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Catalysis Today 111 (2006) 111–118

CATALYSIS TODAY

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Shouldn't catalysts shape up? Structured reactors in general and gas–liquid monolith reactors in particular

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Abstract

In this paper, the advantage of structuring catalytic reactors is discussed. In structured systems, the exact shape of all column internals is determined by design rather than chance. This results in two advantages for the engineer in charge of designing a reactor: (1) the structuring introduces additional characteristic length scales, leading to new degrees of freedom that allow decoupling of phenomena that otherwise would need a sub-optimal compromise and (2) full control over the entire geometry results in higher precision. Taking full control over the geometry boosts performance, especially if the catalyst is tailored to the reactor design.

The monolith structure is the best-known example of a structured catalyst. We discuss the industrial benefits and practical pitfalls of this honeycomb of parallel capillaries that allows the advantages of microfluidics to be applied on an enormous scale. In this paper it is argued that the monolith is most suitable for processes that are (1) stable enough for packed-bed operation and (2) need better mass transfer than can be obtained in any conventional reactor, including the trickle bed and the stirred tank reactor. This includes several large-scale processes such as HDS. Fine chemical synthesis, where the objective of robust scale-up and predictability will never be met using stirred tanks, may equally benefit from the scalable ultra-high mass transfer that is obtained in monoliths.

Keywords: Structured reactors; Monoliths; Multiphase reactors; Reactor design

1. Introduction

Almost all multiphase reactor designs are compromises that try to resolve conflicting wishes. Trade-offs are all too common in reactor engineering, such as selectivity versus activity and catalyst effectiveness versus pressure drop.

In structured catalysts (or structured reactors, which amounts to the same) the entire geometry from particle size to reactor size is fixed by design. Then, the predetermined geometry can be optimised for intra-particle reactions and extra-particle hydrodynamics alike. This is in contrast to the random orientation of particles that results from dumping catalysts in a column, and also in contrast to chaotic eddy patterns in multiphase turbulent systems.

Exploiting precision in geometry is well-known in catalysis (Fig. 1). A classic example of structuring is the egg-shell catalyst. The depth of the active outer layer is a new length scale that introduces a new degree of freedom, which the reactor engineer may use to optimize his design. Another example is the zeolite, in which the size of the channels introduces a degree of freedom that is absent in other silica/alumina supports. Essentially, these two examples use geometric features to optimize the interplay of diffusion and reaction. Apart from these two intra-particle phenomena, multiphase reactor design involves extra-particle heat transfer, mass transfer and momentum balances. The focus of the present work highlights how structuring and geometric degrees of freedom are equally beneficial for these aspects of reactor design.

We demonstrate this for parallel straight channels of capillary dimension in a honeycomb or monolith reactor in multiphase applications. We assume the reader is familiar with the monolith catalyst support and refer to refs. [1,2] for

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URL: http://www.dct.tudelft.nl/race/

0920-5861/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.cattod.2005.10.014

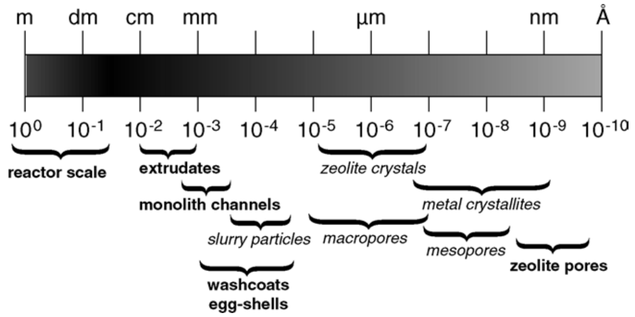


Fig. 1. Relevant characteristics sizes in catalysis engineering. The shapes in bold can be controlled with great precision. For the shapes in italics, control is less precise and a broad distribution is often found.

introductory texts and to refs. [3,4] for more detailed discussions of reactor design and catalyst preparation.

Throughout this text, we will use monolith catalyst structures as the example to demonstrate structured reactor technology, as it is the structure we are most familiar with. Many different examples of catalytically active structures, in which full control over the geometric features allow improved reactor design, are known. Examples include structures similar to distillation internals [5] and woven fibers [6]. More examples are given in a monograph on structured reactors [1] and two special issues of Catalysis Today on the subject [7,8].

