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Chemical Engineering Journal 90 (2002) 47–60

Chemical Engineering Journal

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Alternative multiphase reactors for fine chemicals A world beyond stirred tanks?

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Abstract

Traditionally the intermediate scale and fine chemicals industries have relied on stirred tank reactors, operated continuously or more commonly batchwise, as the work horse of their manufacturing plant to the almost total exclusion of any other type of liquid reactor. The switch to continuous processing has generally been resisted on the basis that this compromises plant flexibility and thus, reduces capital productivity. While the stirred tank and the associated slurry catalyst are of course reliable and flexible to the demands of multi-product plant, it is not always easy to scale up the chemistry from the laboratory and variability in product arises from imperfections in the mixing. This problem is exacerbated for multiphase reactions where the non-uniformity in mixing and mass transfer can lead to significant variance in reaction rate and selectivity, resulting in loss of product quality and productivity. The problem is that while the stirred tank is convenient, it is not in fact a particularly effective mixing device. While historically the stirred tank was one of few options, times are changing. There are many reactor designs now available for multiphase contacting and reaction. Some of these are a proprietary improvement on the simple stirred pot while others are significantly different, such as trickle beds, bubble columns and the use eductors and loop reactors for intense gas/liquid mixing. Interest is increasing into applying process and reactor intensification techniques to batch production through use of small flow channels and structured catalysts, of which monoliths are the best known example. This is however, but one example of work on structured catalysts and reactors that is expected to have an impact on the intermediate scale and fine chemicals manufacturing in the near future.

Keywords: Multiphase; Monoliths; Trickle beds

1. Introduction

Multiphase reactions are important to the “fine chemicals” industry. An extensive review of multiphase reactions carried out in the pharmaceutical and fine chemicals industries is provided by Mills and Chaudhari [1], who highlight that reaction classes carried out include hydrogenation, oxidation, carbonylation and hydroformylation.

The term “fine chemicals” is used to describe a vast array of chemicals of different degrees of complexity: molecular weight, number of functional groups, geometric isomers and enantiomers. The term is commonly used to refer to the chemicals produced at moderate scale, but is also used to infer a degree of complexity and precision in their manufacture or simply a batch production procedure. Does the term “fine chemicals” refer to the finesse of the chemistry or to the small scale of manufacture? It is far from clear. The term is at best imprecise, at worst meaningless. So, for the purposes of this paper, it is useful at least to consider what is meant by the term “fine chemicals”. This will also help highlight the reactor and manufacturing technology opportunities within the “fine chemicals” industry.

The distinction, from the viewing point of an industrialist, is best made in terms the supply route for the product. So called fine chemicals tend to be marketed in one of two ways:

1. *Custom chemical for a specific customer*: this may be produced on a “toll” basis, or be the result of collaboration into developing the manufacturing route or indeed the specific chemistry. The product value for the chemical manufacturer is of dependent on their level of involvement in the process development. Generally, the competitive advantage for the manufacturer lies initially in the rapid development and scale up of new chemistry and catalysis, and only secondarily in the manufacturing costs and technology.
2. *Generic chemical for multiple customers*: the Chemistry and manufacturing technology may be the intellectual property of the company, but more commonly the chemical product will also be available from other suppliers, and thus, manufacturing costs start to have an important impact on competitiveness and operating margins. The

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1385-8947/02/$ – see front matter © 2002 Published by Elsevier Science B.V.
PII: S1385-8947(02)00067-0

competitive advantage here lies in the manufacturing and supply chain costs of the company.

The first of these is considered to be the true “fine chemical”. The second may conveniently be termed intermediate scale chemicals. This of course begs the question of where the line may be drawn between intermediate and bulk scale. A fair question, but one that will not be addressed herein.

2. Intermediate scale and fine chemicals manufacturing

The intermediate scale chemicals manufacturing industry is dominated by batch processing. The overall design of plants is set to accommodate the further requirements for a multi-step manufacturing process, and that a given plant will produce multiple products. Typically, chemicals will be manufactured in campaigns lasting days or weeks, before switching the plant to a different product. Manufacturing plants in fine and intermediate chemicals plants therefore need to be flexible in order to facilitate the multi-step processes and multi-product plant approach. This has led the industry to adopt, almost universally, the stirred tank reactor, operated batchwise, as its primary reactor technology.

Stirred tanks for multiphase reactions, Fig. 1, which will be discussed in detail in later parts of this paper, essentially comprise the autoclave, or pressure vessel, plus a shaft driven impeller and a sparge pipe means of introducing the gas. There may be more than one impeller on the shaft and they may be of common or proprietary design. Heterogeneous and homogeneous catalysts may be used, and if the former presented in the form of a slurry.

