AIDIC *Conference Series*, Vol. 9, 2009
Editor Sauro Pierucci
DOI: 10.3303/ACOS0909040

ISBN 978-88-95608-10-5 ISSN 2036-5969

THE INFLUENCE OF MODULAR STRUCTURE ON THE HYDRODYNAMICS OF CATALYTIC STRUCTURED PACKINGS FOR REACTIVE SEPARATION PROCESSES

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Residence time distribution (RTD) and drainage experiments are used to shed light on the hydrodynamics of the catalytic structured packing Katapak-SP11. The liquid flow behaviour and the dynamic liquid holdup were derived from RTD results and compared with the total liquid holdup obtained from drainage experiments. The liquid considered static from the viewpoint of free-draining experiments becomes dynamic during the normal column operation. The examination of liquid drainage curves and the consistency of different techniques are discussed.

1. INTRODUCTION

The possibility of exploiting an advantageous interaction between separation and reaction has favoured the implementation of heterogeneous catalysis in reactive separation columns. Improvements in this direction are expected from a new generation of modular catalytic structured packings which allows certain flexibility with respect to the variation in the reaction to separation requirements in a single unit.
The commercially available catalytic structured packing under study is the Sulzer Katapak-SP 11 (Figure 1) which is made of wire gauze envelopes filled with catalyst spheres alternated to corrugated metal sheets of the MellapakPlus family.
The geometrical structure of the packing determines the flows development inside the packed bed and consequently the overall column performances. The external wire gauze of catalyst bags allows the liquid flow penetration and prevents the gas cross-over, thus limiting the use of Katapak-SP to those applications where the reaction takes place in the liquid phase. Therefore the liquid holdup inside the catalyst bags influences the reactive performance of the internal. On the other side the liquid holdup on the Mellapak Plus layers is mainly responsible for the interactions with gas.
Hence, the knowledge of liquid holdup represents the key input for the development of mechanistic models and for the prediction of fluid dynamic related parameters, such as pressure drop, capacity, interfacial area and mass transfer volumetric coefficients. However, for Katapak-SP 11 the state of knowledge of liquid holdup is still unsatisfactory. The lack of experiments carried out with this new internal explains only partially this gap. It is also the complexity of the phenomena imposed by the hybrid geometry of Katapak-SP which still requires a detailed comprehensive understanding.
For these reasons, the liquid holdup and flow behaviour in Katapak-SP have been investigated by using both proven gravimetric and tracer based measurement techniques. Hence, information on the different holdup contributions is provided. Moreover, analysis of the residence time distribution (RTD) allows relating the liquid holdup to the flow behaviour in the packing.
In this work we present a comparison of the experimental results obtained with different techniques, stressing the problem of consistency for the measurements times of liquid holdup. The aim is to provide a standardized procedure to be usefully applied to different as well as new catalytic structured packings.

Please cite this article as: Viva A. and Brunazzi E., (2009), The influence of modular structure on the hydrodynamics of catalytic structured packings for reactive separation processes, AIDIC Conference Series, 09, 345-354 DOI: 10.3303/ACOS0909040

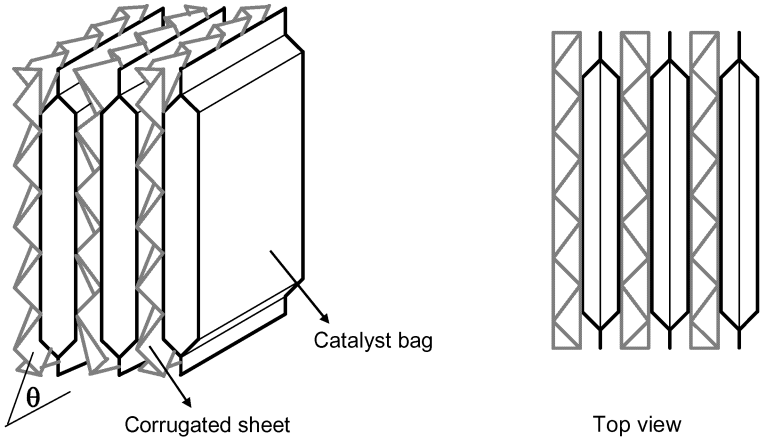

Figure 1. Structure of the modular catalytic packing Katapak-SP11.