2. Design strategies and the window of reality

When considering design strategies, one can choose to start with the catalyst and adapt the reactor, or vice versa, to adapt the catalyst to the characteristics of the reactor.

Krishna and Sie [9] proposed to start with a wish list on three levels: (1) the catalyst itself; (2) the manner of heat and mass contacting in general; and (3) the details of the reactor hydrodynamics. Also, they proposed to keep all options open until the wish list is completed for all three levels. Dudukovic et al. [10] remarked with respect to the three-level approach that, in the current competitive economic environment, companies do not have the luxury to consider these levels sequentially. Rather, process development benefits from ab initio interaction of the chemists that formulate the catalyst with the reactor engineers that design the commercial unit.

Structuring the catalyst/reactor requires the same interaction of chemists and chemical engineers, and both can benefit from the degrees of freedom offered by total control over the reactor geometry. While it remains vital to start with balances over the catalytically active material – the only true ‘reactor’ in the system – changes in catalyst formulation affect the design decisions for the extra-particle space. So, the increasingly common interaction between catalysis and reactor engineering drives the integrated view of the geometric aspects of reactor design in general and the development of structured reactors in particular.

All too frequently, the improvement of catalyst formulation slows down or even stops when further enhancements move the reactor out of the kinetic regime and something else (such as heat or mass transfer) becomes limiting. This “practical ceiling” has given rise to a so-called “window of reality” that suggests that reactors are practically limited to about $10\ \mathrm{mol/m^3_{reactor}/s}$ [11]. An example is hydrodesulphurisation, which used to be a typical slow reaction in a trickle bed. Recent legislation has driven a huge increase in catalyst activity, and now the tried-and-trusted extrudates are increasingly diffusion limited and no longer optimal. Design advances will have to address extra-particle and intra-particle limitations alike to escape the window of reality that, for HDS, not only limits the rate of conversion, but also limits optimal use of the catalyst to selectively convert the right components and limits the catalyst life by deactivation processes that are induced by diffusion limitations.

As experiments in multiphase monoliths have demonstrated [12], fixed-bed reaction rates of at least $100\ \mathrm{mol/m^3_{reactor}/s}$ at minimal pressure drop are easily possible using structured-microchannel reactors.

3. Decoupling length scales

A prominent trade-off in fixed beds is related to the particle size. Small particles are often desired for maximal catalyst effectiveness, which impacts activity, selectivity and stability alike. In trickle beds, using smaller particles implies sustaining a higher pressure drop. At some point, the pressure drop simply becomes too high for practical purposes.

In random packed beds, the particle size determines both the pressure drop and the effectiveness, see Fig. 2(a). A possible escape is the aforementioned egg-shell catalyst, which decouples the characteristic length of diffusion and reaction from the particle size. This approach is effective, but results in a large idle fraction of the reactor volume. Also, egg-shells do not help to improve the mass transfer outside the particle.

Structuring the extra-particle space as well yields the class of structured catalysts of which the honeycomb monolith is the most prominent representative. Now, the characteristic length of diffusion and reaction is the wall thickness and the characteristic length for the momentum balance and the extra-particle mass balance is the channel diameter. There is no reason why these lengths should be coupled (Fig. 2(b)). Thick walls can just as easily be made as thin ones, and a wide range of channel sizes, from ~5 to ~0.5 mm, are commercially available.

The possibility to choose the extra-particle length-scale independently introduces the extra degree of freedom that allows maximum catalyst effectiveness at minimal pressure drop. The added value, in comparison to egg-shell approaches, is that the geometry, the shape of the interstitial voids now becomes part of the design. In other words, the external mass transfer can be optimised as well.

4. Avoiding turbulence

It is almost an axiom in chemical engineering that mass transfer requires energy. Naturally, this stems from the thinning of boundary layers at increased fluid velocities. It also stems from the increased break-up of bubbles by turbulent eddies in multiphase systems.