It is interesting to note that this approach to manufacturing of chemicals on a small and intermediate scale has little changed over the last 500 years. The uncanny resemblance between a 16th century gold plant, Fig. 2, and a modern fine chemicals plant, with both being dominated by the stirred tank reactor, has already been noted [2]. The late Prof. Villermaux made a similar observation [3]. He noted that the technology of Concorde has almost nothing to do with that of the Wright brothers or Bleriot, and that they would probably not be able to fly it. By contrast, technical drawings of chemical processing apparatus, such as batch reactors, taken from patents filed in the 1880s are remarkably similar to those still in use and being installed now. At first sight it does not appear that much progress has been made.

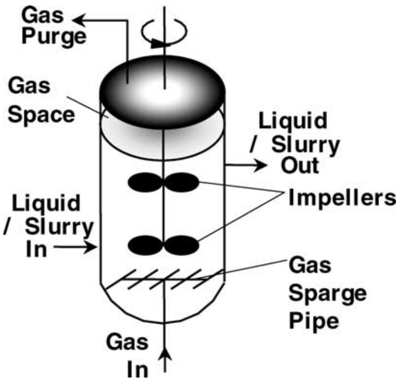


Fig. 1. Stirred reactor with dual agitators and gas sparging.

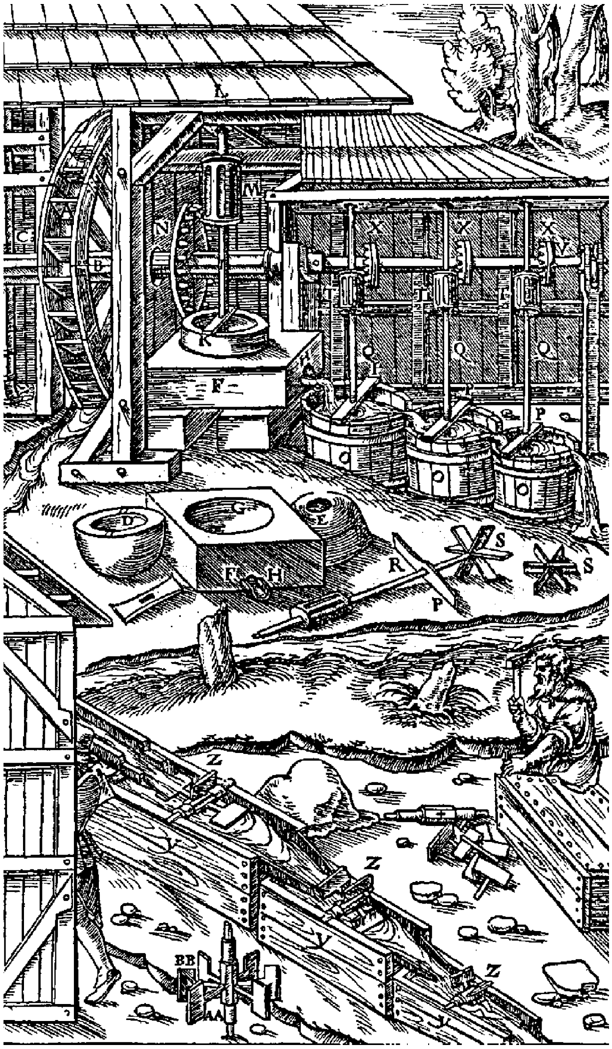


Fig. 2. Engraving of a gold processing plant.

A significant problem with stirred tanks as multiphase reactors is that it is hard to eradicate all transport limitations, whether gas/liquid, liquid/solid or within the homogeneous liquid phase. This means that the reactor may be mass transfer or heat transfer limited, and this can impact on operations by limiting productivity, and may affect both rate and selectivity

These problems are particularly acute during scale up. Geometric, bubble, mixing and kinetic lengths do not scale in proportion. This leads to uncertain changes in heat and mass transfer in scaling from the laboratory to pilot to full scale. Mixing gets harder as the vessel gets larger. Apparent changes in selectivity and activity are observed, and these lead to longer batch times and reduced yields.

