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Applying monolith reactors for hydrogenations in the production of specialty chemicals—process and economic considerations

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Abstract

Monolith catalysts, mainstays in gas-phase automotive and environmental process applications, have found new potential in replacing three-phase slurry reactors for the production of specialty chemicals, especially when their advantages are fully utilized in recirculation loop approaches. Many economic and logistical benefits for removing slurry catalysts drive the investment into monolith technology, both for new capacity and for retrofits onto existing stirred tank reactors. Benefits are most pronounced for fast reaction chemistries, where monolith catalysts can achieve volumetric activities several times higher than slurry reactors. This paper demonstrates how engineering design and scale-up can be performed using fundamental equations and literature correlations in combination with pilot plant measurements and presents an economic analysis emphasizing monolith catalyst life as a critical variable. Efforts to develop replacement catalysts must therefore integrate efficient catalyst fabrication and lab testing into the evaluation process.

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1. Introduction

Hydrogenation in a batch three-phase slurry reactor is a well-established technology, used in the manufacture of many specialty and fine chemical products. Slurry catalysts, however, can present numerous process limitations and drawbacks including hygiene and safety issues associated with handling pyrophoric powders, limitations in incremental productivity expansions due to process filtration and mixing requirements, and yield losses caused by side reactions from the continuous contact of a process reaction mixture with the catalyst throughout the process cycle from charging to filtration.

Catalysts immobilized on monolithic substrates that are integrated with batch stirred tank reactor systems provide a practical alternative to slurry reactors. One option is to configure a slurry reactor with an external flow loop that passes the reaction components through a catalyst-impregnated monolith element. Several examples of such configurations, collectively called monolith loop reactors, have been described. We will discuss the advantages and disadvantages of monolith loop reactors, in terms of both process technology and process economics. We will show that each chemistry brings its own technical challenges and economic constraints, which must be considered in the design and testing of catalysts and ultimately, the design of the final configuration and operation of a monolith loop recycle reactor. In particular, we will highlight the linkage between process economics and catalyst life, which is critical in establishing successful implementation. In fine chemical applications where precious metal catalysts are reused only a few times the monolith catalyst must be capable of at least ten times greater reuse to present a practical alternative. When base metal catalysts such as nickel, copper or cobalt are used, the requirements for monolith catalyst life may be more than one hundred times greater than similar slurry catalyst usage. In many slurry operations precious metal catalysts have not thus far been used because of difficulties in efficiently recovering or

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Nomenclature

$c^*_{H_2}$	concentration of H_2 at saturation (mol/m^3)
d_c	channel diameter (m)
f	friction factor (−)
ΔH	heat of reaction (J/mol)
$k_L a$	gas/liquid mass transfer constant (s$^{-1)}$
k_r	reaction rate constant (s^{-1})
L	reactor length (m)
L_L	liquid slug length (m)
P	pressure (Pa)
Q_{circ}	volume flow rate (m^3/s)
r	reaction rate (mol/m^{3}s)
Re_L	Reynolds number (−)
RR	number of recycles during a batch (−)
T	temperature (K)
t_{batch}	time per batch (s)
u	channel velocity (m/s)
V_L	liquid volume (m^3)
ε_L	liquid hold-up fraction (−)
ε_G	gas hold-up fraction (−)
μ_L	liquid dynamic viscosity (m^2/s)
μ_G	gas dynamic viscosity (m^2/s)
ρ_L	liquid density (kg/m^3)

retaining the catalyst. For these applications the monolith loop reactor provides a practical and economical alternative that makes the use of precious metal catalysts feasible.

2. Monolith reactors versus traditional alternatives

When designing a fine-chemical hydrogenation process, one would consider several conventional reactor types: stirred-tank slurry reactors and bubble columns, in which the catalyst is a finely dispersed powder, and randomly packed trickle-bed reactors, in which the catalyst is in one of various granular or extruded particulate forms. Since monolithic reactors are a form of fixed-bed reactor, the most straightforward technical comparison is to a trickle-bed reactor; one such comparison is presented by Edvinsson and Cybulski [1].

However, in fine-chemical applications the stirred-tank slurry reactor is by far the most frequently used, due to its operational flexibility and its inherent applicability for batch processes. Therefore, it is more useful to compare monolith reactors to slurry reactors. Such comparisons have previously been presented by Cybulski et al. [2] for a general case, and by Boger et al. [3] for hydrogenation of edible oils.

Advantages of monolith reactors over batch stirred-tank slurry reactors include the following:

Lower catalyst cost: In most cases, the overall catalyst cost of a monolith-based catalytic process will be lower than of a slurry-based process. This will be addressed in more detail below.

Higher volumetric reaction rate: The high rate of hydrogen mass transfer that can be attained in a monolith significantly intensifies the reaction rate, especially in processes where mass transfer dominates the overall production rate.

A substantial decrease in catalyst handling: Slurry catalysts are notorious for introducing process complexity and increasing maintenance intensity. The catalysts must be filtered from the process liquid, which adds a unit operation to the process, and often contributes significantly to overall batch cycle time. The catalyst must usually be recycled for reuse. Adding fresh catalyst is labor-intensive and trouble-prone, as are most solid handling procedures in chemical processes. Slurry catalyst tends to build up on process equipment over time, often even downstream of filtration equipment, leading to downtime for cleaning. At the scale required for fine-chemical processes, monolith catalysts can be pre-assembed into canisters. Depending on catalyst life, canisters remain in place for weeks or months, greatly reducing the amount of time and effort expended in catalyst handling.

Increased control over contact between catalyst and reactants: In a slurry reactor, the reaction solution is in continuous contact with the powder catalyst, during the heatup, reaction, and cooldown phases of the batch. Often this extended contact time, especially after the desired conversion has been attained, can allow undesired reactions to occur. This gives rise to a lower selectivity, and byproducts that pose downstream separation problems. The extended contact is difficult to avoid, since it is usually impractical to filter the catalyst before the reaction batch has cooled. In monolith reactor processes, the process liquid contacts the catalyst only when the process conditions are favorable for the desired reaction, and only for as long as is required to attain the desired conversion. Flow is diverted away from the monolith reactor at all other times, so that heatup and cooldown are decoupled from the catalytic reaction.

Increased safety and hygiene: Slurry catalysts are often pyrophoric, and require special handling precautions; even so, catalyst fires are not uncommon. In-process and spent catalyst, which contains organic process chemicals, introduces additional safety and hygiene issues during recycle and disposal or reclaim. For monolith processes, monolith canisters would be produced in a passivated state and activated in situ, giving much less opportunity for personnel exposure.

In the area of reactor equipment, slurry systems and monolith systems each have potential advantages and disadvantages, which must be weighed for individual applications. While slurry reactors feature a maintenance-intensive agitation system, monolith systems add a process circulation pump. Slurry reactors combine liquid holding, reaction, and heat transfer functions into one complex vessel, while monolith systems will usually require separate, simpler vessels for each function. This brings the advantage of flexibility and scalability, at the cost of a larger equipment count.