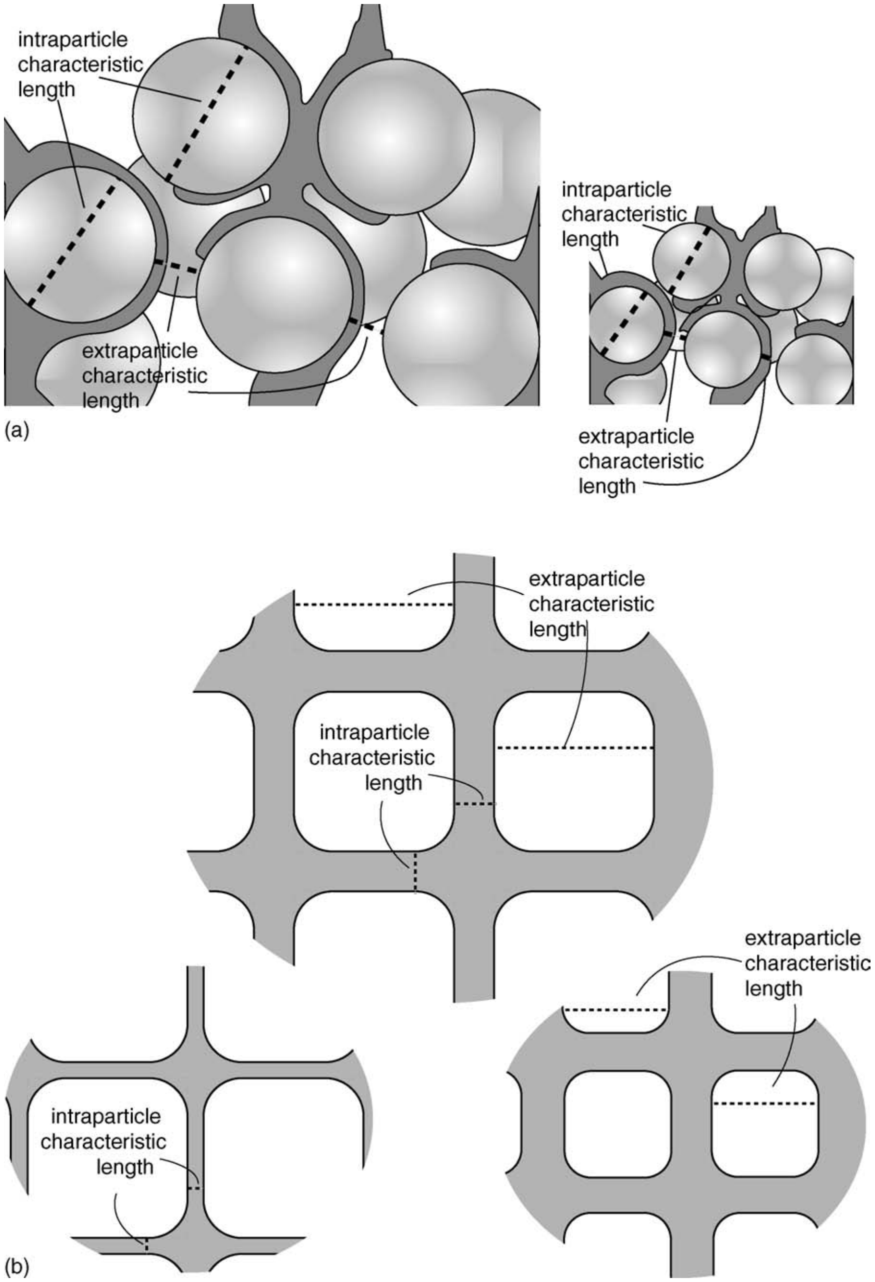


Fig. 2. Coupling and decoupling in catalytic reactors. (a) In a random packing, the extra-particle and intra-particle lengths scale are coupled. The ratio of these lengths is fixed. (b) In a structured packing, the intra-particle and the extra-particle length can be varied independently. The ratio of these lengths is a new degree of freedom that can be optimized in a design.

Indeed, turbulence is an effective method to achieve thin boundary layers and small bubbles, but it has never been an efficient one. Most of the energy supplied to a turbulent system is lost in eddies that do not contribute to mass or heat transfer. As a result, very few industrial unit operations operate in highly turbulent conditions. The reactor engineer may dream of scaling the intense contacting in labscale autoclaves to industrial units, but the energy requirement to do so in large reactors prevents this dream from becoming reality. Apart from the energy requirements, turbulence is a hard-to-understand phenomenon. Due to the anticipated trouble of scaling up a turbulent bubble column, a multitubular system, more awkward to build but more predictable to design, is sometimes preferred for commercial and time-to-market considerations [9].