The understanding of the liquid distribution inside the hybrid packing structure is essential as it governs the performance of the hybrid unit as a whole.

2. LIQUID PHASE RTD MEASUREMENTS

Residence time distribution experiments by injection of a salt tracer in the liquid flow were performed in a 100mm inside diameter column equipped with the catalytic packing Katapak-SP 11. The catalyst bags were filled with glass spheres of 1 mm in diameter. The air-water system was used at ambient conditions.
A schematic of the column set-up is shown in Figure 2a. After the liquid flow stabilisation in the column, the tracer (a 2N aqueous solution of potassium chlorine) was injected via a syringe just before the liquid distributor at the top of the column. At the bottom of the column, the whole amount of liquid was collected in a purposely built mixing cup equipped with a conductometer flow through probe (Figure 2b). The liquid leaving the column was collected into a separate tank (D2). Figure 2c shows the computer data acquisition system. It was connected both at the syringe at the top of the column (trigger signal) and at the flow-through probe at the bottom of the column (conductivity signal), which allowed the tracer concentration to be measured in the liquid stream leaving the column.

Under the assumption of the plug flow model and taking into account of the axial dispersion, the tracer material balance can be written in dimensionless form as in Equation 1.

$$\frac{\partial \mathrm{c}}{\partial \theta} = -\frac{\partial \mathrm{c}}{\partial \mathrm{Z}} + \frac{D_{ax}}{u_L L}\frac{\partial^2 c}{\partial Z^2} = -\frac{\partial \mathrm{c}}{\partial \mathrm{Z}} + \frac{1}{Pe_L}\frac{\partial^2 c}{\partial Z^2} \tag{1}$$

where

$$\theta = \frac{t}{t_m}, t_m = \frac{L}{u_L}, Z = \frac{z}{L},\ Pe_L = \frac{u_L L}{D_{ax}} \tag{2}$$

In the above relations c is the tracer concentration, z the axial coordinate, L the packed bed height, u_L the liquid interstitial velocity, t the residence time, D_{ax} the axial dispersion coefficient and Pe_L the axial Peclet number.
Assuming a pulse function for the tracer and under the proper boundary conditions for closed system, the balance equation can be solved in the Laplace domain.