Monoliths may face disadvantages relative to batch slurry reactors in the areas of temperature management and backmixing. These issues will be addressed in the section below.

3. Modes of operation

Gas–liquid monolith reactors attain high reaction rates because of superior mass transfer rates. To achieve these, a desirable flow configuration must be established, through suitable distribution of gas and liquid to the monolith channels and by maintaining optimum velocity through the monolith channels. Distribution and channel flow phenomena are difficult to separate in practical monolith reactor arrangements; in our experience, performance increases with linear (gas plus liquid) velocity up to velocities of 0.5 m/s. Therefore, monolith reactors perform best in a relatively rapid flow-through mode. This makes them fundamentally different from batch stirred-tank slurry reactors, where the reaction mass does not flow into and out of the reactor, and from trickle-bed reactors, where velocities (especially of the liquid phase) are typically low. Practically, this means that monolith reactors will usually be configured in a flow loop, with a relatively low conversion per pass. A batch hydrogenation is conducted by continuously circulating liquid through the monolith until conversion is complete. With the exception of concept papers describing a monolith pipeline reactor [4], and various monolithic agitator concepts [5,6], all open literature and patent references present some form of recycle system.

Two large-scale gas–liquid hydrogenation processes that use monolithic catalysts have been described: one in hydrogen peroxide production [7], and one in the manufacture of toluenediamine [8]. Both operate as loop systems, with a high ratio of recirculation flowrate to feed and product flowrate. Our focus in this paper will be on batch hydrogenation processes implementing the loop reactor concept.

In an implementation of the concept described by Heiszwolf et al. [9], liquid is circulated through the monolith reactor using traditional liquid distribution devices such as spray nozzles. Gas is introduced into the reactor by gravity-driven natural circulation. Gravity-driven flow is efficient, but limits the range of practicable gas and liquid velocities through the reactor; it becomes impractical when high-density monolith substrates with very small channel diameters are used. High-density monoliths are desirable because they have a large external surface area, and correspondingly high mass transfer and reaction rates.

In an alternative implementation proposed by Air Products and Chemicals, Inc. [10,11] a liquid-motive gas ejector replaces the traditional liquid distribution device. The ejector uses liquid flow to entrain and compress recycled hydrogen. When properly engineered, the ejector also serves as an effective gas–liquid contactor, presaturating the liquid before it enters the reactor, and produces a fine dispersion of gas bubbles in liquid, which results in excellent gas–liquid distribution to the monolith. Because the ejector serves as a gas compressor, the gas-liquid dispersion can be delivered to the inlet of the reactor at a pressure greater than the outlet pressure. While this consumes more energy than gravity-driven flow (the circulation pump must deliver a higher pressure), it greatly expands the range of practical operating conditions, and allows high-density monoliths to be used. Fig. 1 shows schematically the equipment arrangement in an ejector-driven monolith loop reactor.

In a loop reactor system, the circulation flowrate is an additional design and operating parameter, which is conveniently expressed in terms of the recycle ratio: the ratio of batch reaction time to the time required to circulate the batch volume (in other words, the number of recycles completed during a batch):

$$\mathrm{RR} = \frac{Q_{\mathrm{circ}} t_{\mathrm{batch}}}{V_{\mathrm{L}}} \tag{1}$$

At very high recycle ratios, the loop reactor system acts as an ideal stirred-tank reactor. The conversion per pass is so small that concentration and temperature gradients in the system are negligible. As the recycle ratio decreases, the concentration drop and heat generation through the monolith reactor become appreciable. Monolith reactors nearly always operate adiabatically, since radial heat transfer is poor. Therefore, the temperature will rise through the reactor. This sets a practical bottom limit on the recycle ratio, which depends on the maximum acceptable temperature for the process (from considerations of material stability, catalyst selectivity, etc.). Another limit derives from the hydrogen consumption: the conversion per pass can be no greater than dictated by the relative amount of hydrogen delivered to the reactor inlet, which is limited by hydrodynamic considerations. For these reasons, operation at low recycle ratios is only practical in very dilute systems.

Even when recycle ratios are fairly high, monolith loop reactor systems will have more pronounced concentration and temperature gradients than typical slurry systems. This must be taken into account in the process design. The temperature at the reactor inlet may need to be lower than in the corresponding slurry system, to avoid yield losses due to high-temperature phenomena. The loop reactor also introduces an element of backmixing relative to the ideal stirred batch reactor. For kinetically limited reactions whose reaction rates depend strongly on the liquid-phase concentration, this can hamper batch finishing times, because toward the end of the reaction cycle, the average concentration in the monolith reactor is well below the average concentration of the overall batch. Again, this effect decreases as the recycle ratio increases.