The alternative to turbulence is laminar flow in small channels. The small channels ensure a significant contact area between the fluids and the catalyst. Single-phase laminar flow has no convection perpendicular to the wall, and radial diffusion alone results in rather poor mass transfer: very small channels would be needed to reduce the characteristic time of diffusion. On the other hand, the gas–liquid (or liquid–liquid) segmented flow pattern in capillaries has long been known for its excellent mass transfer, even in millimeter-sized channels. The segmented flow has the added benefit of eliminating

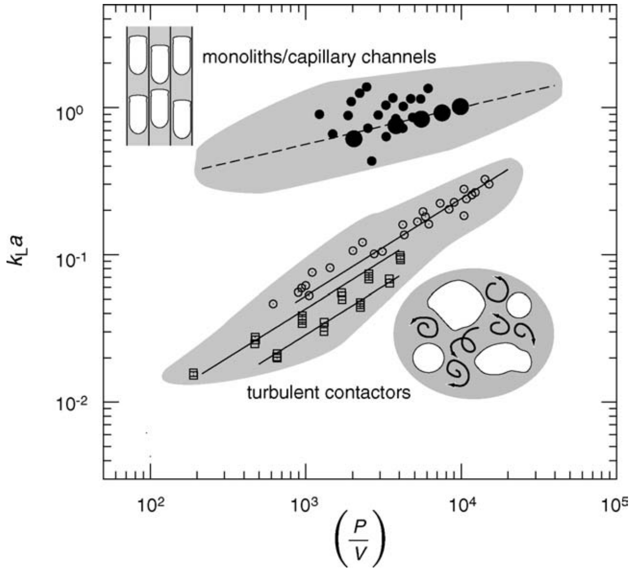


Fig. 3. Comparison of mass transfer group $k_L a$ (s^{-1}) in structured monolith reactors and turbulent bubble columns and agitated tanks as a function of the power input per unit reactor volume (P/V) (W/m^3). All data for oxygen/water adapted from [13].

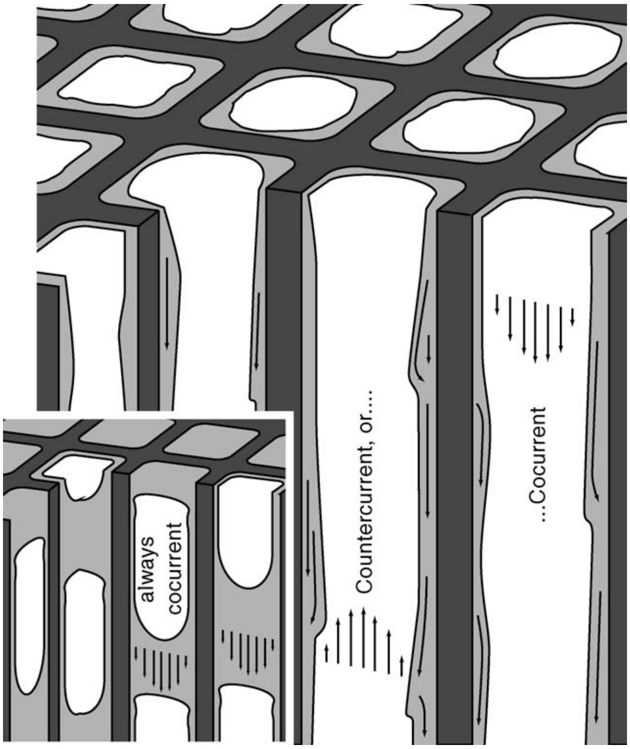


Fig. 4. Counter-current flow in larger monolith, where the liquid trickles down in a falling film on the wall. The gas can flow upward or downward in the center. The inset in the lower-left corner shows the co-current Taylor flow in smaller channels.

coalescence, keeping the bubbles small inside the channel. Fig. 3 shows that an order of magnitude improvement in mass transfer versus power consumption can be obtained in capillary channels.

While Fig. 3 was derived for physical absorption without a catalyst, when a catalyst is coated on the walls of the channel a similar improvement is obtained. For gas components that are transferred to the wall, the thin lubricating film that exists between bubbles and the wall in segmented capillary flow poses an easily surmountable resistance. Also, the bubbles cause circulation inside the slugs that reduces the diffusion distance to the catalyst for liquid-phase components by more than an order of magnitude.

In brief, segmented flow in capillary channels gives more bang for the buck than turbulence.

