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A comparison between the monolithic reactor and the trickle-bed reactor for liquid-phase hydrogenations

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Abstract

A comparison is made between the monolithic catalyst reactor and the trickle-bed reactor for applications in liquid-phase hydrogenations. Their relative merits with respect to factors like cost, flow distribution, pressure drop and scale-up are discussed. Based on a simple mathematic model, computer simulations have been carried out which illustrate the relative performance in terms of productivity, selectivity and pressure drop. A consecutive hydrogenation reaction has been taken as a model reaction.

1. Introduction

Monolithic catalysts are continuous unitary structures which contain many small, parallel passages. Catalytic species are incorporated either into a thin layer of a porous oxide deposited on the channel wall (a washcoat) or into the wall itself. The monolithic reactor (MR) is widely used for gas-phase processes, predominantly in environmental applications including automotive exhaust gas cleaning. It can also be used for multiphase reactions [1,2]. Until now, most of the work has been devoted to hydrogenations. EKA-Nobel operates several plants in which a MR is used in the hydrogenation step of the alkylantraquinone process for H_2O_2 production [3]. Fig. 1 illustrates a MR and the desired flow pattern (Taylor flow) with a series of alternate gas and liquid plugs. This flow pattern has several advantages; good mass transfer characteristic due to the internal recirculation within the liquid plugs and the short diffusion distance through the thin liquid film separating the bubble from the wall. The cross-section of a typical washcoated monolithic structure is also illustrated.

The use of trickle-bed reactors (TBR) for three-phase hydrogenations is common practice. The differences between a TBR and a MR originate from the differences in catalyst geometry which affect catalyst load, internal and external mass transfer resistance, contact areas as well as pressure drop. These effects are analyzed by computer simulations based on relatively simple mathematical models of the MR and the TBR. The simulations illustrate in a quantitative way some of the trade-offs that exist and, more specifically, indicate regions where one of the two has a greater potential.

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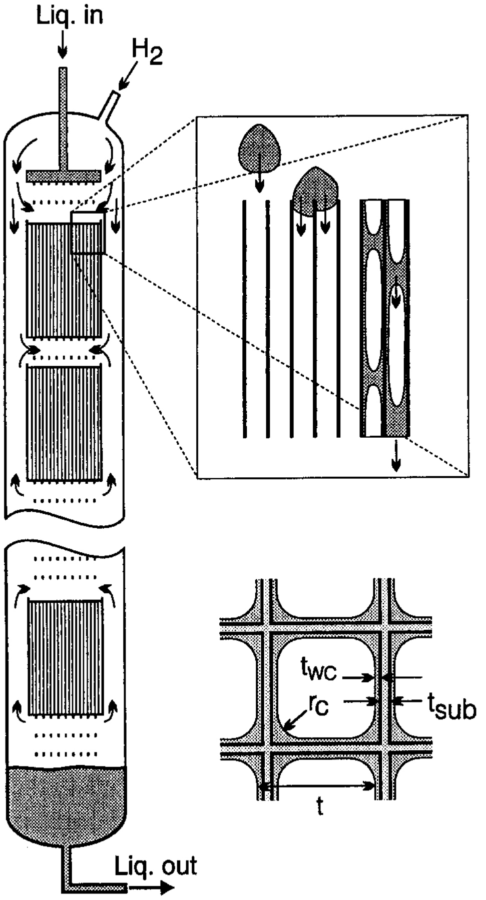

Fig. 1. The monolithic reactor.

2. Monolithic vs. trickle-bed reactors — a qualitative comparison

The most important differences between the TBR and the MR are summarized in Table 1. Obviously, less experience has been accumulated with monoliths, in particular for three-phase applications. They are also more expensive to make. Therefore, the use of monoliths can only be economically justified for three-phase processes in which it offers a distinct advantage, like higher yield (improved selectivity), increased throughput of a plant, or lower investment or running costs. Of particular interest are situations in which a MR substantially simplifies the design or operation of a unit. It should be possible to reduce the cost of monoliths by making use of the experience of manufacturers of modern heat exchangers, which contain similar structures. It should also be noted that the high cost of monoliths is in part explained by the fact that they are mostly designed to meet the demands of high-temperature operation.