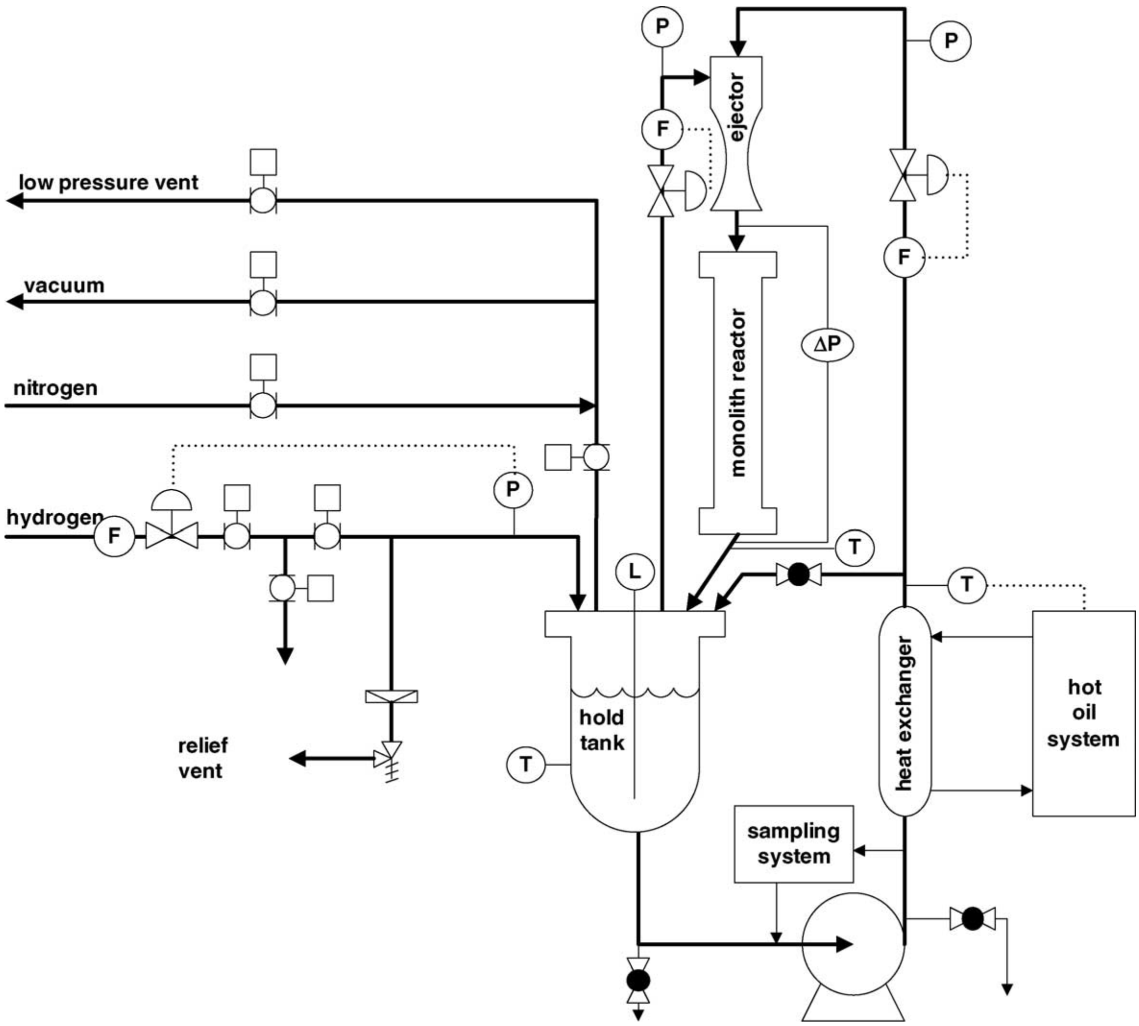

Fig. 1. Schematic of Air Products monolith loop reactor pilot plant with 60 l hold tank and 5 cm × 120 cm monolith reactor configured for hydrogenation.

The monolith loop reactor configuration can easily be extended to continuous operation, by including a liquid feed and product draw into the process. In this case, the recycle ratio is defined as the ratio of circulation flowrate to feed flowrate. While for batch reactions the mixture of plug-flow reactor and stirred reactor characteristics results in a lower overall reaction rate, the reverse holds for the continuous case: here, the plug-flow monolith reactor allows the average reactant concentration in the reactor to be higher than in the product stream (drawn downstream of the reactor, before re-mixing in the hold tank), with correspondingly faster reaction rates. To further increase reaction rates in the main reactor, the system may be operated at somewhat higher reactant concentration, with the final conversion attained in a polishing reactor.

4. Process chemistry criteria

Monolith reactors achieve their volumetric rate advantage over slurry reactors from the superior rate of mass transfer from the gas and bulk liquid phase to the catalytic surface. High rates allow the additional reactor vessel introduced in monolith reactor systems, as well as the amount of catalyst required, to be small, so that overall economics are favorable. This rate advantage holds when the hydrogenation process rates are limited by the rate of hydrogen mass transfer during at least part of the batch cycle. If the reaction is so slow that it renders the process kinetically limited, this advantage disappears: the overall throughput is now set directly by the amount of catalyst in the system. The monolith reactor is no longer small, and a slurry reactor with high catalyst loading may offer better performance. Of course other advantages of monolith reactors (no filtration, safety, etc.) still hold, but may not be sufficient to justify a monolith-based process.

To judge the rate advantage of a monolith, we can compare a representative kinetic rate constant to the mass transfer rate constant in a typical slurry reactor. Both should be expressed as (pseudo)-first order rate constants in hydrogen. The mass transfer rate constant can be expressed by k_La, which, depending on the reaction equipment and conditions, ranges from 0.02–0.2 s^{-1} for typical stirred-tank slurry reactors. The kinetic rate constant can be more difficult to define—here we will evaluate it from the hydrogen consumption rate at 50% conversion at saturated hydrogen conditions:

$$K_{r1} = \frac{r_{H_2}(c^*_{H_2}, 50\%)}{c^*_{H_2}} \tag{2}$$

For example, from nitrobenzene hydrogenation experiments we derived a kinetic rate expression with a first-order dependence on hydrogen concentration. At process conditions, we evaluate k_{r1} to be 1.4 s^{-1}. Since this is significantly larger than typical k_La values, a monolith reactor can significantly intensify the reaction by providing faster mass transfer (we have measured monolith mass transfer constants up to 2 s^{-1} in the isopropanol/nitrobenzene reaction system).

Repeating this analysis for glucose hydrogenation [12], we find that the best catalyst identified yields a k_{r1} of 0.33 s^{-1} at process conditions. Since mass transfer of hydrogen through viscous aqueous carbohydrate solutions is slow, the k_La for this reaction system will not be at the high end of the range suggested above, and the monolith still holds an advantage over slurry processes. However, other considerations beyond catalyst productivity may be necessary to fully justify a monolith-based process.

5. Catalyst development

Monolith process development depends on the availability of an active, selective, long-lived, mechanically robust monolith catalyst. While monolith catalysts are commercially available for gas phase applications, liquid phase applications require custom development. Options for preparation of these catalysts include: (1) adapting widely practiced processes developed for gas phase automotive monoliths. This typically means coating a low surface area cordierite mechanical support with a higher surface area washcoat containing a catalytic metal. Metal monolith skeletons, such as used for structured packing, or ceramic open-cell sponge structures can also be used. (2) Extruding high surface area materials, which serve as both monolith skeleton and catalytic metal support. Carbon extrudates are commercially available. (3) Modification of another fabricated (e.g cellulose or fiberglass) monolith structure.

A mechanically stable monolith skeleton must be identified first. The most common option is the application of a ceramic cordierite monolith currently used in gas phase, automotive and environmental applications. Ceramic or carbon extrudates are stable in organic reaction media if mounted such that abrasive loss due to movement at the mounting surfaces is eliminated. Less common monolith materials used in gas-phase applications, such as paper or laminated fiberglass, disintegrate in liquid systems.

Where reaction rates are governed by liquid phase pore diffusion, only the outer layer (up to about 20 μm) of the catalytic coating effectively contributes to the reaction rate. Hence, a structure made from an inert material coated with a thin porous catalytic layer is most attractive. The overall performance is then governed by the external surface area of the catalyzed structure. Both extruded ceramic and fabricated metal structures can offer high geometric surface area per volume.

The catalytic metal/washcoat combination will likely resemble the slurry catalyst currently used in the process. In many hydrogenation processes the slurry catalyst is a carbon-supported precious metal, which suggests that high-surface-area activated carbon would be a desirable washcoat. However, activated carbon powder adheres poorly to monolith skeletal material such as cordierite. Alternative techniques include in situ coating preparations using precursors such as polyfurfuryl alcohol and heating the coating [13,14]. The performance of a monolith with a heat treated polyfurfuryl alcohol polymer coating is illustrated in Fig. 3 for nitrobenzene hydrogenation.

For rapid catalyst development, it is preferable to rely on a proven support for which manufacturing infrastructure is in place. Since washcoating is an established process, whereas in situ coating is developmental, the primary effort to fabricate potentially commercial monolith catalysts for use in liquid processes focuses on conventional washcoat technology. This allows one to adapt a variety of slurry catalysts to a monolith skeleton. To emulate the active-carbon slurry catalysts, inorganic supports with carbon-like properties are desired.