5. Counter-current flow

Multiphase processes that suffer from product inhibition can benefit from counter-current flow of gas and liquid. Again, hydrodesulphurisation is a good example [14]. The perennial problem with counter-current flow is flooding, i.e., upward flow of liquid due to the drag exerted by the gas. For such applications, one should prevent vigorous contact of the gas and liquid, which may be achieved by using large channels. Fig. 4 shows how monoliths with larger channels allow liquid to trickle down in the corners of the monolith channels while the gas flows upwards. The gas–liquid interface can be further stabilized by using fins on the channel walls, see Fig. 5 [15].

Again, the ability to precisely define the geometry, and to independently choose channel diameter and wall thickness gives the engineer the ability to optimize the complex interplay of flooding tolerance and diffusion/reaction phenomena.

6. Precision

In structured reactors, the geometry typically consists of many repeats of a simple building block. This holds for monoliths, but also for the corrugated sheets that are used in Katapak and similar packings. Repeating the exact same geometry over and over suggests that a design for that single building block is sufficient to describe the entire reactor.

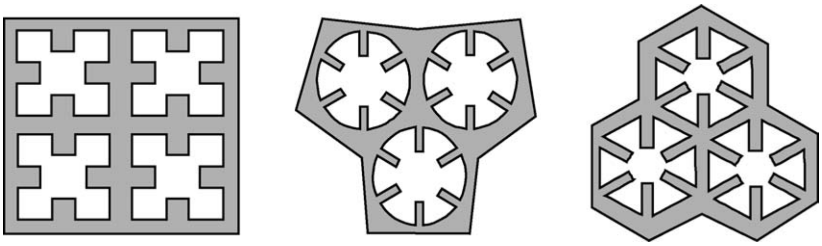


Fig. 5. Several monolith geometries with internal fins, used to stabilize the gas–liquid interfaced in counter-current flow.

The well-defined repeating shape is accompanied by a well-defined laminar flow pattern that does not suffer from the uncertainties associated with turbulence. As a result, a phenomenal precision in reactor design can be achieved. In fact, in the first study of multiphase monoliths known to us, Özel [16] coined the phrase ‘‘controlled channeling’’, in combination with ‘‘the uniformity of passageways’’, to describe their observed better distribution in comparison to trickle beds, especially at low flow rates.

Whether that precision can actually be achieved has recently been doubted. Tomographic studies have revealed that hold-up and velocity vary from channel to channel [17,18]. For the falling film reactor, it was found that variations within the channel, from corner to corner, cause significant backmixing [19]. For segmented flow in monoliths, a careful analysis of the hydrodynamic stability reveals that, provided the reactor is operated in the proper downflow regime, the effect of maldistribution is very limited. Whilst the hold-up distributions are alarming at first, the impact of hold-up on the residence time and on mass-transfer performance is minimal [20]. Results in full-scale commercial units [21] confirm that the high precision of the single channel can be achieved, even when significant hold-up variations are present.

The deviations from plug flow are easily eliminated by the stacking of several monolith blocks. Of course the gas–liquid distribution and stacking procedure require some consideration, but considerable progress has been made. In fact, the distribution techniques outlined by Satterfield and Özel [22] several decades ago are useful and have been succesfully used for film flow and segmented flow alike.

7. Structuring the channel wall

Another level of structure may be obtained inside the wall of monolith channels. Fig. 6 shows a cross section of a monolith with a needle-like wall structure [23]. The permeability of these walls can be chosen such that the capillary pressure of a passing gas bubble ($\Delta p \sim \gamma/d$) is enough to appreciably push the liquid into the porous wall, i.e., to pump perpendicular to the axial direction and enhance the mass transfer to the otherwise stagnant liquid inside the wall structure. Note that this allows us to have an order of magnitude shorter length for diffusion and reaction, without altering the channel diameter.

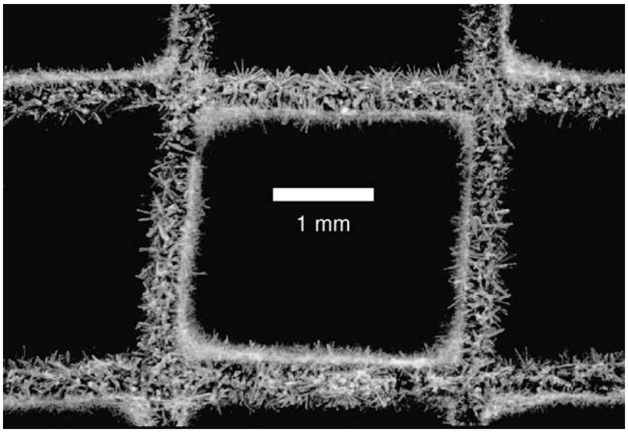


Fig. 6. SEM micrograph of monoliths where the channel walls have a permeable needle-like structure of acicular mullite.