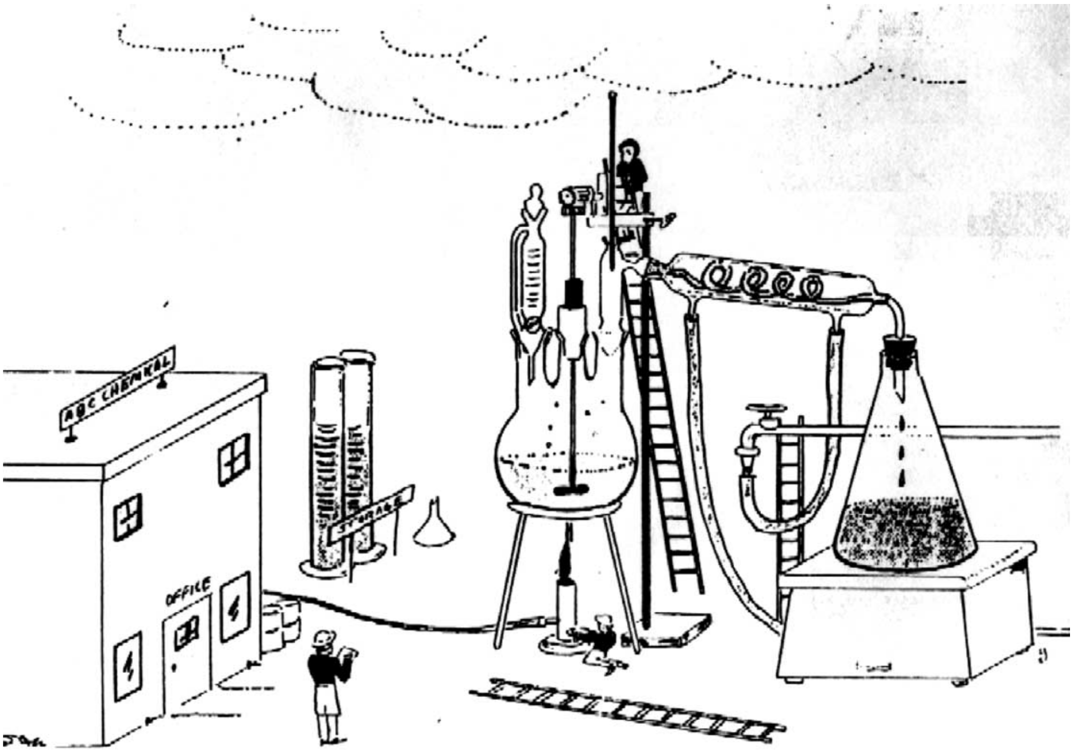


Fig. 3. "The bench scale results were so good that we by-passed the pilot plant."

"So what's the fuss about scale up?" This is a question often posed by colleagues in chemistry and catalyst research; implying sometimes that reaction engineers have an irrational fear of scale up. The truth is of course that there is nothing irrational about the caution with which scale up is treated, but rather that the irrationality tends to lie in the scale up itself. If it did not, then fine chemical plants may in fact resemble that presented in Fig. 3. They do not of course; although note particularly the presence of the same, ubiquitous stirred tank even in this light hearted representation.

There is now a growing awareness in the intermediate scale and fine chemicals companies that traditional manufacturing methods do not give cost advantage. This is especially true for the intermediate scale chemical products, where they lead to expensive unit costs and potential loss of selectivity and production because of the limitations of the stirred tank reactor at a medium and large scale. Further, in fine chemicals, it is difficult to reliably scale up new chemistry, leading to expense on scale up and transfer of laboratory chemistry to production scale as well as delayed new product introduction to the market (viz. delayed sales income).

Here lies an opportunity, therefore, for alternative approaches to the engineering of multiphase reactors for intermediate scale and fine chemicals, to improve the manufacturing cost base and speed beneficial production of new products. This is a technology based opportunity for improved profitability in this sector of the chemical industry.

3. Stirred tank reactors

The batch stirred tank reactor is the workhorse of the intermediate scale and fine chemicals industries. They are used at the small scale ($<1\,\mathrm{m}^3$), at large diameters, and notably in the bulk chemicals industry for continuous production units at the very large scale, 15–30 m^3, for example in terephthalic acid and aniline plants. As noted above, the catalyst may be in the form of slurry or a homogeneous catalyst. Slurry catalyst particle sizes vary from one catalyst to another, and significantly from one support material to another, but diameters in the range of 20–250 μm are typical.

The gas may be sparged, or pulled in from the bulk gas–liquid interface using a gas inducing type impeller. Importantly, however, in many batch reactors, the gas addition is on a pressure controller, maintaining constant pressure; so called "dead end reactors" [4]. Thus, at the start of the batch, while the reaction is fast, high gas sparge rates are required to maintain the pressure and thus, gas–liquid dispersion is best maintained through efficient breaking up of the sparged gas into small bubbles. As the reaction slows, the gas feed rate declines. The mass transfer of the gas from the bulk space above the liquid then becomes more important if high gas reactant concentration levels in the liquid phase are to be maintained. Correct design and selection of the impeller and sparge arrangements are thus critical to the mass transfer performance of the reactor.