5.1. Lab testing in an autoclave

To facilitate rapid catalyst testing it is advantageous to utilize existing laboratory resources such as standard stirred autoclaves. One example of a catalyst testing apparatus designed to fit an autoclave is illustrated in Fig. 2 where the hollow shaft turbine serves the same function as the ejector in the monolith loop configuration and produces a fine dispersion of gas bubbles in the liquid phase, which is continuously circulated through the monolith.

The use of this equipment allows screening as well as in-depth testing of numerous hydrogenation chemistries. As an example, Fig. 3 shows results of lifetime testing for both a polymer-coated and an inorganically washcoated monolith. For nitrobenzene hydrogenation, used as a screening reaction, the inorganic material washcoat demonstrated greater performance and durability.

To identify opportunities for monolith catalysis in batch processes, monolith catalyst candidates should be evaluated to determine the overall rate of reaction, selectivity to the desired products and life, and compared to their slurry catalyst equivalents. Results for a number of chemistries are listed in Table 1. Enantioselective syntheses using chiral modifiers have also been demonstrated. In each of these

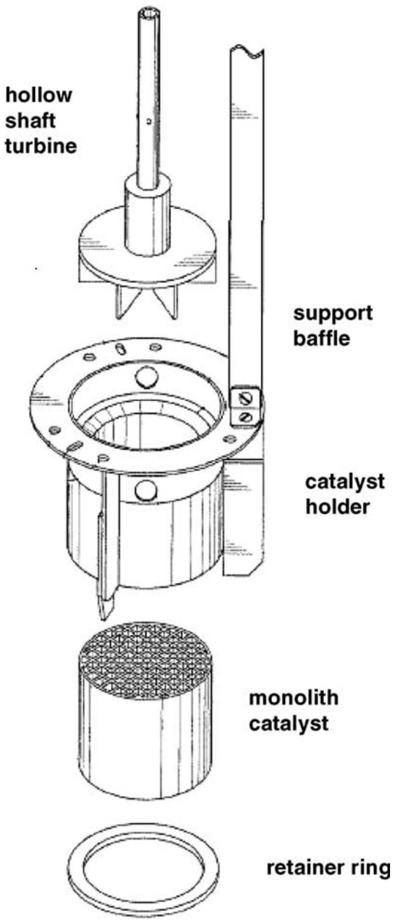

Fig. 2. Exploded view of a monolith testing apparatus designed as a retrofit to a laboratory autoclave. The hollow shaft turbine impeller creates a gas–liquid flow that circulates bottom to top in the monolith catalyst. The support baffle keeps the unit from rotating within the autoclave and the retainer ring fixes the catalyst in the holder. (Patent pending.)

cases, to maintain the catalyst a regeneration step (e.g. solvent wash) was required for sustained activity. Lifetime of the catalyst has been the most significant issue in monolith catalyst development.

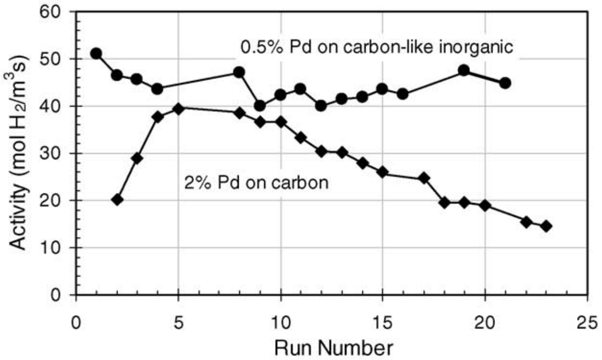

Fig. 3. Lifetime testing of palladium based monoliths for nitrobenzene hydrogenation in an autoclave using the monolith testing apparatus (Fig. 2). Carbon monolith prepared from polyfurfuryl alcohol. Reaction conditions: $V_{\mathrm{monolith}}/V_{\mathrm{liquid}} = 0.075$; 40% nitrobenzene in isopropanol; 60 °C, 12.8 bar.

6. Engineering and scale-up

6.1. Process design basis

Having identified a suitable catalyst, the next challenge becomes designing a process that integrates this catalyst. We have found that in many cases, monoliths hold advantages significant enough to favor a monolith loop retrofit to an existing stirred tank reactor; in this case, the monolith must integrate with pre-existing equipment. When the monolith reactor is part of a newly designed process, the designer has greater flexibility. In either case, the most likely alternative or displaced technology is a stirred tank reactor (STR). Therefore, we will examine process design by comparison with slurry STRs.

Like a STR, the monolith process must include means of containing the reaction batch, effecting the reaction (providing contact between catalyst, hydrogen, and liquid reactants), and removing the heat of reaction. The STR achieves these in one vessel, using high-power agitation to effect the reaction, and internal coils or a jacket to remove the reaction heat.

In retrofit cases, the new process may take advantage of the heat transfer capacity of the existing tank (which requires that the agitation system be maintained as well), but in most cases an external heat exchanger will need to be placed in the circulation loop, between the circulation pump and the monolith reactor. An independent heat exchanger can be designed to increase flexibility, for example to decrease heat-up and cool-down times and shorten the overall batch cycle.

6.2. Gas–liquid distribution to monolith reactor

The means of achieving contact between catalyst, hydrogen, and liquid reactants is of course the heart of the monolithic process, provided by the gas–liquid distributor and the gas–liquid flow through the monolith channels. The most prevalent flow pattern in monolith channels is Taylor flow, characterized by gas bubbles alternating with liquid slugs. Research has shown that Taylor flow is established over a wide range of gas and liquid properties and velocities, and gives rise to high rates of mass transfer of gaseous and liquid reactants, due to both the thin liquid film separating the gas bubble from the catalytic surface and the circulating flow patterns within the liquid slugs. Mass transfer phenomena in monoliths have been analyzed in several recent papers [15,16].

Gas and liquid may be distributed to the monolith reactor using various distribution devices. Since it is not practical to design a reactor for full conversion of hydrogen per pass, gas must be recycled from the headspace of the hold tank to the inlet of the monolith. We already noted gravity-fed operation, along with its inherent limitations. To provide more driving force for flow through the monolith channels, the gas must be compressed relative to its pressure

Table 1
Comparison of reactor productivity in model reactions with slurry and monolith catalysts in an autoclave reactor using the testing apparatus in Fig. 2