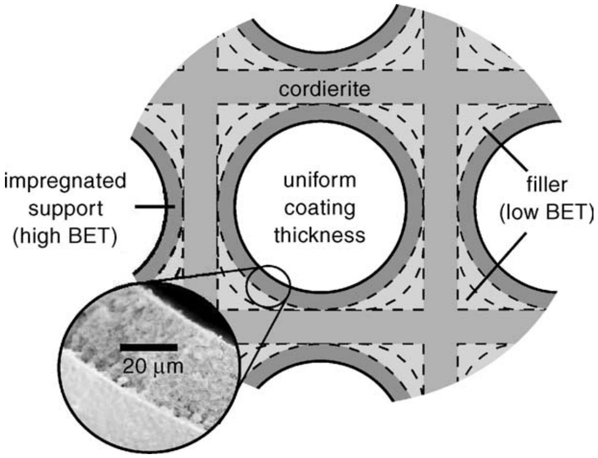


Fig. 7. Egg-shell monolith catalyst.

A somewhat less exciting but equally useful example of structuring the catalyst wall is the preparation of egg-shell structures, similar to the ones used in packed beds. Fig. 7 shows how subsequent coating steps may be used to apply low-BET layers (e.g. α-alumina) and high-BET layers (e.g. γ-alumina). The first layers are applied to fill up the corners, and a final coating is applied to a round channel to generate an egg-shell layer of uniform thickness [24]. During later impregnation of a catalyst precursor, most of the material will adsorb on the outer layer with the higher surface-area. The first coating layers may also be used to block the macropores of the bare walls, which otherwise might fill up with poorly accessible active material.

8. Areas of application

So far, we have discussed the benefits of using a defined structure inside a reactor in general terms. It remains to be determined in what kind of processes these advantages play out best. Table 1 shows a brief comparison of the monolith with the

Table 1
Reactor comparison

	Trickle bed	Monolith reactor		Slurry reactor
		Counter-current	Co-current	
Intraparticle effectiveness	+/−	+/−	+/−	++
Catalyst inventory	++	+/−	+/−	−
k_La	−−	−−	++	+
k_Sa	−−	−−	+	+
G → L → S mass-x-fer	+/−	+/−	++	+
Pressure drop/power in-put	−−	+	++	+/−
Counter-current possible	−	++	−−	
Plug flow	+	+/−	+	−−
Scalability	+/−	+/−	+/−	−−
Safety, quick shutdown	−	+/−	++	−

archetypes of multiphase reactors, the slurry reactor (including bubble columns and agitated tanks) and the trickle bed reactor.

The main advantage of the trickle bed is the high catalyst inventory and the plug flow behaviour. Monoliths do not improve these aspects, but they outperform the trickle-bed in terms of mass transfer performance. This might suggest that monoliths are good alternatives to trickle bed reactors. Recently, Enache et al. [25] of Johnson Matthey evaluated the use of a monolith for pyrolysis gas hydrogenation, which is typically performed in a trickle bed. The study showed that the monolith outperformed the trickle bed, but the improvement was of the order of percentages rather than of multiples and as such, the improvements were not spectacular enough to warrant a retrofit of the existing commercial unit. In fact, trickle beds are typically used for rather slow reactions (that is, expressed per unit catalyst volume) and the rates per unit reactor volume are appreciable only due to the high catalyst inventory. For such processes the excellent mass transfer of the monoliths does not come to its own. The analysis of Johnson Matthey was quite specifically conducted to investigate the possibility of a retrofit, which imposed some restraints that prevented the monolith from operation at ideal conditions. Of course, monoliths may well be reasonable alternatives to trickle beds for designs that start from scratch.