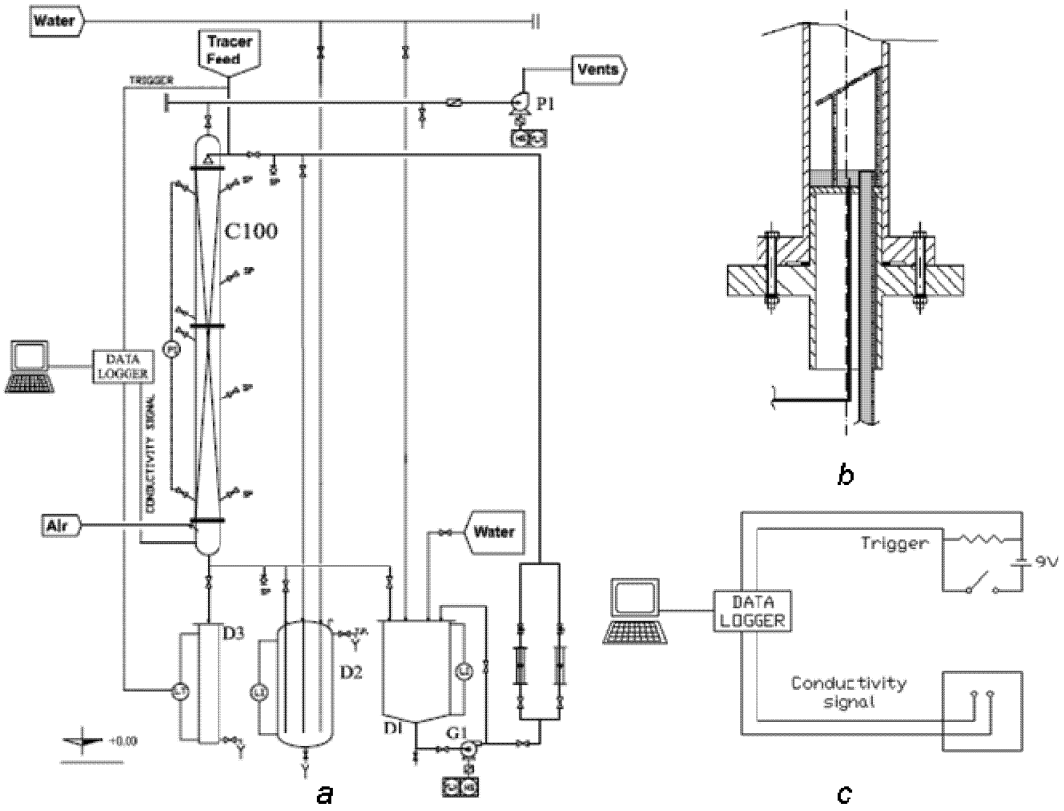

Figure 2. Schematic of the experimental setup: (a) column, (b) conductometer flow through probe, (c) data acquisition system.

The residence time distribution function *E(t)* is demonstrated to be defined as:

$$E(t) = \frac{V^* \cdot c(t)}{\int_0^\infty V^* \cdot c(t)dt} \tag{3}$$

where V^* represents the volumetric flow of liquid.

The *n*-th moment of *E(t)* is

$$m_n = \int_0^\infty c(t, L) \cdot t^n dt \tag{4}$$

For n = 0, 1, 2 the following equations can be derived.
The zero moment represents the mass of tracer:

$$m_0 = \int_0^\infty c(t, L)dt = \frac{M}{V^*} \tag{5}$$

The first moment represents the mean residence time of the tracer and it is the parameter of interest for the evaluation of liquid hold-up:

$$t_m = \int_0^\infty t \cdot E(t)dt = \frac{L}{u_L} = \frac{3600 \cdot L \cdot h_{RTD}}{u_{SL}} \tag{6}$$

where h_{RTD} is the liquid holdup in the column and u_{SL} is the liquid superficial velocity.

According to Levenspiel (1999), the axial Peclet number is determined by iteration from the relation connecting Pe_L to the second moment of the function $E(t)$, that is the variance σ:

$$Pe_L = \frac{2 \cdot t_m^2}{\sigma^2 \cdot Pe_L}\left(Pe_L - 1 + e^{-Pe_L}\right) \tag{7}$$

$$\sigma^2 = \mu_2 - t_m^2 = \int_0^\infty t^2 \cdot E(t)dt - t_m^2 = \int_0^\infty (t - t_m)^2 \cdot E(t)dt \tag{8}$$

After recording the RTD curve, it is possible to calculate the moments and then Pe_L and h_{RTD}.

Experimental RTD results were taken into consideration only if the difference between the zero moment calculated from the experimental curve agreed with the mass of the injected tracer.
The trend derived experimentally of RTD curves is presented in Figure 3, where the influence of liquid rate is shown. Increasing the liquid load leads to taller and thinner curves and thus smaller residence time distribution with peaks shifted towards shorter times; this is a common and expected behaviour.

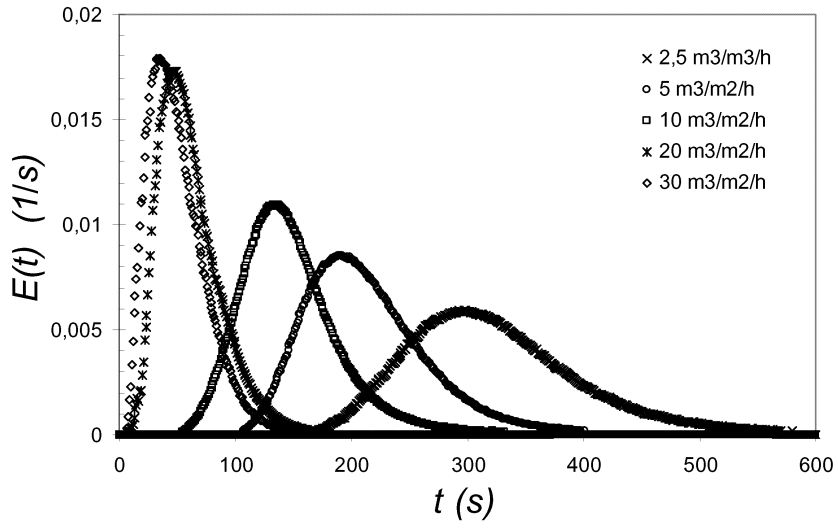

Figure 3. Influence of the liquid rate on the liquid residence time distribution.