For simple reactions occurring fully in the kinetic regime, the TBR will outperform the MR due to the higher load and the lower cost of the catalyst. In processes involving faster reactions, especially if there are selectivity concerns (like the intermediate product being the desired one), it is not obvious which reactor is best suited for the process. The diffusion length in a particulate catalyst is longer than in a monolithic catalyst and hence the effectiveness factor is typically lower for the TBR [5]. As a consequence, the conversion per unit volume of catalyst is lower in the TBR. Moreover, the diffusion length can influence the selectivity of the reaction if the rate is controlled by diffusion. Two ways to reduce the diffusion length in TBRs are: (1) to use smaller catalyst particles, or (2) to use a catalyst with the catalytically active species located only near the outer surface of the particle (an egg-shell). The first remedy, however, will increase pressure drop and the second one reduces the catalyst load in the reaction zone, making the loads of a TBR and a MR comparable. For instance, the volumetric catalyst load for a bed of 1 mm spherical particles with a 0.1 mm thick layer of active material is 0.27, while for a catalyst made from a commercial cordierite structure (square cells, 400 cpsi, wall thickness 0.15 mm), also with a 0.1 mm thick layer of active material, it is 0.25.

The frictional pressure drop is always lower in the MR, up to two orders of magnitude, for all relevant sizes of catalyst particles (shell catalysts too). For a MR operating in downflow mode, it is possible to balance the frictional pressure drop with the hydrostatic pressure of the liquid inside the channels. The essentially zero net pressure drop provides an opportunity to operate the MR with internal recirculation of hydrogen. Since the

Table 1
Characteristics of trickle-bed and monolithic reactors for three-phase processes

Aspect	TBR	MR
Catalyst		
Manufacture	Well established techniques	Established for gas phase at developmental stage for liquid phase
Cost	Low	Moderate–high
Volumetric catalyst load	0.55–0.6 for conventional packings; < 0.3 for shell catalysts	0.05–0.25
Handling	Replacement using well established procedures	Monolithic blocks are assembled in frames that can be stacked on top of each other
Size	Pellets, 1–5 mm	Channels, 1–4 mm, possibly with a washcoat, 50–150 μm
External surface area	1000–3000 m^2/m^3	1500–2500 m^2/m^3, external mass transfer better than in TBR [4]
Diffusion length	0.1 (shell)–2.5 mm	50–150 μm
Operating conditions		
Superficial velocities	Liq. 0.005–0.05 m/s Gas 0.05–1.5 m/s	Liq. 0.03–0.15 m/s Gas 0.05–1.0 m/s, preferably the sum of superficial velocities should be ~ 0.4 m/s
Pressure drop	High for small particles	Very low
Mode of operation	Pseudo steady-state	Inherently unsteady
Design		
Experience	Many units in operation	Only one full scale process in operation
Gas recirculation	External, needs compression	Internal, no pump needed
Scale-up	Gas/liquid maldistributions can appear	Simple [3]
Inlet distribution	Good distribution required; liquid tends to flow towards the wall	Very good distribution needed

gas does not need to be recompressed, an open passway from the bottom of the reactor to the top is all that is needed (see Fig. 1).

3. Monolithic vs. trickle-bed reactors — mathematical modelling

The mathematical models of the monolithic and the trickle-bed reactors, as well as the methods used to evaluate the model equations, are given in [5]. The correlations used for the MR are taken from [2] and those used for the TBR are given in [6].