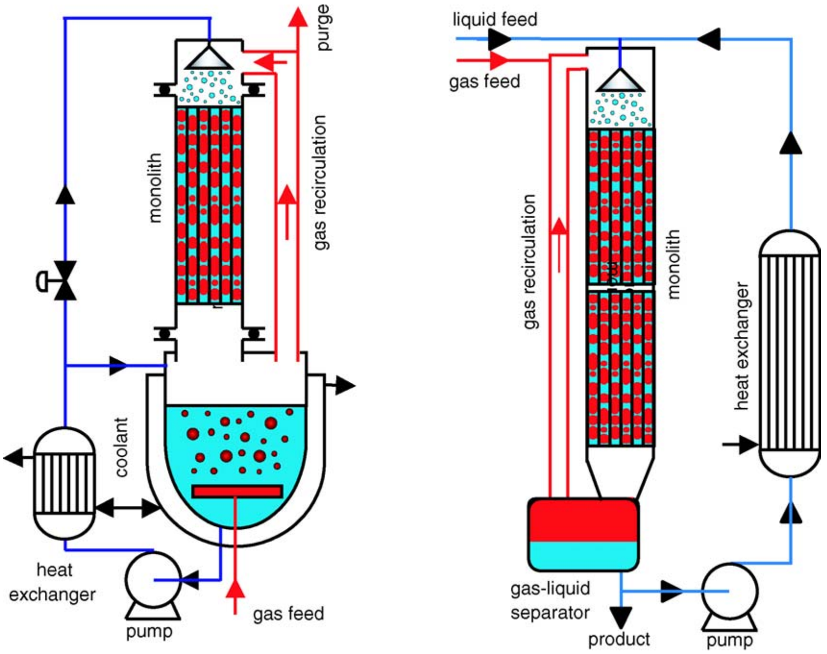
The comparison of monoliths with slurry systems is more favourable. Table 1 shows that co-current monoliths are ‘‘slurry systems on steroids’’, outperforming stirred tank systems also in those areas where stirred tank are better than normal fixed beds.

Monoliths have drawn the most interest from industry as slurry replacement.

Akzo-Nobel commercially uses monoliths in the anthraquinone process for peroxide synthesis, which is a fast reaction that is normally carried out in a slurry process [21]. Air Products and Chemicals, Inc. have used monoliths in loop configurations for nitroaromatic hydrogenations [26]. In both of these applications, the monolith outperforms slurry systems and adds additional advantages: for the Akzo-Nobel process, the fixed-bed character of monoliths eliminates the critical filtration step, whilst for the Air products process, the low pressure drop of monoliths was instrumental in allowing the high recycle ratio needed to prevent excessive temperature rise in the column. The most obvious downside to monoliths, in comparison to slurry systems, is the required long-term stability. If the catalyst deactivates too quickly, then the frequent replacement of the fixed-bed monolith is too costly. An overview of such cost arguments has recently been given by Machado et al. [27].

Monoliths are structured reactors that go beyond the classical egg-shell catalyst in the sense that the extra-particle voids, or the interstices, are also fixed by design. Outside the catalyst, mass transfer to the catalyst, gas–liquid contacting and momentum exchange (pressure drop) are the most important design considerations. For processes where any of these are an important aspect, monoliths will perform excellently. Typically, fast reactions that are performed in slurry systems fall into this category. For processes where external mass and heat transfer, pressure drop and energy requirement are not important, monoliths are less appealing, but the increased precision that can be obtained in design may trigger the selection of monoliths as a viable design option.

We expect that many attractive applications will be discovered in the next decade. In particular, the use of



Monolith Loop Reactor
(batch version)

Monolith Loop Reactor
(continuous version)

Fig. 8. Monolith loop reactor configurations, from [28].

monoliths outside heterogeneously catalysed reactions has not been studied in detail. The high mass transfer at low power input, combined with the high precision might make monoliths suitable structures for reliable and untroubled scale-up of homogeneous reactions in fine chemicals.

9. Reactor layouts

The most common process schemes involving monoliths are recycle systems. There are two reasons for choosing a loop. Firstly, monolith reactors are adiabatic. Combining an adiabatic column with an external heat exchanger allows independent scaling of the heat removal equipment, at the expense of added equipment and backmixing. Secondly, monoliths are often operated at higher superficial velocities than trickle beds, and the residence time may be too short to achieve full conversion in a single pass.