Analysis of RTD data allows identifying the variation of flux regime in the column (see previous studies on Katapak-S and Multipak by Kolodziej et al. 2005, Götze et al. 2001, Moritz and Hasse, 1999). In fact, the RTD curves point out the transition from a condition of partially wet reactive zone to a regime named liquid Load Point, characterized by catalyst bags completely filled with liquid. When the liquid load exceeds the Load Point, the catalyst bags reject the exceeding liquid which thus flows as a by-pass over the Mellapak Plus layers. This

behaviour is recognizable in the dimensionless RTD curves because of the different residence time of liquid flowing inside the catalyst bags compared to that flowing over the corrugated layers. The shape of RTD curves and consequently the distribution of liquid inside the packing are strictly related to the modular configuration and to the geometry of the packing.

The shape of the dimensionless E as a function of the dimensionless time θ for different liquid loads is shown in Figure 4. At low liquid loads (2.5 and 5 m^3/m^2h) the curves are narrow. The tails are due to the presence of stagnant zones inside the catalyst bags that are not completely filled with liquid. The fraction of liquid flowing outside the bags increases with liquid load, although the Load Point is not yet reached (10 m^3/m^2h). The shorter residence time of liquid flowing over the Mellapak layers implies the anticipation of the RTD curve. This effect is even more visible for liquid loads above the Load Point. The mean residence time is reduced because of the high fraction of liquid flowing directly over the Mellapak Plus layers outside the catalyst bags. In this condition, a strong back-mixing of liquid can be supposed, due to the crossing liquid from and towards the catalyst bags especially at the contact points of the wire gauze envelopes with the corrugated layers. The back-mixing generates long tails in the RTD curves and a strong deviation from the desired ideal plug flow.

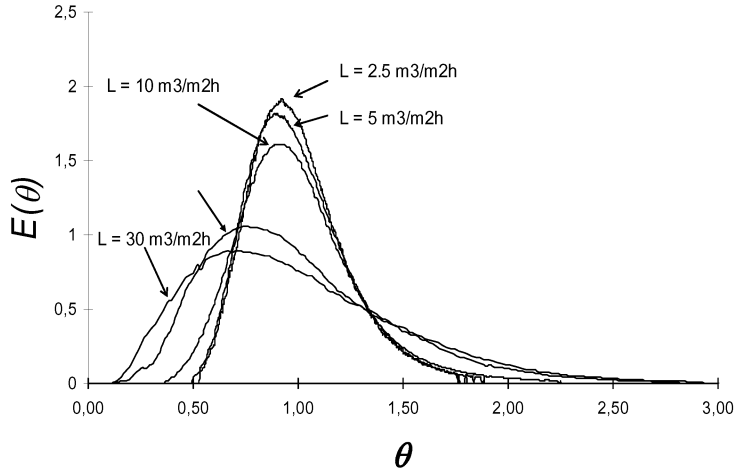

Figure 4. Dimensionless RTD curve at different liquid loads.

The behaviour of the liquid inside Katapak-SP 11 can not be compared with the one observed by Götze et al. (2001) for Katapak-SP 12. Above the liquid Load Point, for Katapak-SP 12, the RTD curve does not show neither the anticipation in the mean residence time nor the presence of long tails. This difference is due to the combination of two effects. The first is the reduced mixing of liquid between reactive and separation zones, because only half of the Mellapak layers are in close contact with the catalyst bags and so the liquid flowing outside the bags has a stronger effect in the mean residence time also for low liquid loads. Secondly, the volumetric fraction occupied by catalyst bags in the packing is smaller in Katapak-SP 12 than in Katapak-SP 11, thus reducing the influence on the residence time of the stagnant zones delay.

