Catalysis Today 259 (2016) 354–359

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Catalyst testing in multiphase micro-packed-bed reactors; criterion for radial mass transport

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ARTICLE INFO

Article history:
Received 11 December 2014
Received in revised form 22 May 2015
Accepted 24 May 2015
Available online 23 June 2015

Keywords:
HDS
Reaction kinetics
Radial dispersion
Micro-packed bed reactor

ABSTRACT

In catalyst activity testing, micro-packed-bed reactors are the most commonly used devices. However, the small particle sizes (typically 0.05–0.2 mm) inherent with these microreactors in multiphase systems do exhibit special hydrodynamics characteristics, that are not generally recognized.

Cold three-phase model investigations show that in micro-packed-bed reactors segregated flows of gas and liquid occur in a broad range of conditions. This situation is dramatically different from the hydrodynamics in industrial-scale trickle-bed reactors. Since in a broad range of conditions the gas flow follows preferential pathways through the micro-packed bed, the average thickness of the liquid layers is relatively large. Because the transport through these layers occurs mainly by molecular diffusion, the observed reaction rate potentially will be limited, resulting in poor radial dispersion. Even for a rather slow reaction as the hydrodesulfurization of dibenzothiophene (HDS), radial mass-transfer limitations were observed. This counterintuitive result is due to the combination of (i) the presence of apparent stagnant liquid layers with several particle diameters thickness, (ii) the low rate of radial transport, and (iii) the strong inhibition by the reaction product H_2S. A general criterion, analogous to the Weisz–Prater criterion for internal diffusion limitations, is proposed for the estimation of the influence of poor radial dispersion in catalyst performance testing in micro-packed-bed reactors. For use in practice, it is advised to start with a worst-case scenario and dependent on the outcome to relax this strict criterion.

1. Introduction

Beds packed with particles of 3 mm and larger in size are generally used in industrial applications. In multiphase operation they behave very differently from beds packed with small particles (typically 0.05–0.2 mm diameter). A good illustration is the result of hold-up measurements in micro-packed beds, reported by Márquez et al. [1], see Fig. 1.

The observations are remarkable. Firstly, the values of the liquid hold-up are high in a micro packed bed, between 0.65 and 0.85. In literature of trickle beds typically much lower values of the liquid hold-up, varying between 0.05 and 0.20, are reported [2]. Secondly, the liquid hold-up is hardly dependent on the gas-flow rate. When the gas and liquid flow were stopped, no liquid came out of the column: the dynamic hold-up is close to zero. In Fig. 2 these data are compared with typical data for industrial trickle beds.

Apparently, the inherent small particle size in the small packed beds causes the hydrodynamics to be dramatically different, compared to the industrially applied trickle-bed reactors. For particles smaller than typically 0.2 mm the capillary forces predominate over the viscous and gravitational forces in sharp contrast with large-scale industrial reactors [2]. The negligible influence of gravity is clear from the observation that essentially the hold-up is fully static. The observation that the dependency of the liquid hold-up is not very sensitive to gas- and liquid-flow rates shows a small interaction between gas flow and liquid flow. It should be noted, though, that at the lowest gas-flow rates the hold-up values are slightly higher, the higher the liquid flow rate, indicating that some interaction exists between liquid and gas flows.

In our work on the scaling down of trickle-bed reactors we extensively performed cold-flow investigations [3]. In impulse–response experiments residence times were measured for several combinations of gas (N_2) and liquid (ethanol) flow rates. A coloured dye tracer (dissolved in ethanol) was analyzed by a spectrometer. The residence time for the liquid phase τ_L (s) was calculated from the position of the peak maximum from the derivative

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http://dx.doi.org/10.1016/j.cattod.2015.05.025
0920-5861/

Notation

a_{GL}	effective gas–liquid interfacial area [$m^2\ m_{bed}^{-3}$]
Cap_L	capillary number [–]
C_s	concentration at the G-L interface [$mol\ m_{liq}^{-3}$]
d_p	catalyst particle diameter [m]
d_{slab}	thickness of the slab representing the liquid zone [m]
d_t	internal reactor tube diameter [m]
$D_{e,i,L}$	effective radial dispersion component i in the liquid phase [$m^2\ s^{-1}$]
D_L	bulk diffusivity in the liquid phase [$m^2\ s^{-1}$]
h_L	liquid hold-up (*i.e.* fraction of bed voidage filled with liquid) [$m^3\ m_{void}^{-3}$]
k_{GL}	gas–liquid mass-transfer coefficient for component i [$m\ s^{-1}$]
k_V	reaction rate constant (unit depends on n)
L	thickness of the slab representing the liquid zone [m]
n	reaction order
Re_p	particle Reynolds number [–]
$R_{v,i}^{obs}$	observed volumetric reaction rate of component i [$mol\ m_{particle}^{-3}\ s^{-1}$]
Sc	Schmidt number = $\mu_L/(\rho_L D_L)$ [–]
u_G	superficial gas velocity [$m\ s^{-1}$]
u_L	superficial liquid velocity [$m\ s^{-1}$]
WHSV	weight-hourly space velocity: ratio liquid mass-flow rate/catalyst weight [h^{-1}]

