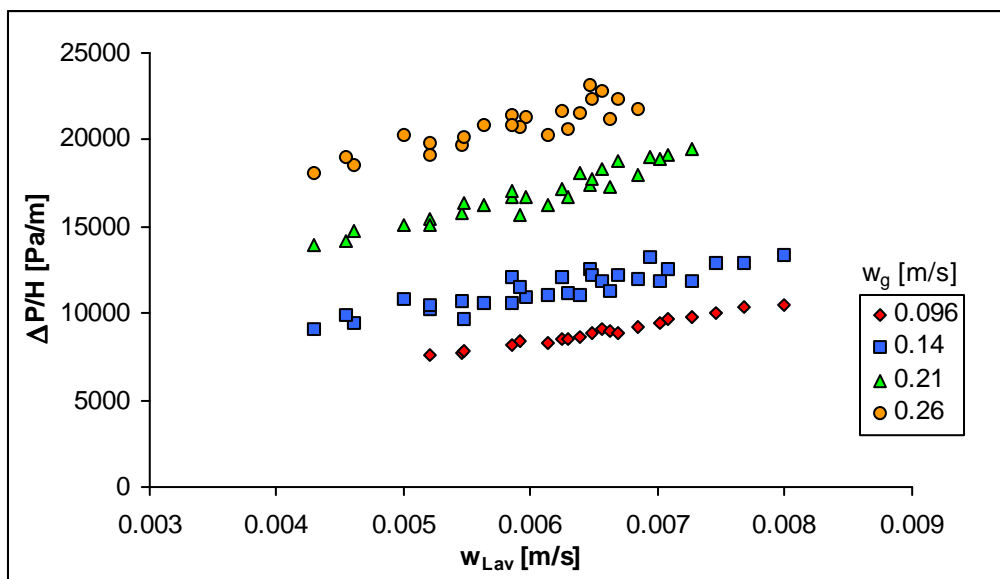The influence of the velocities of flowing media on gas pressure drop in bed was shown in Fig.6.

Fig.6. The influence of the mean liquid and gas velocities on gas pressure drop in bed for solution No 4.

Statistical tests showed that irrespective of the tested system and the method of forcing pulsation in the reactor the $\Delta P/H$ values calculated from Sai and Varma (1987) equation are close to the ones obtained in the presented experiments. The correlation derived by these authors takes into consideration the physicochemical properties of the liquid studied via dimensionless modules in which these properties

are related to those of pure water. Thus, the values of pressure drop were correlated using the form of equation derived by the above authors. The following dependence was obtained as a result of the estimation of the constant and exponents of the equation:

$$F = 5775.6 \cdot \left(\frac{Re_g}{Re_{Lav}} \right)^{0.912} \left(\frac{\sigma_w}{\sigma_L} \right)^{0.05} \left(\frac{\mu_w}{\mu_L} \right)^{1.1} \left(\frac{\rho_L}{\rho_w} \right)^{1.3} \qquad (3)$$

where $F = f_c \cdot Re_{Lav}^{0.624}$. This equation with the mean relative error of $e_y = 8.1 \%$ and standard deviation of $\sigma_{st} = 6.7 \%$, correlates 702 experimental points (Fig.7).
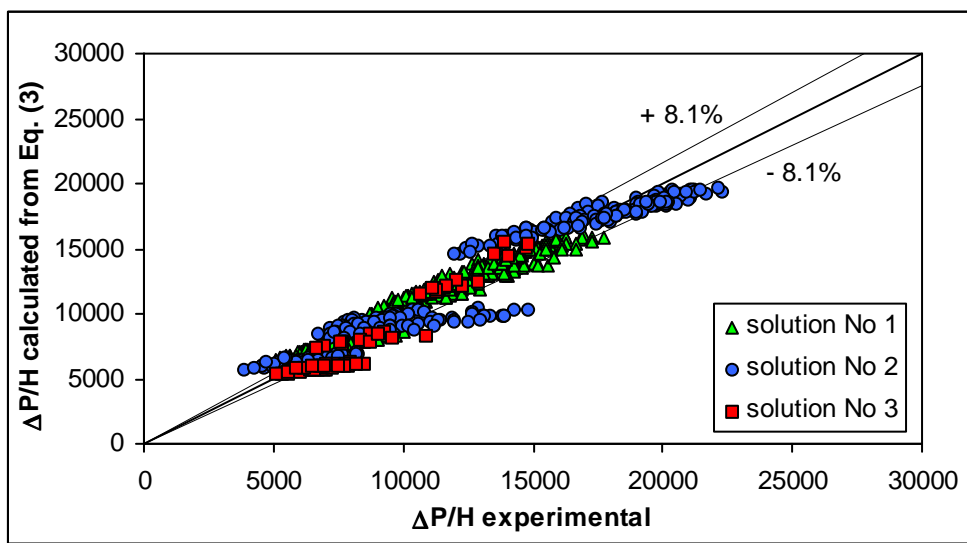