	Conditions	Catalyst: loading	Reactor productivity (mol H_2/m^3 s)	Conditions	Catalyst: loading	Reactor Productivity (mol H_2/m^3 s)
Butyronitrile → mono, di and tri *n*-butylamine	125 °C; 33.4 bar	5% Pd on carbon; 2 kg/m^3	0.31	125 °C; 33.4 bar	Pd on carbon-like washcoat; 3.17 kg Pd/m^3	74
Ethyl pyruvate → ethyl lactate	20 °C; 12.8 bar	3% Pt on carbon; 0.9 kg/m^3	0.28	20 °C; 12.8 bar	Pt on inorganic washcoat; 3.04 kg Pt/m^3	21
Methyl acetoacetate → methyl hydroxybutyrate	80 °C; 12.8 bar	Raney Nickel; 20 kg/m^3	0.45	50 °C; 12.8 bar	Pt on inorganic washcoat; 3.2 kg Pt /m^3	3.2
4-*t*-butylcyclohexanone → 4-*t*-butylcyclohexanal	100 °C; 12.8 bar	5% Pd on carbon; 2 kg/m^3	0.007	100 °C; 12.8 bar	Pd on inorganic washcoat; 3.32 kg Pd /m^3	2.7
2-ethyl-2-hexenal → 2-ethylhexanal	50 °C; 12.8 bar	Raney Nickel; 10 kg/m^3	1.1	50 °C; 12.8 bar	Pd on inorganic washcoat; 3.23 kg Pd /m^3	22
Nitrobenzene → aniline	60 °C; 12.8 bar	1.65% Pd on inorganic washcoat; 0.167 kg/m^3	0.042	60 °C; 12.8 bar	Pd on inorganic washcoat; 3.52 kg Pd /m^3	55
Glucose → sorbitol	120 °C; 54.2 bar	5% Ru on carbon; 2 kg/m^3	0.51	120 °C; 61.0 bar	Ru on carbon-like washcoat; 17.7 Ru kg/m^3	10

Monoliths were 5 cm × 5 cm dia, washcoated 400 cpsi cordierite; tested in CatRak with $V_{cat}/V_L = 0.075$. Slurry catalyst loadings = total catalyst wt/liquid volume; monolith catalyst loadings = catalytic metal/monolith volume. Reactor productivity measured at <50% conversion. Reactor productivity: units for monolith = mol $H_2/m_{monolith}^3$ s; units for slurry = mol H_2/m_{liquid}^3 s.

downstream of the reactor. Conventional mechanical compressors may serve this purpose; the pressurized hydrogen may be combined with the liquid using any number of distribution devices, for example static mixers. However, hydrogen compression equipment is inefficient and can be trouble-prone, especially when the hydrogen is laden with solvent vapors.

For this reason, we have focused our efforts on gas–liquid ejectors as distribution devices. The ejector uses the pressure energy of the circulating liquid to draw in and compress the hydrogen gas, eliminating the need for rotating equipment. The thermodynamic efficiency of ejectors operated in this fashion is low, i.e., only a small fraction of the pressure energy of the liquid is converted into pressure energy of the gas. However, the additional energy dissipation ensures that the gas and liquid form a fine dispersion, which can be delivered to the monolith reactor entrance without further conditioning. In most cases, the liquid will be fully saturated with hydrogen at the monolith inlet, due to the excellent mass transfer in and downstream of the ejector. We have found that gas holdups of 40–50% yield optimal results.

6.3. Pressure drop through monolith reactor

The ejector does pose a few limitations, most notably in the amount of pressure boost it can provide the hydrogen. For example, in our efforts using off-the-shelf ejectors fed by a pump delivering up to 5 bar differential pressure, the practical limit was about 1 bar hydrogen pressure boost. The higher the desired hydrogen flowrate, the lower the resulting pressure. This sets a limit on the pressure drop through the monolith reactor. There is an extensive literature describing and modeling pressure drops in monoliths and capillary channels. All useful models include the slug length (the average length of a liquid slug plus a gas bubble) as a critical parameter. For example, the following model considers each liquid slug to be in developing channel flow [17]:

$$\Delta p_{\mathrm{fric}} = 4 f_{\mathrm{LG}} \frac{1}{2} \rho L (u_{\mathrm{L}} + u_{\mathrm{G}})^2 \frac{L}{d_{\mathrm{c}}} \varepsilon_{\mathrm{L}} \qquad (3)$$

$$f_{\mathrm{LG}} = \frac{16}{Re_{\mathrm{L}}} \left[1 + a \left(\frac{Re_{\mathrm{L}} d_{\mathrm{c}}}{L_{\mathrm{L}}} \right)^{b} \right] \qquad (4)$$

While slug lengths may be set or analyzed using specialized laboratory equipment, the important question of slug length distribution in industrial distributor/monolith reactor systems has not been adequately addressed. Using the best available models, we have been able to back-calculate slug lengths and bubble sizes from pressure drop measurements [10], but there is no guarantee that this parameter will remain constant upon scale-up.

6.4. Demonstration at pilot scale

Similarly, mass transfer relationships also depend on the slug length parameter. Consequently, for scale-up of a particular chemistry in a monolith reactor, it is necessary to obtain rate and pressure drop data using the reaction system of interest at the desired process conditions. Since catalyst screening and optimization is most effectively conducted at smaller scales, for example in autoclave retrofits as described above, separate equipment, most likely at a larger scale, must be used to generate the engineering data required for scale-up.

The considerations above point to the need for a pilot facility, to demonstrate monolith-based processes beyond the laboratory scale. For our studies, we constructed an intermediate-scale pilot plant, capable of delivering up to 40 l/min of process liquid at up to 5 bar differential pressure to a 0.05 m diameter, 1.2 m long tubular monolith reactor

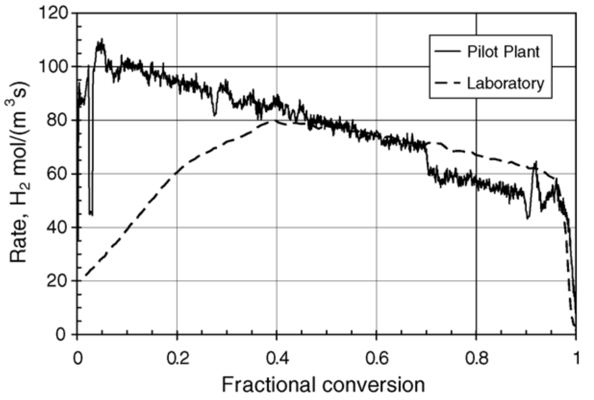

Fig. 4. Comparison of batch hydrogenation results obtained in the laboratory and at the pilot scale for 40% nitrobenzene in isopropanol. Target reaction conditions were 14.8 bar(a) and 120 °C. In the laboratory reactor, the reaction is partially completed by the time the desired temperature is attained, which causes the ramp-up in rate seen in the figure.

(Fig. 1). Other system parameters (pressure and temperature rating, material of construction, hold tank volume) were chosen to accommodate almost any industrial hydrogenation process. The pilot plant is fully instrumented to capture both reaction information (hydrogen uptake rate, temperature rise, etc.) and hydraulic information (gas and liquid flowrates, pressure drops). The equipment was used for several hydraulic studies using water and isopropanol, nitrogen and hydrogen, and for hydrogenation pilot trials of nitrobenzene and glucose.