3.1. Major assumptions

The following assumptions are made: (I) concurrent downflow, (II) isothermal operation, (III) no axial dispersion, (IV) pseudo steady-state operation, (V) the physical properties do not vary in the reactor, (VI) complete wetting of the catalyst, (VII) a consecutive hydrogenation reaction of the type:

$$A+H_2 \overset{r_1}{\Rightarrow} B; \quad B+H_2 \overset{r_2}{\Rightarrow} C \tag{1}$$

with the reaction rates given by:

$$r_1 = k_1 \frac{K_{H_2}c_{H_2}}{1+K_{H_2}c_{H_2}} \frac{K_A c_A}{1+K_A c_A + K_B c_B};$$

$$r_2 = k_2 \frac{K_{H_2}c_{H_2}}{1+K_{H_2}c_{H_2}} \frac{K_B c_B}{1+K_A c_A + K_B c_B} \tag{2}$$

These rate expressions are taken as prototypes for Langmuir–Hinshelwood (LH) type kinetics. This is obviously a gross simplification knowing

Table 2
Parameter settings used in the calculations

Catalyst		*Liquid*	
Porosity	0.50	Density	800 kg/m^3
Tortuosity	3	Viscosity	$5\cdot10^{-4}$ Pa s
		Diffusivity of H_2	$8\cdot10^{-9}$ m^2/s
Gas		Diffusivity of A and B	$1\cdot10^{-9}$ m^2/s
Density	Gas law	Inlet conc. of A	400 mol/m^3
Viscosity	$1\cdot10^{-5}$ Pa s	Henry's constant, H_2	$3\cdot10^{4}$ Pa m^3/mol
Kinetic parameters		*Monolith* (*notation in Fig.* 1)	
k_1	4–400 mol/m^3,s	Pitch, t	1.27 mm
k_2	0.4–640 mol/m^3,s	Wall thickness, t_{sub}	150 μm
K_A,K_B	0.0025 m^3/mol	Washcoat, t_{wc}	30–100 μm
K_{H_2}	0.0296 m^3/mol	r_c	0–350 μm t_{wc}(wc), 0(inc)
Trickle-bed		*Operation*	
Bed void		Pressure	10 bar
Fraction	45%	Sup. gas. vel.	0.40 m/s $- u_{L,sup}$
		Sup. liq. vel	0.02–0.05 m/s

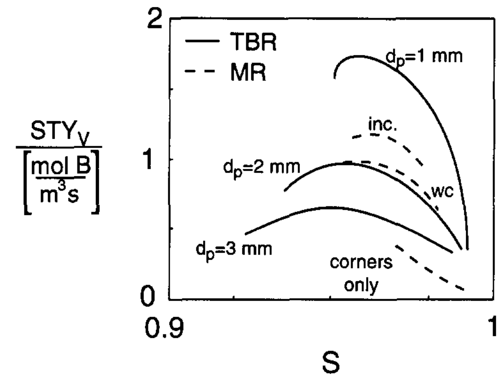

Fig. 2. Attainable productivity and selectivity with various catalyst geometries. On each curve the thickness and load of the catalyst decrease from left to right. $k_1 = 40$ mol/m^{3}s, $k_2 = 0.1\ k_1$. Volumetric catalyst loads: TBR, 4.0–55%; MR: incorporated type (inc) 15.1–35.5%, washcoated (wc) 8.6–28.6% and washcoated with all active material in the corners (corners only) 0.6–6.6%.

that hundreds of different LH equations have been reported in the literature for various reactions [7,8]. Each expression has been tailored to match a particular hypothesized reaction mechanism or to provide a good fit to a set of kinetic measurements. In spite of that, the kinetic expressions above can be informative in many situations since they capture two key aspects of heterogeneous catalysis; the rate of the reaction and the saturation of the surface by the reactants. The values assigned to the various kinetic and adsorption parameters in this work produce rates that agree well with those reported in the literature.

The TBR is assumed to be filled with spherical catalyst particles with the active material present in a shell of thickness $r_p x_{shell}$. The MR is assumed to operate in the Taylor flow regime. The channels have square cross-section and a cell density of 400 cpsi. The catalytically active material is assumed to be either incorporated into the support structure itself (inc) or in a slightly non-uniformly distributed washcoat (wc). Some of the assumptions made above are in part justified by the fact that this is a comparison between two reactor types, e.g. the particular kinetic expressions used are not assumed to have a strong effect on the *relative* performance between the MR and the TBR.