Fig.7. The comparison of the $\Delta P/H$ values experimentally determined and calculated from equation (3).

4. Liquid/solid mass transfer.

Mass transfer coefficients between liquid and packing surface were determined by means of electrochemical method. It consists in measuring the density of the electrochemical reaction current whose rate is controlled by diffusion of ions to the surface of an electrode (cathode). The electrode reaction used was the cathodic reduction of potassium ferricyanide. The solution was a mixture potassium ferri/ferrocyanide and a large excess of potassium chloride as so-called current carrier. The rudiments of the discussed technique can be found in the works of Selman and Tobias (1978) and Mizushima (1971). The viscosity of the basic solution was increased to $2 \cdot 10^{-3}$ Pas by adding glycerol. Further increase in viscosity made the work of the column impossible due to forming of strong foam. The cathode was platinum spheres with the diameter equal to inert packing diameter (3mm) positioned along the axis of the bed at the distance of 0.245m each other (the first electrode was placed at the height of 0.48m from the top). Platinum strips padding the inner wall of the column were the anode.

The aim of the carried out experiments was to prove whether the operation of the reactor in LIPF regime, forced by cyclic changes in the liquid feeding and carried out by means of BASE-IMPULSE method, is favourable as regards the rate of the mass transfer processes. Thus, the findings of the measurements were shown in the form of the so-called "enhancement coefficient" defined as the ratio of the value of mass transfer coefficient (k_{Ls}) determined in the tested by us LIPF regime to the value of this coefficient determined in the steady state for $w_L = (w_{Lav})_{LIPF}$ and w_g = idem. For such velocities of liquid and gas phases the reactor operates in the gas continuous flow regime (GCF). Both values, that is $(k_{Ls})_{GCF}$ and $(k_{Ls})_{LIPF}$ were experimentally determined for each of four electrodes placed along the axis of the apparatus. Fig.8 shows the dependence of the enhancement coefficient on the velocity of both phases and the liquid impulse duration.
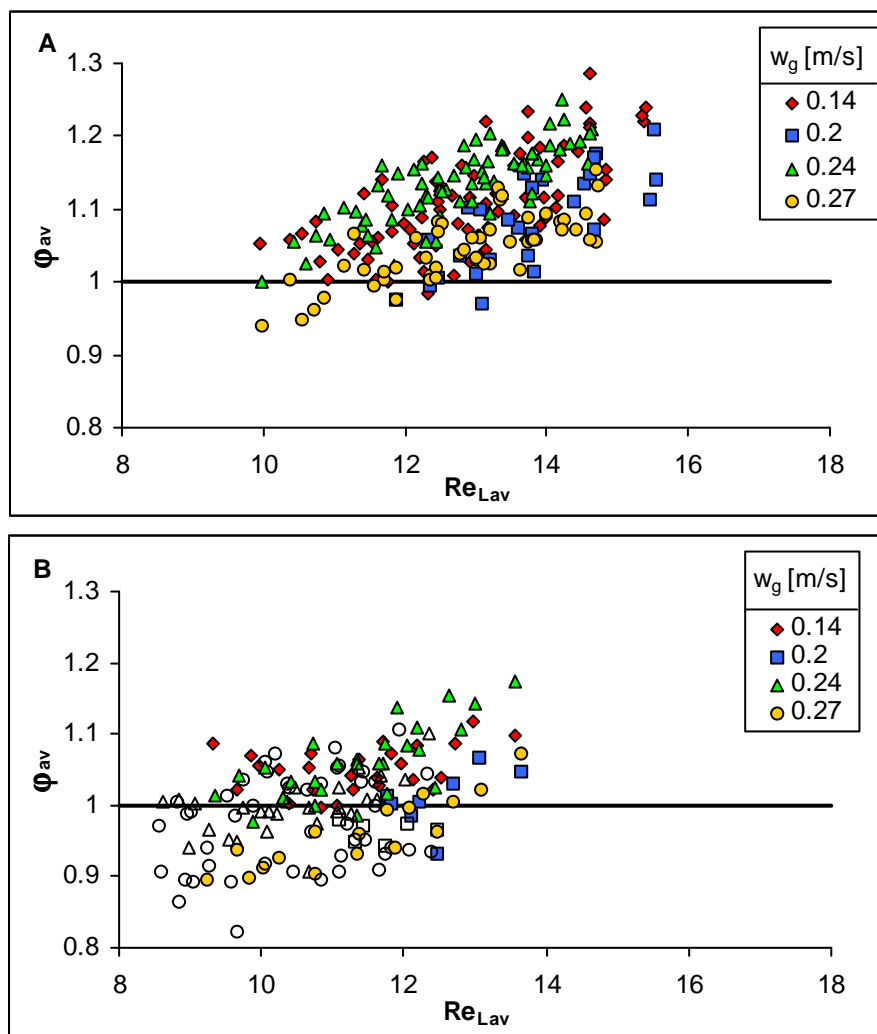