Greek

ε_b	bed voidage [$m^3\ m_{bed}^{-3}$]
ϕ	Thiele modulus [–]
ϕ_i	actual flow rate ($i = L$: liquid, $i = G$: gas) [$\mu L\ min^{-1}$]
Φ_{rad}	Weisz modulus for radial mass-transfer [–]
η	catalyst efficiency [–]
μ_L	liquid viscosity [$kg\ m^{-1}\ s^{-1}$]
ρ_L	liquid density [$kg\ m^{-3}$]
τ_b	tortuosity of the bed [–]
τ_L	liquid residence time [s]
τ_θ	dimensionless residence time [s]

of the breakthrough curve of the dye. In the usual way τ_L was converted in the dimensionless τ_θ, using $u_{total} = u_L + u_G$:

$$\tau_\theta = \frac{\tau_L}{L/u_{total}} \quad (1)$$

For single-phase (ethanol) experiments we found $\tau_\theta = 1$, independent on the flow rate, as expected. However, for multiphase systems the results are very different, as illustrated in Fig. 3.

At low liquid fractions (and thus large gas fraction) $\tau_\theta \gg 1$ (Fig. 3a). Not surprisingly, at the highest liquid fraction (Fig. 3b), $\tau_\theta \to 1$, τ_θ is independent of the liquid fraction of the flow. Thus, for low gas flows the result is similar to the single flow experiments, whereas for high gas-flow rates this is not the case. The interpretation is straightforward and is related to the hydrodynamics.

At a high liquid fraction in the flow, the gas bubbles travel with the liquid flow through the bed, and as a result of this, the residence times of gas and liquid are the same and can be predicted from the sum of gas and liquid flow rate, resulting in $\tau_\theta = 1$. Good examples, where $\tau_\theta = 1$ holds, are bubble flow and segmented flow in capillaries (Taylor flow).

However, if a part of the gas by-passes the liquid phase the value of τ_θ will be >1. The occurrence of by-passing in packed beds is due to capillary forces that keep the liquid together if there is only a

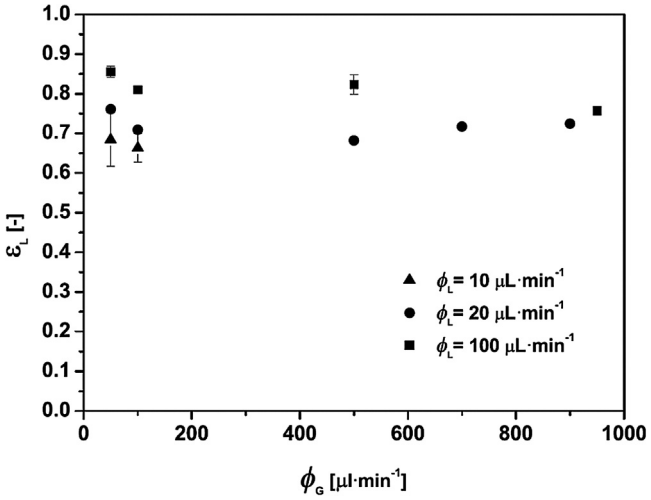

Fig. 1. Liquid hold-up ε_L (liquid volume/void volume) for several combinations of gas flow rate (ϕ_G) and liquid flow rates (ϕ_L) for a flow of N_2 and tetradecane over $106 < d_p < 125$ µm non-porous glass beads in a 2.0 mm internal diameter glass tube. Figure taken from [1].

limited interaction between gas and liquid (low-interaction mode). The gas thus follows preferential pathways (a kind of snake flow). The data in Fig. 3 show for most conditions extensive by-passing of the gas. The extent of by-passing increases with increasing gas-flow rate.

The question arises whether extensive by-passing does impact the interpretation of results observed in catalyst testing research. In multiphase operation in packed beds the by-passing of the gas phase implies more or less apparent stagnant liquid zones, *i.e.* liquid zones that stay in the same place, but in fact there is a laminar down flow of liquid [4]. One of the consequences of the occurrence of these apparent stagnant zones is that radial transport on the reactor scale is reduced; the thicker the apparent stagnant zone is, the slower the radial transport will be and, therefore, a lower conversion could be anticipated.

2. Criterion for radial dispersion in packed beds with segregated flows

Regarding catalyst testing, a sound theoretical basis needs to be developed resulting in convenient criteria to assess in advance the interference of mass-transfer gradients within the particle, in the film surrounding the particle or between the gas and the liquid phase. In addition non-ideal reactor behaviour due to extensive

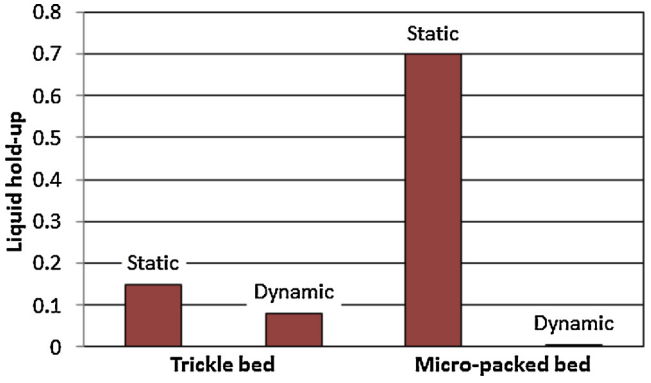

Fig. 2. Comparison of typical liquid hold-up values for industrial trickle beds and micro-packed beds; the dynamic hold-up for micro-packed beds is close to zero.