The monolith loop reactor (Fig. 8) with external heat exchanger is most suitable for violently exothermal reactions. Such reactions are normally carried out in stirred tank reactors in diluted concentrations, so most other design alternatives, such as venturi loop reactors, are equally back-mixed. In fact, a diluted feed may, in plug flow, be converted to completion in a single pass over the loop if the product can be recycled after cooling as the diluting solvent [26].

A very important advantage of monoliths is safety: if the recycle flow is shut down, monolith reactors drain within seconds, because gravity readily overcomes friction in the open structure without bends. This rapid draining can interrupt a violent temperature rise in seconds. This is in sharp contrast to all slurry systems, including venturi loop reactors, where the suspended catalyst cannot be filtered instantaneously and where stirring has to be maintained to cool the reactor in the event of a temperature excursion.

Monoliths may also prove useful in single-pass columns without a recycle. The single-pass reactor configuration is the traditional stronghold of the trickle beds, where calm reactions with mild temperature effects benefit from as much catalyst as can be squeezed the column. There are reasons for considering monoliths for such applications, especially if coking can be reduced by avoiding hydrogen limitations [29]. The main drawback of monoliths is the higher flowrates, i.e., lower residence times, in comparison with trickle beds. At very low flowrates monoliths become unstable: from channel to channel variations of throughput and hold-up become significant. Recent research in this area has provided experimental data in large scale systems [21] and small scale systems [17], and a stability analysis for flow behaviour now provides good criteria to determine the minimal allowable fluid velocities.

An interesting niche-application is the monolith stirrer, Fig. 9. Monoliths structures can be mounted on a stirrer shaft to create a stirred tank reactor with a fixed-bed catalyst, eliminating the need for filtration. Downtime to allow catalyst settling, often as time-consuming as the reaction itself, frustrates production targets in the fine chemical industry. The monolith reactor has distinct advantages over other ‘‘Carberry’’ reactors that are often used for extrudate-size catalyst testing: one may design very thin channel walls to ensure, in part due to segmented flow in the channels, absence of mass transfer limitations. Fine chemicals synthesis is often conducted under time constraints that do not allow elaborate scale-up studies. Overdesign of mass transfer, which is feasible using monoliths, is most welcome to minimize surprises during the batch campaigns.

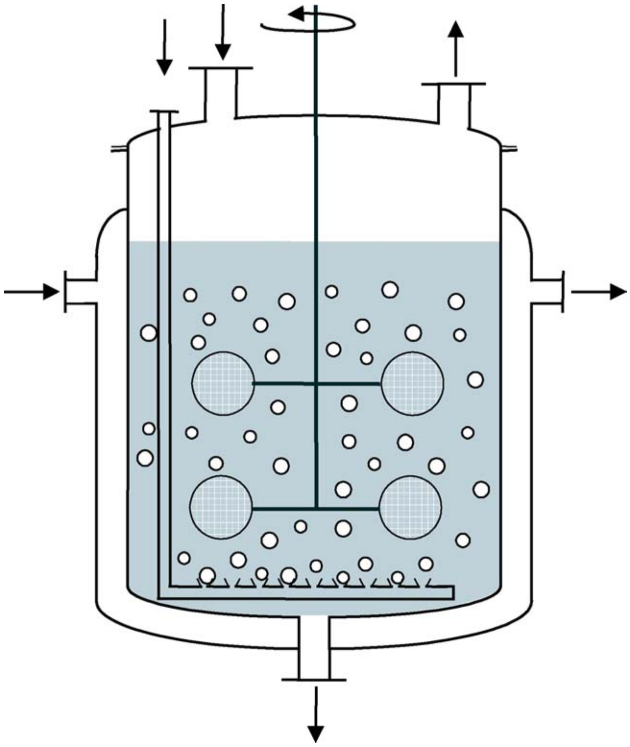


Fig. 9. Monolith stirrer reactor.

10. Conclusions

The structuring of reactors and catalysts helps to escape from the many tradeoffs that frequently occur in the design of multiphase reactors. Taking complete control over the shape of the voids between the catalytically active material automatically introduces new independent length scales that allow decoupling of intra-particle phenomena from extra-particle phenomena.

The extra length scale can also be obtained using egg-shells, but the added control over the voids in a catalyst bed allows for more precision in general. The fluid mechanics in the reactor can be better adjusted to the catalytic conversion at hand. As a result, structured reactors are best used in applications where mass transfer outside the catalyst and pressure drop are important.

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