Heat transfer (cooling or heating) may be provided by an external jacket or by internal coils or tubes. The internal fittings provide the opportunity for a higher heat transfer area, but makes cleaning more difficult (in fouling or multi-product applications) and disrupt the fluid mixing patterns within the vessel. External jackets are generally inevitable if the reactor is lined, for example with glass.

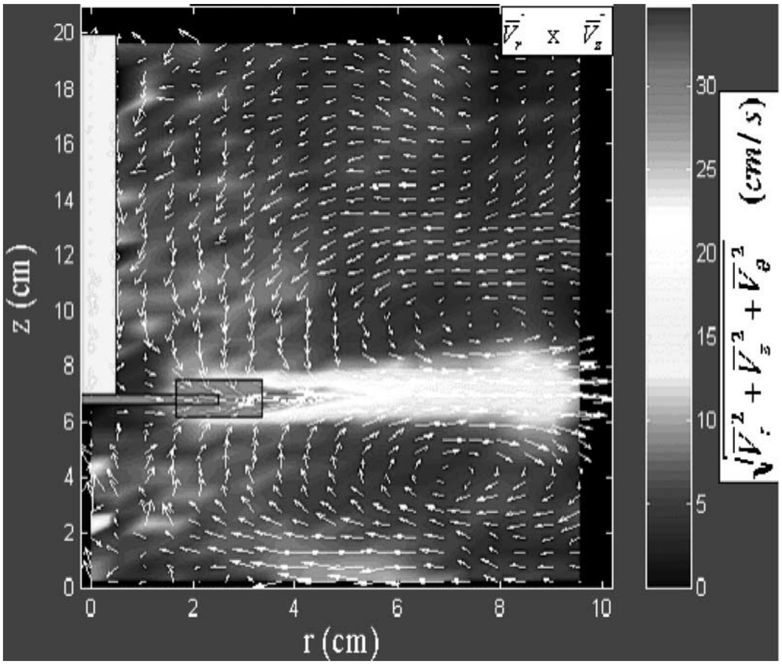
From the above, in the case of poor mixing design (or operation) or insufficient heat transfer (area or coefficient), then one or more of these transfer processes may limit the rate of the reaction. This can result in variable concentrations of chemical species in the liquid phase and adsorbed onto the catalyst surface. This can impact on the reaction selectivity and in some cases the stability of the catalyst itself. Inadequate heat transfer will result in overheating for an exothermic reaction and thus, changes in selectivity, or a lower temperature for endothermic reactions, resulting in low activity and longer batch times. The mixing and fluid flow is complex, and thus, the mass and heat transfer are difficult to predict and design with any accuracy. There is considerable experience in the industry and academia in mixing, and understanding is increasing rapidly. It is still not possible, however, to model a mechanically agitated vessel with multiple phases in predictive fashion. As noted before, it is also not possible to predict with confidence how these will change with scale up and the increase in vessel diameter and/or height.

3.1. Stirred tank mixing patterns

It is worthwhile to consider briefly the mixing problems of stirred tanks. In order to do this, flow visualisation based on the mathematical reconstruction of data measured by tracking the motion of a radioactive particle will be used. The particle density may be chosen to be neutrally buoyant (and thus, mimic the liquid) or to resemble a catalyst particle. Two techniques are referenced here: one based on a γ-ray emitting particle, the other based on a positron-emitting particle. Both of these techniques are presented comprehensively in [5] and will not be discussed in detail here.

The first data set is based on a 200 mm diameter stirred tank, with four planar baffles and stirred by a six blade Rushton turbine [6]. The velocity data measured using a γ-ray emitting neutrally buoyant particle are presented in Fig. 4. The plot shows clearly the high velocities in the impeller region, with these dissipating as the flow progresses radially outwards. Two clear circulation patterns are evident, one each below and above the impeller. Also discernible are quiescent zones, for example, below the impeller, and two near the wall above the impeller. Clearly the momentum transfer, required to achieve uniform mixing, is relatively poor even at this small scale.