Fig.8. Enhancement coefficient depending on the mean Reynold's number of liquid (A - $t_{ip} = 20 \div 7$s. B - $t_{ip} = 5$s (solid points) and $t_{ip} = 3$s (open points).

The shown in the above figure φ values represent the mean arithmetic value of enhancement coefficients calculated for four electrodes placed along packing. While

analysing this chart, it can be concluded that a great number of experimental points lies above the $\varphi = 1$ value. It means that the mean value of mass transfer coefficients in LIPF regimes is higher than in GCF regime, at the same velocities of both phases. Experimental points whose impulse duration was very short ($t_{ip} = 3s$ and $5s$) and the reactor operated at a relatively great velocity of the gas phase ($w_g = 0.28$ m/s) are below the $\varphi = 1$ value. The presented comparison shows that is possible to select the parameters of the cyclic work of the column in such a way as to intensify the liquid/solid mass transfer.

Figures 9 and 10 presents the changes in the enhancement coefficients values on individual electrodes and influence of the duration of base and impulse on the φ value.
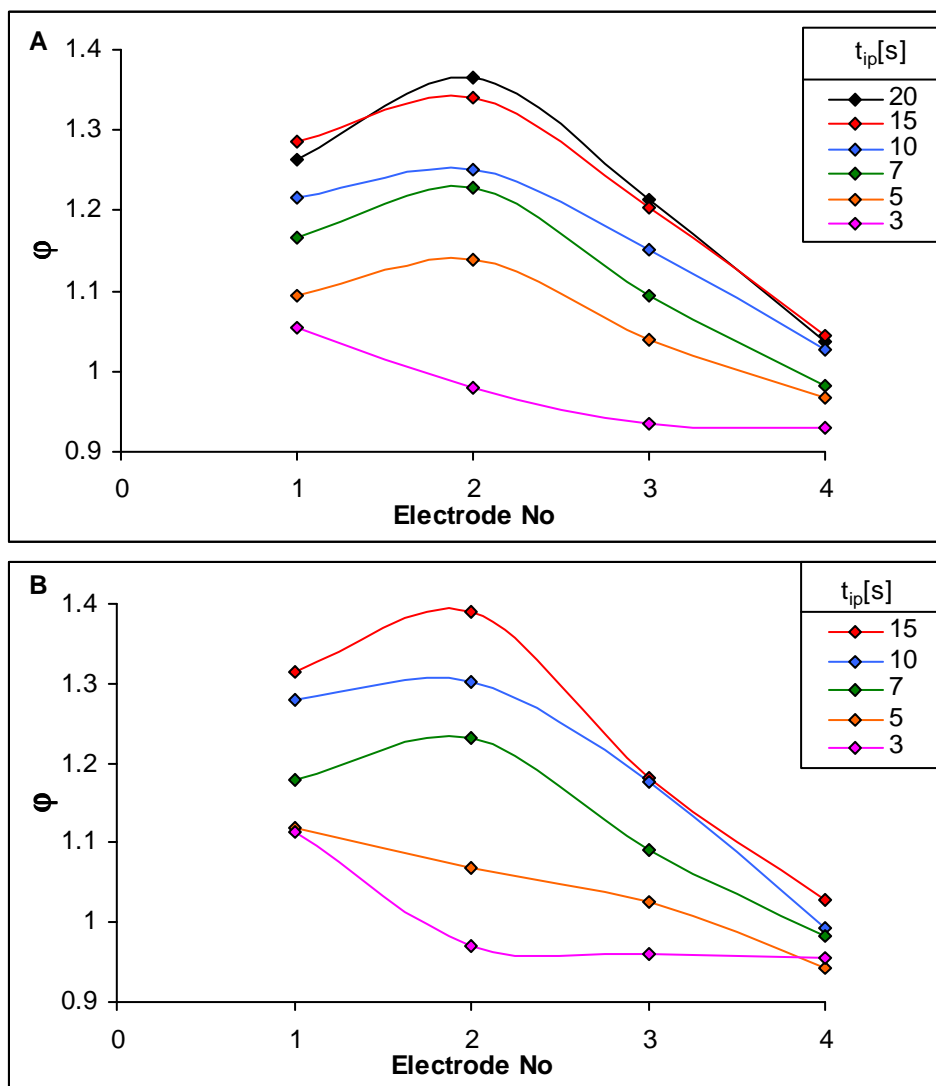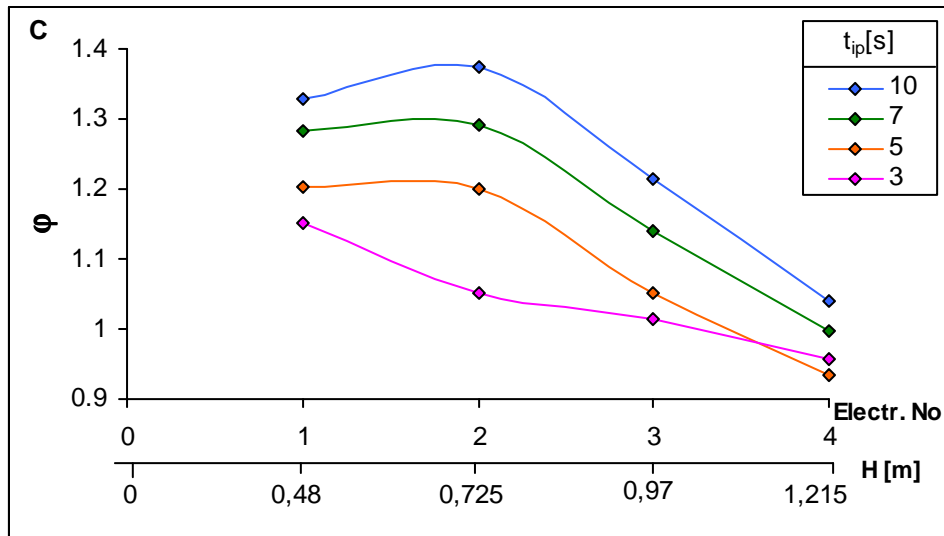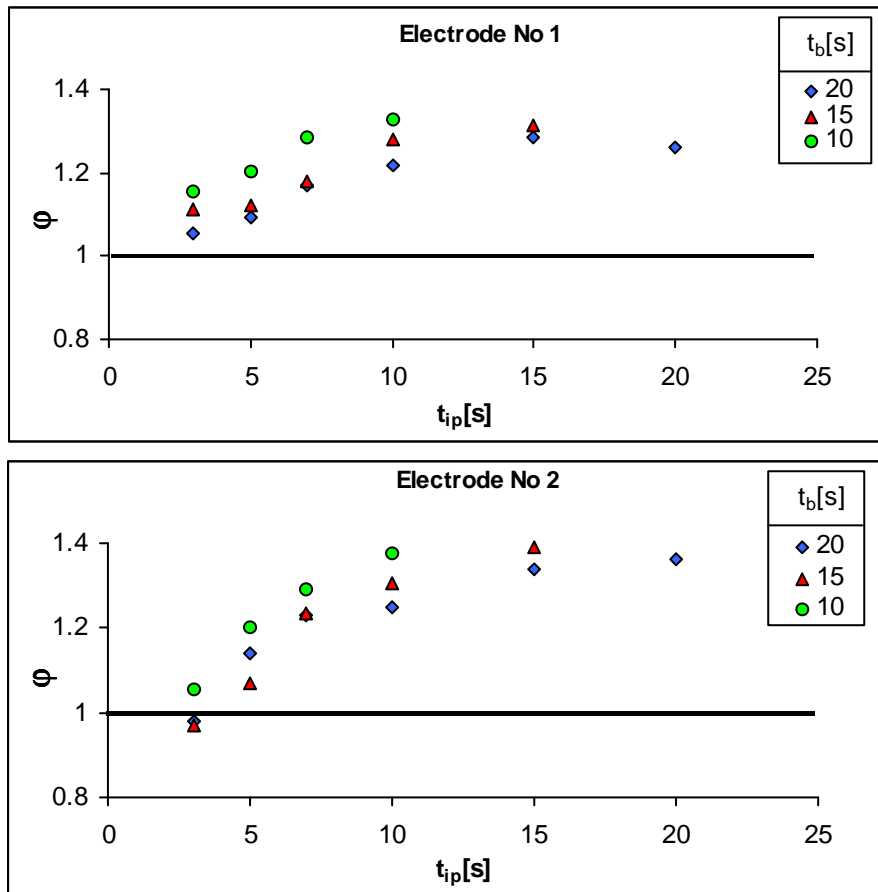
Fig.9. Changes in the φ value along packing; solution No 1, w_g = 0.14 m/s, w_{Lb} = 0.032m/s, w_{Lip} = 0.0068m/s; A – t_b = 20 s; B – t_b = 15 s; C – t_b = 10 s.
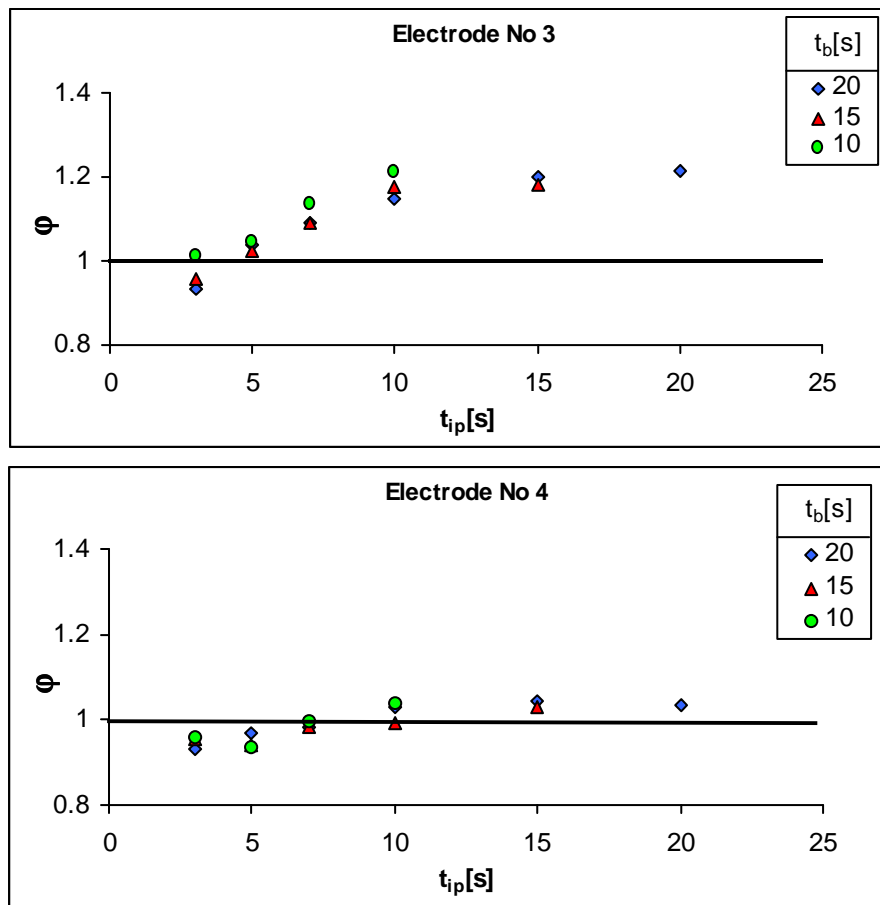
Fig.10. The influence of base and impulse duration on the enhancement coefficient value; solution No1, $w_g = 0.14$ m/s, $w_{Lb} = 0.0032$ m/s, $w_{Lip} = 0.0063$ m/s.