Nitrobenzene hydrogenation was the first chemistry that we carried all the way from catalyst development and laboratory studies through to the pilot plant. Fig. 4 shows that the volumetric productivity observed during pilot trials closely matched lab results. No significant catalyst deactivation was observed over the course of 26 batch hydrogenations, which again was consistent with laboratory observations.

The next pilot trial, on the other hand, underscores the importance of going beyond laboratory experiments. For glucose hydrogenation, operating at pilot scale allowed us to use more representative feedstocks (cornstarch hydrolysates rather than crystalline glucose) than were available for lab studies. Also, due to the relatively high viscosity of glucose/sorbitol solutions, we could not be sure that adequate circulation was attained in lab-scale equipment (designed for low-viscosity liquids). Our pilot trial showed that the volumetric productivity at the pilot scale was similar to that attained in the lab, suggesting that the mass-transfer effects at both scales were comparable. However, while the catalyst had been relatively stable in lab studies, at the pilot scale with a commercial feedstock the catalyst deactivated more rapidly, indicating the need for further catalyst development and optimization.

During both trials, reactor pressure drops were measured; the results are applicable to commercial scale-up. Since accurate values of liquid viscosities at process conditions were unavailable in both cases, pressure-drop models were not applied. However, the trends were as expected, and consistent with bubble sizes of several mm.

6.5. Process design

In the preceding sections we have touched upon several factors that affect the design of the monolith loop reactor system: reaction and mass transfer rates; recycle ratio and its effect on temperature rise and hydrogen depletion; ejector performance and pressure drop; and residence time (distribution) considerations such as continuous versus batch operation and backmixing effects. We must consider all these factors in the design of the equipment.

As with any reactor, the reactor size is determined by the required processing rate. For a batch reactor, this means the desired batch size and reaction time. Since the reaction rate in a batch process will vary with degree of completion, the reactor size follows from integration of the rate expression. However, the required size can be more straightforwardly calculated from the batch completion time at the laboratory scale, using an experiment in which the catalyst and reaction conditions are the same as for the full-scale process:

$$V_r = V_{\mathrm{Cat,lab}} \frac{t_{\mathrm{lab}}}{t_{\mathrm{batch}}} \frac{V_{\mathrm{L,batch}}}{V_{\mathrm{L,lab}}} \tag{5}$$

The minimum circulation flowrate follows from the maximum temperature rise that can be tolerated, or from hydrogen depletion considerations:

$$Q_{\mathrm{circ}} \geq \frac{V_r r \Delta H_r}{\rho_L c_{p,L}(T_{\max} - T_{\mathrm{in}})} \tag{6}$$

$$Q_{\mathrm{circ}} \geq n V_r r \frac{V_{\mathrm{mol,G}}(1-\varepsilon_G)}{\varepsilon_G} \tag{7}$$

For relatively small-scale applications, the monolith shape and size will most likely be determined by the catalyst fabrication technology and economics. For example, the diameter may be set by the monolith size that can be extruded, which is currently about 0.33 m. The required reactor length follows from the diameter and the reactor size. Assuming a single reactor and setting the gas holdup, we may also calculate the superficial liquid and gas velocities. If the velocity is too small (<0.10 m/s), mass transfer will not be optimal, and a smaller reactor or higher liquid circulation flowrate should be chosen.

The pressure drop through the reactor follows from the calculated velocity and an appropriate pressure drop model (preferably based on pilot data in the system of interest). If the pressure drop is too large for the ejector to overcome, a larger, custom reactor diameter may be necessary. Alternatively, the design may be modified to include two or more reactors in parallel. Doubling the number of reactors reduces the reactor pressure drop by a factor of four or more. The multiple-reactor approach also avoids the increasingly difficult gas–liquid distribution as the reactor diameter increases.

If the design of the circulation pump and heat exchanger allow, scale-up beyond the original production rate becomes a matter of installing additional monolith reactors in parallel (or, subject to the constraints above, increasing the length of the original ones).

7. Economics

In the industrial environment the economic and operating benefits must ultimately be weighed against the risks to drive the decision to invest in new technology. Often a broader view of the economic impact is necessary to capture the full value of new technology. This is certainly true when considering monolith catalysts as replacement of conventional batch slurry catalysts. A complete economic evaluation should include the cost of catalyst, the impact of reduced maintenance and equipment cleaning, the elimination of filtration cost, the reduction of solid waste including environmental impact and improved return on capital investment for incremental capacity expansion.

7.1. Investment options

During plant capacity expansions slurry catalyst handling can become a major bottleneck requiring investment into catalyst filtration and handling operations. This investment can be redirected into an installation of a monolith loop reactor. On a capital basis these investments are often similar in magnitude, each requiring a pump, piping and a vessel or reactor housing. However, the investment into a monolith reactor also brings with it the additional benefits of eliminating the slurry catalyst altogether.

Increasing the amount of catalyst alone in a batch slurry process may not enhance productivity or process economics unless a complementary increase in heat transfer, mixing and gas–liquid mass transfer can be obtained from existing equipment or additional equipment investments are secured. A monolith loop reactor fitted with a high capacity ejector provides simultaneous gas–liquid mass transfer and catalyst liquid solid mass transfer with the retrofit of a monolith loop reactor design to the existing tank reactor. Heat transfer is not specifically enhanced with this upgrade, but can be flexibly addressed by adding a heat exchanger to the loop.

7.2. Catalyst cost savings

The cost per gram of catalytic metal is generally higher for a monolith catalyst than for the corresponding slurry catalyst, due to higher monolith substrate and fabrication costs. Experimental studies can define the amount of catalytic metal required to achieve the same selectivity, yield and batch time as in the existing slurry process. It is often found that the amount of catalytic metal required in the monolith process is the same as or higher than the amount needed for a corresponding slurry process, due to imperfect coating methods, washcoat thickness, or metal dispersion. For a monolith catalyst to be advantageous, it must have the capacity to be effectively reused numerous times. These considerations lead to the following important process variables:

M = amount of catalytic metal per batch required to complete the batch (at given process conditions and batch time)
$R = M_{\text{monolith}}/M_{\text{slurry}}$
n = average number of batch cycles a catalyst charge remains in the process

Table 2 compares practical ranges of economic factors for slurry and monolith catalysts in precious metal catalysis applications.