In slurry catalyst systems, interest relates not only to the liquid recirculation patterns, but also the suspension of the catalyst particle, its recirculation and the mass transfer from the fluid to the solid. Using positron emitting particle tracking, the circulation patterns of the liquid and two representative particle densities have been studied [7]. The set up was a 100 mm diameter baffled vessel with a pitched blade turbine impeller-intended to give improved up-draft over the Rushton turbine used in the above study. The liquid mixing patterns, again from use of a neutrally buoyant particle, are shown in Fig. 5. There are a number of observations to be made here. Firstly, the up draft does not progress past



From [6]

Fig. 4. Liquid velocity flow patterns from computer automated radioactive particle tracking experiments (tank diameter 200 mm, Rushton turbine speed 150 min^{-1}) [6].

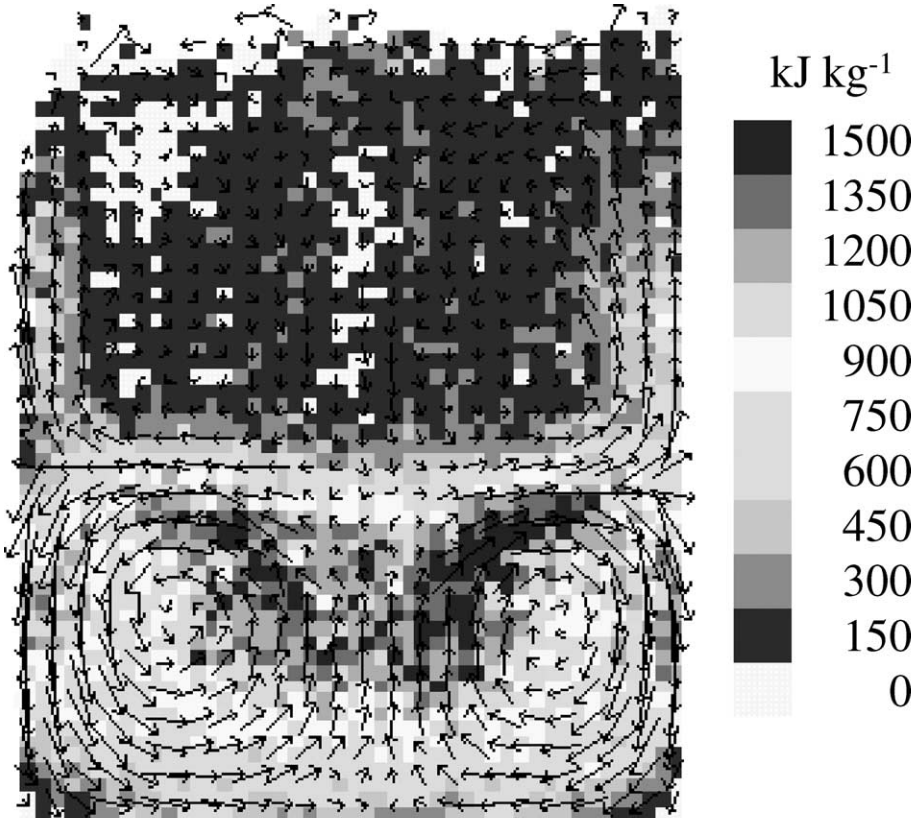


Fig. 5. Liquid kinetic energy and flow patterns in a stirred tank with a pitched blade turbine impeller from positron emission particle tracking (vessel diameter 100 mm, impeller diameter 35 mm, impeller speed 800 min^{-1}).

the plane of the impeller. Secondly, two distinct circulation patterns are evident, in the upper and lower portions of the vessel, with the upper part of the vessel being far less intense. The extent of this difference is emphasised by the velocity probability density function, Fig. 6. The distribution shows a clear shoulder, indicative of a bimodal distribution; effectively a different distribution for the upper and lower circulation patterns, Fig. 6a. The same is true, Fig. 6b, for the 1300 kg/m^3 particle (taken to be representative of a γ-alumina supported catalyst). For the heavier particle (3000 kg/m^3 roughly equivalent to Raney nickel), the distribution appears to become uni-modal, but this is essentially because the particle does not penetrate into the upper portion of the vessel. While the extent of mixing could of course be improved by increasing the impeller speed, this study indicates clearly the problems that will occur in portions of the vessel where the liquid momentum is insufficient, which is inevitable in large-scale vessels.

There are a number of general observations that can be made from the above flow visualisations:

- large variations in local velocities;
- high shear and high velocities in the impeller region;
- impeller induced up-and down-drafts may not progress far past the plane of the impeller;
- areas of low velocity and near stagnation are seen;
- uncertain inter-penetration between upper and lower circulation patterns of both the fluid and the catalyst.