The lowest values of the enhancement coefficient were obtained on electrode 4 lying at the distance of 0.235m from the bottom of the column. As research shows, long impulse duration is favourable from the point of view the enhancement coefficient. However, the base duration seems to influence the ϕ value to a lesser extent (lower base duration influences the enhancement coefficient very little).

Trying to interpret the obtained results the following were compared: mass transfer coefficients in base with k_{Ls} values determined for GCF regime at $(w_L)_{GCF} = (w_{Lb})_{LIPF}$ and k_{Ls} in impulse with k_{Ls} values determined for self-inducing pulse flow where $(w_L)_{PF} = (w_{Lip})_{LIPF}$. Such a comparison requires, on the one hand carrying out measurements for GCF and PF regimes with adequately chosen velocities of the liquid phase and next processing the signal from the electrodes from which one has to cut out the parts that refer to base and impulse and calculate the mean k_{Ls} value for these parts. The calculation of the k_{Ls} value were generally higher in base than in GCF regime, however, lower than in PF regime in impulse. An example of a signal from the electrodes is shown in Fig.11.
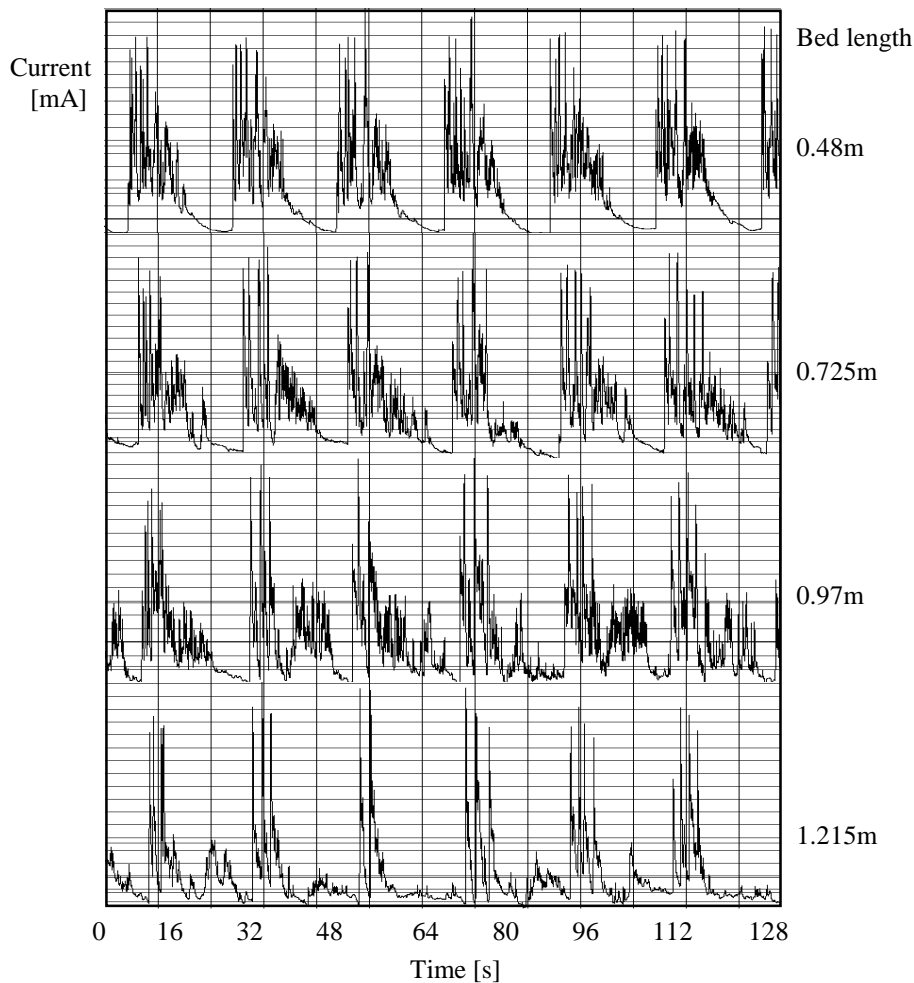
Fig.11. Signals from the electrodes placed along packing; solution No 2, $w_g = 0.27$ m/s, $w_{Lb} = 0.0014$ m/s, $w_{Lip} = 0.0038$ m/s, $t_b = 10$ s, $t_{ip} = 10$ s.