3.2. Computer simulations

The assumptions made above lead to a nonlinear system of ordinary differential equations, which together with the inlet conditions constitute an initial value problem. The system was integrated using a semi-implicit Runge–Kutta method [9]. The effectiveness factors were estimated using a one-dimensional finite difference method. For the non-uniformly distributed washcoat, the effectiveness factors were evaluated using an approximation presented in [5,9]. The simulations were performed on a PC-486 using the MATLAB software package [10].

3.3. Simulation results

The parameters used in the simulations are, if not otherwise stated, those given in Table 2.

Catalyst geometry

As mentioned above, the most obvious difference between the MR and the TBR lies in the shape of the catalyst support and in the distribution of active material. Fig. 2 illustrates the relationship between the catalyst geometry, the productivity (or space time yield per volume, STY_v, expressed as net moles of the intermediate product B formed per m^3 and s) and the selectivity (S, here defined as net moles of B formed per moles of A consumed). The comparison is made for the same superficial flow rates and conversion ($x_A = 10\%$). A low conversion level was chosen so that the effect of different pressure drops should not considerably confound the comparison. For each curve the thickness of the catalytic layer, and hence the catalyst load, decreases to the right. Selectivity increases with decreasing thickness while the productivity goes through a maximum. For the TBR this can be explained by the lower effectiveness factor associated with thicker catalyst layers. In addition, for the MR the external surface area decreases as the washcoat becomes thicker. It can be concluded that for a reasonably fast reaction the best performance in terms of STY_v and S can be attained using low diameter shell catalysts. The performance of a monolithic catalyst is comparable to that of a 2 mm particle. Moreover the incorporated type is somewhat better than the washcoated one. The performance of a MR with a very poorly distributed washcoat, all active material in the corners, has been added to illustrate the negative effect of non-uniform distribution.

Reaction kinetics

For slow reactions without side reactions the TBR is favored simply because higher catalyst loads can be used. Fast reactions and/or competing side reactions make large particles unsuitable and smaller particles or shell catalysts must be used. Fig. 3 illustrates the trade-off between catalyst volume on one side and surface area and diffusion length on the other. The curves shows lines of equal STY_v in the MR and the TBR for the catalyst geometry indicated. The rate of the first reaction (in the absence of mass transfer) at the reactor inlet (r_{1s}) is used as the abscissa and the ratio of rate constants k_2/k_1 is used as the ordinate. The lower left corners in the figure corresponds to a slow reaction with small selectivity problems, while the upper right corner represents the reverse situation. In general, a MR can perform better than a TBR if the initial rate exceeds 10 mol $m^{-3}s^{-1}$ for model parameters and design/operating variables considered. The area of the higher performance of a MR shifts to the left with the increase of a particle size and/or a shell thickness in a TBR. This is strictly related to the increasing diffusion path inside the particles. The border lines

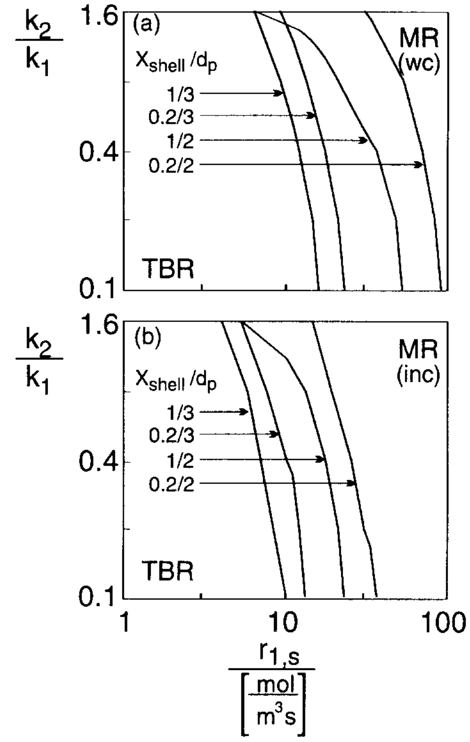

Fig. 3. Contours indicating equal productivity for a TBR and a MR as a function of the rate constants. Monolith geometries: (a) washcoated, $t_{wc} = 50$ μm, $t_{sub} = 150$ μm, $r_c = 150$ μm; (b) incorporated, $t_{wc} = 50$ μm, $t_{sub} = 50$ μm, $r_c = 0$ μm. TBR geometries are given in the figure.