These observations are of course made for small diameter vessels, and it is well known that mixing heterogeneity increases with the size of the vessel!

3.2. Improvements to stirred tanks

There are numerous approaches to improving the mixing capability of stirred tanks. These involve largely modifications to the fixed internals and to the impeller design.

For fixed internals, vertical wall baffles are the oldest and most obvious example. Flow segregation baffles have also been used to encourage, most commonly, a core upward flow with an annular downflow circulation pattern. The cylindrical baffles may be an integral part of the impeller (rotor–stator systems) or be a discrete vessel internal, such as the Praxair LOR [8].

Impeller design is the most common variable, with the redesign normally intended to give directional flow: up draft, down draft (gas inducing), radial or vortex. This can involve “simply” changing the shape of the blades, such as imposing a curvature on the blades of a classic Rushton

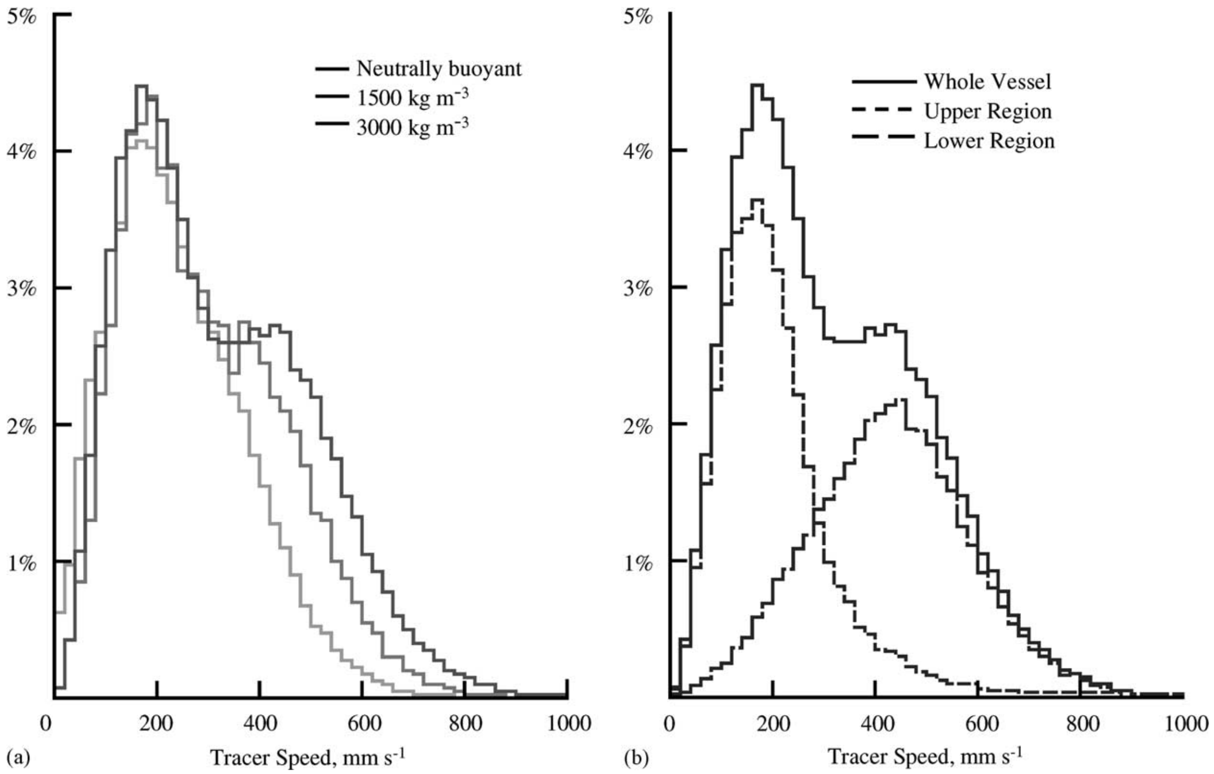


Fig. 6. Probability density function for different density particles from positron emission particle emission experiments: (a) for a neutrally buoyant particle and (b) for particles of different densities. Vessel diameter 100 mm; pitched blade turbine 800 min^{-1}.

turbine. This is effective in improving the gas dispersion characteristics. Alternatively, turbine and hydrofoil type impellers are also available commercially for ostensibly the same operation—dispersing a gas into a liquid continuum. The combination of different impeller designs mounted on the same shaft is also practised, with the lower impeller designed to break up the gas coming from the sparger and the upper impeller designed to draw down the gas from the bulk interface. An enormous variety of impeller designs is available commercially, with frequently a single supplier offering a dozen or more designs, each proposed for different types of applications . All major commercial suppliers can present impeller designs that show significant improvements over classic designs such as the paddle, the six blade Rushton turbine and the marine impeller.