The purchase price of a catalyst can be estimated from the following simplified equation:

$$\begin{aligned}&\text{catalyst price}(\$/\text{kg catalyst})\\&\quad=\text{manufacturing charge }(\$/\text{kg catalyst})\\&\qquad+\text{wt\%}_{\text{Metal}}/100\%\times\text{metal price }(\$/\text{kg metal})\qquad(8)\end{aligned}$$

where wt%$_{\text{Metal}}$ is the amount of metal in the catalyst, and the manufacturing charge includes profit and all costs except for the catalyst metal. The metal cost fluctuates depending upon market conditions and how metal ownership is

Table 2
Comparative economic and performance factors for slurry and monolith precious metal catalysts

Factor	Slurry			Monolith		
	Units	Low	High	Units	Low	High
Catalytic metal loading	wt%	0.5	10.0	wt% g/m^3	0.5 1100	6.0 14,000
Manufacturing charge which includes fabrication, profit and raw materials costs excluding metal	$/kg	40	70	$/kg $/m^3	160 35,000	420 95,000
R, relative catalyst metal charge per batch monolith vs. slurry to achieve same batch time	–	–	–	1.0	1.0	3.0
Metal recovery per batch	wt%	80	95	wt%	95	99

assigned between the catalyst supplier and the catalyst user. The net cost of catalyst, allowing for a metal recovery credit, follows from:

$$\begin{aligned}&\text{net catalyst cost } (\$/\text{kg catalyst})\\&\quad = \text{catalyst price } (\$/\text{kg catalyst})\\&\qquad + \text{recovery charges } (\$/\text{kg catalyst})\\&\qquad - (\text{wt\%}_{\text{Recovery}}/100\% \times \text{metal price } (\$/\text{kg metal}))\end{aligned} \tag{9}$$

where wt$\%_{\text{Recovery}}$ is the metal recovered per mass of catalyst. Note that the catalyst manufacturing charges are not recoverable. Therefore catalysts with higher manufacturing charges will always require net lower usage amounts or longer life to be competitive with catalysts which have lower manufacturing charges.

The contribution of the catalyst cost to the product can be estimated according to:

$$\begin{aligned}&\text{catalyst contribution cost } (\$/\text{kg product})\\&\quad = \frac{M}{n} \times \text{net catalyst cost } (\$/\text{kg catalyst})\\&\qquad \times \frac{100\% \times 100\%}{\text{wt\%}_{\text{metal}} \times \text{wt\%}_{\text{product}}}\end{aligned} \tag{10}$$

where wt$\%_{\text{metal}}$ is the percent by weight of catalyst metal in the catalyst, and wt$\%_{\text{product}}$ is percent by weight of product in a batch.

The key to reducing the catalyst contribution cost to a process is the number of times the catalyst can be reused and the amount of catalyst metal required to achieve the process goals. A summary of economic and performance factors comparing slurry and monolith processes for a precious metal catalyst is illustrated in Table 2.

7.3. Additional savings

Batch slurry catalyst processes are labor-intensive, requiring loading, unloading, waste disposal and cleaning of equipment. The monolith allows the elimination of all routine catalyst handling and cleaning steps. The reduction in maintenance costs can be equated directly to labor cost, which for a dedicated reactor and filtration system can be one full time equivalent of labor.

Metal recovery in slurry catalysts can be poor due to losses in handling and in equipment hold-up. For the monolith, catalyst handling losses are minimized. Cleaning and decontamination is also more facile, because the monolith catalyst can be washed in place before being removed for reclamation.

Where monolith technology offers an alternative to the use of environmentally harmful catalysts, such as nickel, additional savings and environmental benefits may be gained by their implementation.

7.4. Replacement of a Pt slurry catalyst with a Pt monolith

A potential candidate for the application of a monolith to replace a slurry catalyst is a fine chemical or pharmaceutical hydrogenation process with limited slurry catalyst reuse. In these applications the catalyst is often used only once before reclamation, to maintain consistent product profiles and batch times. If catalyst is reused, accurately quantifying the amount being returned to the subsequent batch is difficult, since the spent slurry catalyst is wet and may be diluted with filter aid. This is not the case with a properly designed monolith, which maintains stable performance between batches.

The following example illustrates the potential catalyst contribution savings from converting a fine chemical or pharmaceutical application from a slurry catalyst to a monolith. We will assume that the monolith formulation has been optimized to yield acceptable selectivity; this analysis focuses on the impact of catalyst life on the monolith economics. The batch slurry reactor process hydrogenates a solution with 30% substrate using a 5% Pt catalyst with a reactor loading of 0.5% by weight. The catalyst is used once and is then recovered for reprocessing by the catalyst supplier. A summary of the process and economics are shown in Table 3.

The comparison case is a 60-l monolith reactor retrofitted to the batch tank. We will assume here that lab studies have shown that, compared to the slurry process, between one and three times as much platinum is required for the monolith (i.e., $1 < R < 3$).

The variable with the least certainty is the manufacturing charge for the monolith. This depends on substrate cell density, washcoat materials, technology fees, the number of manufacturing steps and the annual volume of catalyst purchased. The anticipated range for this charge is between \$35,000 and \$95,000 per m^3 for volumes necessary to support a single application. The sensitivity of the point at which the process contribution cost of the slurry and monolith are equal as a function of the monolith manufacturing charge is illustrated in Fig. 5. The monolith catalyst must achieve multiple uses between 3 and 15 compared to the slurry catalyst to achieve cost contribution parity with the slurry catalyst. This is typical for processes using precious metal catalysts.

As the catalyst usage increases, the savings over the slurry catalyst increase correspondingly. The sensitivity of saving to catalyst use and manufacturing charges are illustrated for an example in Fig. 6. The ultimate catalyst contribution savings for a monolith is the cost of the slurry catalyst which can be achieved with high use levels which are a factor of 10 times the slurry catalyst use level.

The monolith catalyst is more conveniently regenerated than slurry catalysts; washing steps can be conducted while the catalyst is in place whereas slurry catalysts require additional process vessels and filters. Regeneration

Table 3
Comparison of performance and economics for a Pt slurry catalyst compared to monolith catalysts with different loadings and life

	Unit	Slurry	Monolith case 1	Monolith case 2	Monolith case 3
Pt in each reactor to achieve similar batch times.	g	284	426	426	852
R = Pt in monolith/ Pt in slurry	kg/kg	–	1.5	1.5	3.0
Pt on catalyst (dry)	wt%	5	3.1	3.1	6.2
	g/m^3	–	7060	7060	14100
Manufacturing charges including fabrication,	\$/kg	50	290	290	290
profit and raw materials cost excluding metal	\$/m^3		65000	65000	65000
Cost of metal recovery as a % of the initial catalyst cost	%	5	10	10	10
Number of batches for each catalyst		1	10	20	20
Net metal catalyst recovered for reclamation credit	%	90	90	82	82
Net catalyst cost after recovery credits and costs*	\$/kg of product	0.854	0.347	0.173	0.347
Net savings per batch based on total number of batches processed	\$	–	577	774	577

Pt price assumed to be \$490/troy ounce = \$15.75/g. Feed solution (3790 kg) contains 30% substrate in 70% solvent. Monolith reactor volume is 0.06 m^3 attached to the main reactor in a monolith loop reactor configuration. The monolith is made of 400 cells per square inch cordierite. The stirred tank volume is 5.0 m^3.

procedures will depend on the particular chemistry conducted. For example, the processing of highly functional organic substrates can generate oligomers and condensation products, which can occlude the porous catalyst surface reducing catalyst activity. Solvents can be recirculated under heating and hydrogen pressure to remove these heavy products while regenerating the catalyst surface. In the case of amines, hot water with a dilute organic or inorganic acid can be used to remove adsorbed products or dilute caustic solutions can be used to release the amines from the surface.