The RTD of liquid inside a single bag of catalyst spheres has been analyzed by Behrens (2006). His study contributes to a better understanding of the modularity effect on the behaviour and performances of the whole packing. According to Behrens (2006), the mean residence time in the bag decreases by increasing the liquid load. Above the Load Point, the tracer response shows a split-up, the residence time of the excess liquid being much smaller than that of the liquid flowing inside the catalyst bag. This split-up is not visible in the RTD curves of the packings fitted in the column, both because of the liquid exchange between catalyst bags and Mellapak layers in one single packing and also because of the mixing at the transitions between consecutive packing elements. Consistently with this analysis, the axial dispersion coefficient of modular catalytic packing is two orders of magnitude higher than the one obtained for a single bag. While a single bag behaves as a trickle bed

reactor, in structured catalytic packings the non ideal flux is determined by the hydrodynamics and not by molecular diffusion effects. In Figure 5 the trend of the axial diffusion coefficient and the axial Peclet number are shown as a function of the liquid velocity and the liquid Reynolds number, respectively. The liquid phase Reynolds number is calculated as:

$$Re_L = u_L \rho_L d_{eq} / \eta_L \tag{9}$$

where for Katapak-SP 11 the hydraulic diameter is d_{eq} = 0.01404 m.
The axial dispersion of Katapak-SP 11 follows the same trend of Multipak (Kolodziej et al., 2005). The two lines refer to two variants of the Multipak packing. This packing has a modular structure similar to Katapak-SP 11 (Ratio Catalyst Bags over corrugated Layers 1:1) and a similar behaviour in the column can be supposed.

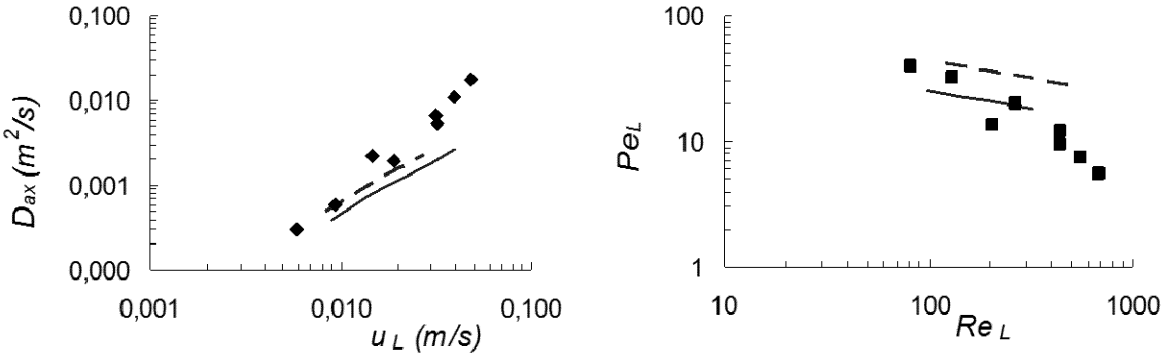

Figure 5. Axial dispersion coefficient and axial Peclet number for Katapak-SP 11 (points). Data for Multipak (lines) are taken from Kolodziej et al. (2005).

According to Equation (6), RTD experiments allow determining the total liquid holdup inside the column from the first moment which represents the mean residence time of the tracer. Figure 6 shows t_m as a function of the liquid superficial velocity.

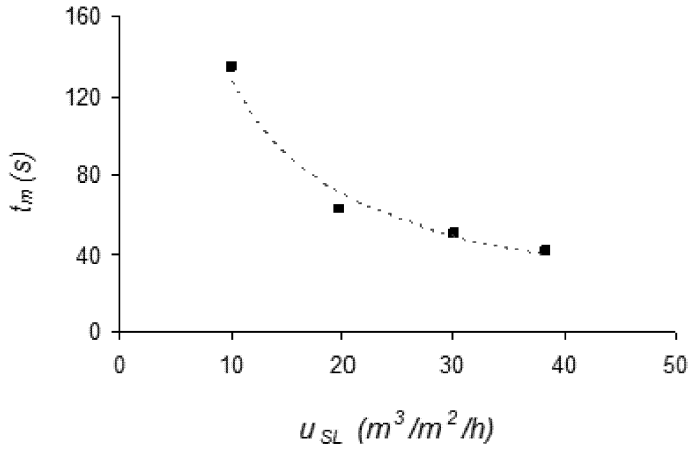

Figure 6. Mean residence times at different liquid superficial loads.