In addition to the significant improvements in mixing devices that have been made, improvements in understanding are possible using the many flow visualisation techniques available today and judicious use of computational fluid dynamics codes. Even with these advances, mixing heterogeneity is still the norm and it remains unavoidable that changes in the characteristic lengths of the key rate processes change with the diameter of the vessel. It remains impossible, especially for multiphase systems, to predict this with any certainty. The use of the stirred tank still therefore, is still characterised by slow mixing and transport and uncertainty on scale up. Recent advances have significantly reduced, but not solved the problem.

4. Whither fine chemicals reactors?

Stirred tanks are workhorse of the medium to fine scale chemical industries. They are used on a small and a large scale, with slurry and homogeneous catalyst, with the gas normally sparged. The impeller and sparger design is critical and poor mixing patterns can occur even in small vessels. Proprietary designs do help significantly, and considerable improvements have been made over the last 25 years.

The inescapable fact however, is that stirred tanks are fundamentally poor mixers; and the larger they get the worse they get. Not only this, but also they do not scale up well.

If this is the case, then this begs the question, in what type of reactor might intermediate and fine scale chemicals be better manufactured? Considering the drivers that have led to the widespread adoption of stirred tanks, this raises the following pointed questions regarding manufacturing practice.

1. Can continuous operation cut cost? Is batch manufacture always the right approach? At what scale of operation does continuous, automated and controlled operation become the economically preferred route?
2. Must a flexible reactor be a stirred tank? Is it used simply because of its resemblance to a round bottomed flask, or is it really the best (slurry) reactor for the job?
3. Can non-slurry plants be flexible? Can fixed bed (or immobilised catalytic) reactors be designed able to cope with multi-product and multi-step processing at low cost?

4. Can we ease scale up problems through different technology?

These questions are the heart of this paper, and the remainder of the paper will try to address some of them. They are fundamental to the progress of intermediate and fine scale chemicals manufacturing, and maybe progression beyond the traditional stirred tank approach.

5. Multiphase reactions—a world beyond stirred tanks

Multiphase reactors can be classified into families, in similar fashion to the consideration of gas–solid reactors of van Swaaij [9]. The most convenient classification is according to whether the heterogeneous catalyst is mobile or fixed, with subdivisions of each genus according to the source of energy input and the nature of the gas–liquid dispersion. For present purposes, it is more convenient to limit the degree of classification to the nature of the catalyst and the technology status, Table 1.

This is only a selection of the reactors available and proposed for gas–liquid and three phase systems. For a more comprehensive coverage see Mills et al [10]. Some of these reactors will now be considered in the context of the questions posed above.

A key benefit of a fixed bed catalyst over a slurry catalyst is that the need for catalyst filtration, separation and recycle is circumvented, at the expense traditionally however, of a loss of multi-product flexibility. This loss of flexibility is a major inhibitor in terms of the take up of fixed bed reactors in the intermediate scale chemicals manufacturing.

5.1. Trickle bed reactor

In a trickle bed reactor, the liquid and gas flow co-currently downwards through over a fixed bed of catalyst, Fig. 7, with the liquid trickling over the catalyst surface as a film within a gas continuum. The catalyst will normally be an extrudate of relatively high aspect (L/D) ratio, of cylindrical or tri-lobe cross-section. Trickle beds are widely used in the refinery and petrochemicals industries for hydrogenation based reactions, with some of the reactors being of very large diameter.

Table 1
Multi-phase reactors—a selection

Fixed catalyst	Mobile catalyst
Conventional reactors	Conventional reactors
Trickle bed	Stirred tank
Packed bubble column	Proprietary impeller designs
	Ebullated bed
Developmental	Three phase fluidised bed
Pulsed trickle bed	Slurry bubble column
Structured catalysts	Loop/jet reactors
Monolith catalysts	

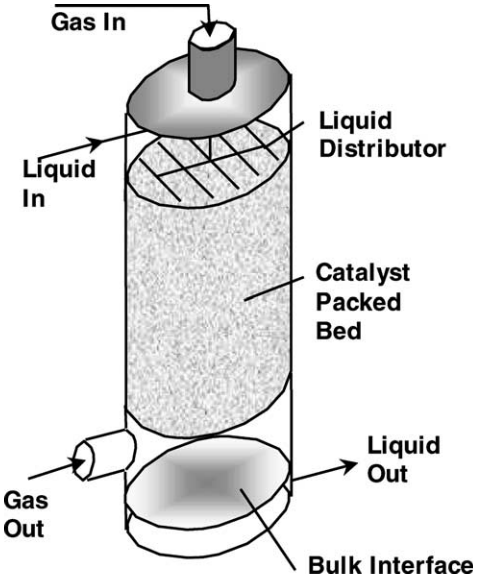


Fig. 7. Schematic diagram of a trickle bed reactor.