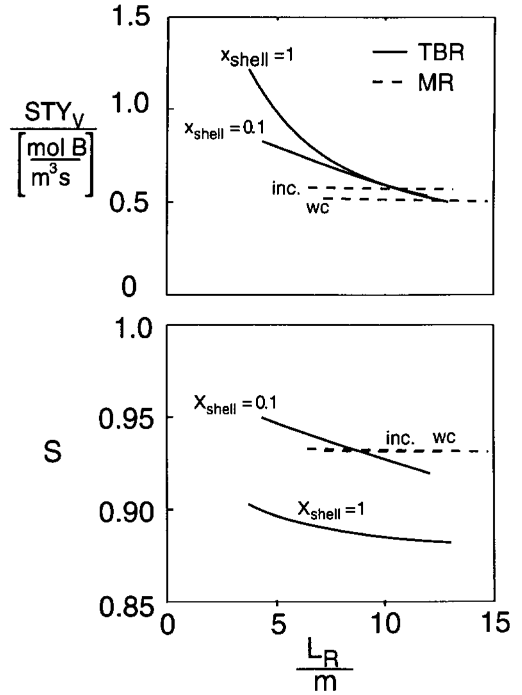

Fig. 4. Productivity and selectivity as a function of the reactor length. MR: $u_{L,sup}=0.02$–0.04 m/s, (wc) washcoated $t_{wc}=50$ μm, $r_c=150$ μm, (inc) incorporated $t_{wc}=50$ μm, $t_{sub}=50$ μm, $r_c=0$ μm; TBR: $d_p=1.0$–2.5 mm, $u_{L,sup}=0.019$–0.037 m/s.

of equal performance for a monolithic catalyst of incorporated type (Fig. 3b) are shifted more to the left than for washcoated monoliths. This can be attributed to the higher volumetric catalyst load for the 'incorporated' monolithic catalysts.

Pressure drop

The advantage of small particles in the TBR is limited by the acceptable pressure drop. As the size of a TBR is increased it is necessary to increase both the reactor length and the diameter since the ratio between them must be kept reasonable. As a consequence, the acceptable pressure drop per unit length decreases and this necessitates the use of larger particles. This also causes the external surface area to decrease and the diffusion distance to increase. In Fig. 4, productivity and selectivity of a TBR is plotted against the length of the reactor which is filled with the smallest particles producing an acceptable pressure drop (2 bar) for a fixed conversion ($x_A=0.50$). The lines for a MR of the same length operated with zero pressure drop (i.e. with balance between the frictional and the hydrostatic pressure drop) are also plotted. The productivity of a TBR for the range considered is higher than that of a MR, obviously at the cost of a much higher pressure drop. This is due to the higher volumetric catalyst load in the TBR. Contrary to this, selectivity is rather higher for a MR, except for very thin shell catalysts in the TBR. It is worthwhile to mention that the MR is almost insensitive to variations in bed depth. The importance of this difference will depend on the acceptable pressure drop, the required space velocity and the viscosity of the liquid.

4. Conclusions

A monolithic reactor can be an attractive alternative to a trickle-bed reactor for hydrogenations proceeding consecutive reaction scheme with an intermediate as the product desired. For the model parameters and design/operating variables considered, a MR can perform better for fast reactions characterized by initial rates higher than 10 mol $m^{-3}s^{-1}$. For such reactions, performance indices are better than those for a TBR with particles larger than 2 mm. A TBR is characterized by much higher frictional pressure drop which is negligible in a MR and is balanced with hydrostatic pressure. This creates an unique possibility of operation with an internal hydrogen recirculation without using a pump.

Acknowledgements

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