7.5. Replacement of a Ni slurry catalyst with a precious metal monolith catalyst

The conventional hydrogenation of sugars to sugar alcohols using Raney® nickel catalyst leads to a batch product containing dissolved nickel, which must be treated with ion-exchange resins to make an acceptable product. Ruthenium catalysts avoid this problem, reducing the costs of the ion-exchange operations and waste disposal. Raney® nickel is relatively dense, and can be separated and recycled by settling [12]. Unfortunately, typical ruthenium/carbon catalysts do not readily settle and cannot be directly substituted in a process designed for Raney® nickel without investment in additional catalyst handling equipment. A monolith loop reactor design, which avoids filtration issues, holds particular promise in this case.

In Table 4 the parameters necessary to economically justify such a process are examined. If the monolith catalyst can conduct 300 batches (30 times more than Raney® Nickel), annual catalyst contribution savings up to \$370,000 may be realized. This level of savings can justify a capital investment between \$500,0000 and \$1,000,000. In addition, an economic analysis should include the additional benefits associated with the reduction of nickel waste disposal and ion-exchange operating costs which can save between \$0.005–\$0.01/kg based on the final product. For a single 29,000 metric ton per annum sorbitol reactor operating 1895 batches per year this would provide an additional \$145,000 to \$290,000 of savings for the new monolith process, which is similar in magnitude to the catalyst contribution savings.

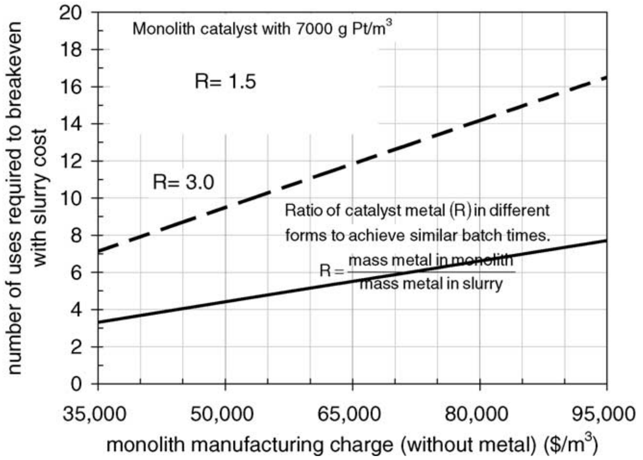

Fig. 5. Sensitivity economic analysis showing the minimum number of catalyst uses required for the monolith catalyst to achieve identical catalyst contribution costs compared to a slurry reactor when the slurry catalyst is only used once before reclamation. The process is summarized in Table 3.

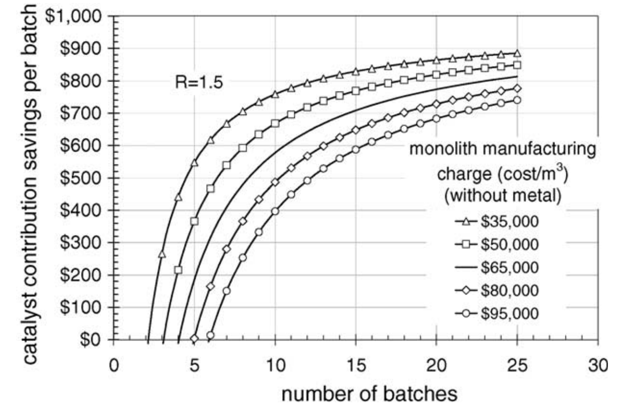

Fig. 6. Sensitivity of catalyst contribution savings to the number of times the monolith is reused and the manufacturing charges, for the general process summarized in Table 3.

Table 4
The comparison of performance and economics for a Ru monolith catalyst in a monolith loop reactor configuration with a Raney® Nickel slurry catalyst process to produce 29,000 metric tons of sorbitol from glucose in a single reactor system

	Unit	Raney® slurry	Ru monolith case 1	Ru monolith case 2	Ru monolith case 3
Catalyst metal in each reactor to achieve similar batch times	kg	181	22.4	22.4	22.4
R = Ru in monolith/Ni in slurry	kg/kg	–	0.13	0.13	0.13
Metal on catalyst (dry)	wt%	95	6.3	6.3	6.3
	g/m^3	–	14100	14100	14100
Manufacturing charges including fabrication, profit and raw materials cost excluding metal	$/kg	26	223	290	357
	$/m^3		50,000	65,000	80,000
Cost of metal recovery as a % of the initial catalyst cost	%	5	10	10	10
Number of batches for each catalyst		10	300	300	300
Net metal catalyst recovered for reclamation credit	%	82	97	97	97
Net catalyst cost after recovery credits and costs*	$/kg of product	0.035	0.022	0.027	0.032
Annual catalyst savings compared to a slurry catalyst for 1895 batches per year per reactor	$	–	370,000	220,000	70,000

Ruthenium metal price is assumed to be $55/troy ounce ($1.22/g); nickel metal price is assumed to be $11/kg. The slurry reactor volume is 30 m^3, filled to 80% volume with 55% glucose (28,000 kg solution). Monolith reactor volume is 1.6 m^3 attached to the main reactor in a monolith loop reactor configuration. The monolith is made of 400 cells per square inch cordierite.

The formation of organic acids such as gluconic acid is well known in the manufacture of sorbitol and regeneration of the monolith can be facilitated by washing with dilute base and acid to remove organic acids and salts that may build up on the catalyst surface. Particular regeneration recipes can easily be developed by washing the catalyst in situ followed by rate and selectivity testing.

8. Conclusions

The monolith catalyst, an established technology in gas phase catalysis, is poised to find its place as an alternative to slurry catalysts in the fine and specialty chemical industry. Important considerations and design parameters of operating a monolith catalyst in three-phase applications include recycle rate, residence time, mass transfer, pressure drop and mixing. These are now sufficiently understood and most engineering challenges have been met, so that a combined engineering analysis based on models and well instrumented pilot equipment can provide reliable scale-up implementation for any new chemistry challenge.

At the heart of the technology however is the ability to design, rapidly test, and manufacture new robust catalysts with long life. This challenge requires that established monolith fabrication methods be used to create catalysts whose performance matches that of slurry catalysts, yet whose formulation is often quite different. Developing inorganic washcoats which can provide the same performance as carbon based slurry catalysts is key to successfully replace many slurry processes. The higher manufacturing costs of monoliths compared to slurry catalysts will always require that monolith catalysts have long life. At the same time the elimination of slurry catalyst from a process can have far-reaching economic advantages that cannot be simply represented by the catalyst cost. A holistic economic analysis that includes the impact of reduced maintenance, environmental charges, elimination of filtration, lower waste disposal and high metal recovery will provide the best basis for understanding the ultimate advantage of the monolith technology.

Each process chemistry will provide its own challenges and likewise unique economic advantages with the removal of slurry catalysts. While not every chemistry will benefit from this approach, monolith catalysts hold sufficient potential for economic benefits that their use should be considered in the development of new three-phase processes.

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