Hence, from the RTD curve the holdup in the column can be estimated and this holdup actively participates to mass transfer operations. For conventional packings, the RTD holdup corresponds to the dynamic holdup determined by draining experiments. For catalytic structured packing, on the contrary, the holdup derived from RTD measurements agrees with the total holdup given by the sum of the dynamic and the static contributions derived from draining experiments on condition that consistent measurement times are used (Viva and Brunazzi, 2007).
In the following the results obtained with the drainage method for Katapak-SP 11 are reported and compared with the above mentioned RTD holdup.

3. DRAINAGE EXPERIMENTS

3.1 Static holdup

Viva and Brunazzi (2007) have shown that the static holdup can estimated by extending the model proposed by Behrens (2006) for single catalyst bag to the Katapak-SP 11 geometry. According to Behrens, the static holdup is comprised of three contributions: the pore holdup, the capillary rise holdup and the residual holdup. Since the catalyst bags in our test case are filled with glass spheres, the pore holdup fraction is not present. The capillary rise holdup is estimated from the balance bewteen the capillary forces and the gravity. The predicted capillary rise height value agrees with the experimental value observed by Aferka et al. (2007) on the catalyst bags holdup obtained with tomography experiments carried out on Katapak-SP 12. The residual liquid is retained by capillary forces at the contact points of the glass spheres above the capillary height after the drainage. This fraction can be estimated with correlations developed for trickle beds of spheres and described in Van Hasselt et al. (1999).
For Katapak-SP 11 the predicted static holdup has found to be equal to 6%, and in good agreement with the experimental value obtained after 1 h of drainage of the packing. The details on the used correlations and the experimental procedures are reported in Viva and Brunazzi (2007).

3.2 Dynamic holdup

To measure the dynamic free-draining holdup the procedure was as follows (Brunazzi and Viva, 2006). The column was first operated at high liquid load to ensure thorough wetting of the packed bed. Then the liquid stream was shut off and after some period of time the liquid flow-rate was set to the desired value. After stabilisation, the liquid feed valve was closed while the liquid was allowed to drain from the packing in a purposely built liquid collecting tank (D3, Figure 2a). The time-dependent liquid dropping was measured by means of a Differential Pressure transmitter and the signal stored on a PC. Brunazzi and Viva (2006) observed a strong dependence of the volume of draining liquid on time. The dynamic free-draining holdup was calculated as the volume of liquid drained per unit of column volume (the part filled with packing). In particular a reference time of 1h was set as a proper draining time for the dynamic holdup evaluation.
In order to confirm this statement, the approach proposed by Urrutia et al. (1996) for the holdup analysis of trickle beds has been extended to Katapak-SP 11. In the original model, developed under the assumption of laminar liquid film flow in a draining packed bed, it was found a linear dependence of the draining liquid volume on $t^{-0.5}$. According to Urrutia et al. (1996), the free-draining liquid holdup may be evaluated by extrapolating the dimensionless drained liquid volumes at infinite time (i.e. $t \rightarrow \infty$ or $t^{-0.5} \rightarrow 0$).
In the present work, a linear dependence of draining liquid volume on time has been observed for all the tested liquid loads also for Katapak-SP 11. The drainage kinetics is evident in Figure 7 where the experimental drained liquid volumes divided by the values extrapolated at time $t \rightarrow \infty$ are plotted versus $t^{-0.5}$.