It seems that the basic parameters necessary to interpret the results will be the analysis of the structure of signals from the electrodes placed along packing.

5. Summary

The basic aim of the present study was to prove that it is beneficial to carry out processes in a trickle bed reactor in the pulse regime forced by periodic changes in liquid feeding the apparatus using the BASE-IMPULSE method. It was shown that the operation of the reactor in the tested range of operational parameters changes (natural pulses are induced in the impulse) ensures even distribution of liquid on the bed considerably limiting the danger "hot spots" forming on its surface. Basic hydrodynamic parameters of the reactor were determined and equations correlating the obtained results were formulated. The collected hydrodynamic data base will be the comparative base for simulations of cocurrent gas and liquid flow through packed bed conducted by means of the computational fluid dynamics procedures (CFD) (numerical package – Fluent 6.1.22). It was also prove that, due to proper choice of cyclic reactor operation parameters, the increase in liquid/solid mass transfer coefficient in relation to the value of the obtained under stationary operation of the apparatus (GCF) can be obtained.

The collected base of mass transfer coefficient k_{Ls} for GCF, PF and LIPF regimes will the subject to further analysis, whose aim will be a better understanding of the reactor functioning in the forced by periodic liquid feeding pulse flow.

Notation

a   – specific packing surface, 1/m
d_p – diameter of packing, m

$$e_Y = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{Y_{exp,i} - Y_{cal,i}}{Y_{exp,i}} \right| \cdot 100\%$$ – mean relative error, %

$$f_c = \frac{2\Delta P \cdot d_p}{\rho_L w_{Lav}^2 H}$$

H   – bed height, m
k_{Ls} – mass transfer coefficient, m/s
ΔP – pressure drop, Pa
t   – time, s
w_α – superficial velocity, m/s

Greek letters
ε – bed porosity
ε_{Ld} – dynamic liquid holdup
μ – viscosity, Pas
ρ – density, kg m^{-3}
σ – surface tension, N m^{-1}

$$\sigma_{st} = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} \left(\left| \frac{Y_{exp,i} - Y_{cor,i}}{Y_{exp,i}} \right| - e_Y \right)^2} \cdot 100\%$$ – standard deviation, %

φ - enhancement coefficient

Dimensionless numbers

$$Ga_L' = \frac{d_p^3 \rho_L (\rho_L g + \Delta P / H)}{\mu_L^2}$$ – liquid phase modified Galileo number

$$Re_\alpha = \frac{w_\alpha \cdot d_p \cdot \rho_\alpha}{\mu_\alpha}$$ – Reynolds number

Subscripts
av   – average value
b   – base
g   – gas
i   – local parameter
ip   – impulse

L   – liquid
w   – water
α – α-phase, α = g, L

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