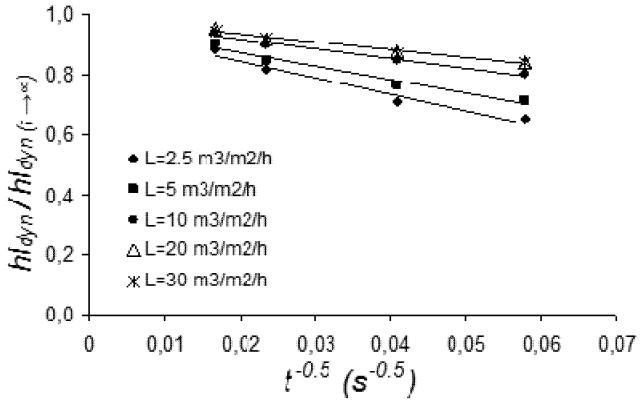

Figure 7. Dependence of the dimensionless draining liquid volume on $t^{-0.5}$.

4. COMPARISON AND CONCLUSIONS

The dynamic holdup values at infinite draining time differ from the experimental values obtained with the gravimetric method after 1h of draining for a maximum deviation of 5%. This confirms the suitability of the chosen draining reference time of 1h for the estimation of the dynamic holdup in the used column configuration. Of course for taller columns the infinite draining time method allows the reduction of the experimental draining time that otherwise would be extremely long.
Finally the static holdup value has been added to the dynamic holdup value extrapolated at infinite time and to the dynamic experimental value at 1h of draining. The comparison between these total holdups obtained from drainage measurements with the total RTD holdups is reported in Figure 8. The results and the consistency of these different techniques are therefore validated also for the complex modular structured of Katapak-SP.

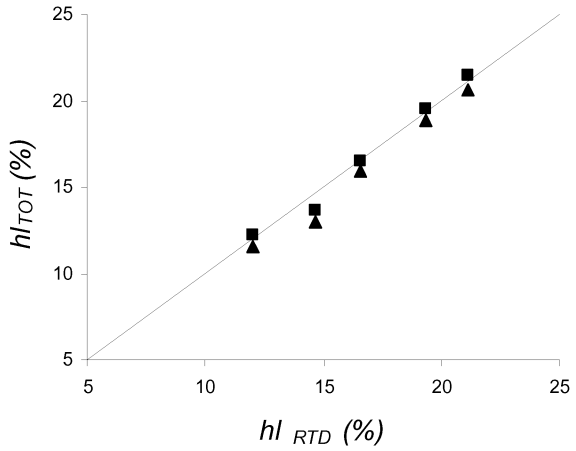

Figure 8. Total liquid holdup vs RTD holdup. Total holdup is given by the sum of the static holdup and the dynamic holdup measured after 1h of draining (▲) or the dynamic holdup from the infinite time method (■).

Acknowledgements

We acknowlegde the financial support provided by the European Commission within the 6th Framework Programme, Project "INSERT Integrating Separation and Reaction Technologies", Contract-No: NMP2-CT-2003-505862.

5. NOTATION

c	tracer concentration, $kmol/m^3$
d_{eq}	hydraulic diameter of the packing, m
D_{ax}	axial dispersion coefficient, m^2/s
$E(t)$	residence time distribution function defined by eq.(3), $1/s$
$E(\theta)$	dimensionless residence time distribution
hl_{DYN}	dynamic holdup from draining experiments, m^3/m^3
hl_{RTD}	RTD holdup, m^3/m^3
hl_{TOT}	total holdup from draining experiments, m^3/m^3
L	packed bed height, m
M	mass of the tracer, $kmol$
m_n	n-th moment of the RTD function, $kmol\ s^{n+1}/m^3$
Pe_L	axial Peclet number
Re_L	liquid phase Reynolds number
t	time, s
t_m	mean residence time, s
u_L	liquid interstitial velocity, m/s
u_{SL}	liquid superficial velocity, $m^3/m^2/h$
V^*	volumetric liquid flow, m^3/s
z	longitudinal coordinate, m
Z	dimensionless longitudinal coordinate

Greek

η_L	liquid dynamic viscosity, $Pa\ s$
μ_2	2nd moment of the residence time distribution function, eq.(8), s^2
θ	dimensionless time
ρ_L	liquid density, kg/m^3
σ	variance, eq.(8), s

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