The trickle bed is inherently continuous in operation. It has low operating costs, nominally plug flow of the gas and liquid phases and thus, good control over product quality. Because of the random packed nature of the catalyst bed, it is inherently a single product plant, or more correctly a single catalyst plant. There is no provision for heat transfer within the bed. A reaction exotherm must be absorbed either as an adiabatic temperature rise, transferred to a high gas flow rate, dissipated by partial evaporation of the liquid or mitigated by dilution of the reactant. An alternative is to recycle the liquid, but this removes the plug flow design thus, depressing average rates, but with little effect on selectivity if the non-selective reaction is parallel rather than series. At high rates, the reactor can be gas–liquid mass transfer limited.

Scale up from laboratory is not straightforward. This is essentially because the mass velocities (which dictate the hydrodynamics and thus mass transfer) and space velocities (or residence time) do not scale linearly. Scale up is however, reliable with correct know-how and methods.

The key question here is at what size are they competitive? Opinions vary considerably. The literature has a number of evaluations, but these are for the most part of doubtful general validity. There are widely differing base cases and widely different assumptions for design costing. Particularly, the base case designs for trickle bed and batch plants are based on different flow rates, and to different levels of specification, and the cost extrapolations contain gross over-simplifications (e.g. single cost scaling exponent and no step changes). The essential element of a cost comparison is that designs and costing should be done on a comparable level, and extrapolations performed with caution.

So what is a general rule? Take the example where a fine chemical manufacturer is capacity constrained, but has a single product that currently occupies one of the (flexible) batch plants for 50% of its operation. Is the best option to build a new batch plant, or build a single stream continuous plant with a trickle bed reactor to free up the batch unit? The answer is very dependent on the application: reaction network, reaction kinetics, conversion, pressure and temperature. There is also considerable variability in "local" factors, such as manpower costs and capital location factors.

Unfortunately, the recommendation is to consider each case on its own merits. Specifically, beware generalisations in the literature and examine carefully the validity of the design and cost comparisons, and the cost scaling.

5.2. Pulsed trickle beds

At low liquid mass velocities trickle bed performance can be relatively poor. Operation at low liquid rates may occur due to design for high conversion. The low performance arises due to poor wetting of the catalyst surface, and thus, low mass transfer area and low catalyst surface utilisation. This can be overcome by liquid recycle, which also allows heat transfer. In the case where high conversion and high purity are required however, this may not be permissible and an alternate solution to the problem is required.

One proposed solution is to pulse the liquid feed [11,12]. Typical pulse cycles are in the range of 15–60 s, and the benefits at low time averaged liquid rates are proven at small scale. The technique probably works by periodic total wetting of the catalyst, followed by partial drainage prior to the next liquid pulse. The net effect is that the time averaged wetting of the catalyst is significantly increased relative to steady-state operation. Periodic surface renewal due to the pulse liquid flow may bring additional mass transfer benefits. This is a very interesting development to improve trickle bed efficiency, operability and flexibility.

5.3. Slurry bubble columns

In the slurry bubble column, Fig. 8, the gas flows upwards though the liquid/slurry phase. The energy input into the column is via the gas sparge, in contrast to the stirred tank were the primary input is via the impeller. The overall flow pattern of the liquid is that in the axial portion, the liquid is in up-flow, essentially due to an "air-lift" (or gas pumping) type phenomenon induced by the gas flow. Near the walls the liquid and solids tend to be in downflow, with little gas hold-up. This is demonstrated in Fig. 9, that shows the gas phase hold-up, represented as the density measured by γ-ray transmission based computer tomography [13]. This shows clearly the high gas hold up in the axial part of the column and the low gas hold up near the column walls. Radioactive particle tracking has also been used to confirm this flow pattern [14]. This circulation pattern leads to the liquid/slurry phase being essentially fully backmixed, in common with the stirred tank. Gas–liquid mass transfer is generally quoted as being good. It has been deployed commercially for methanol synthesis from coal-derived syngas, Fischer Tropsch synthesis and natural oil hydrogenation.

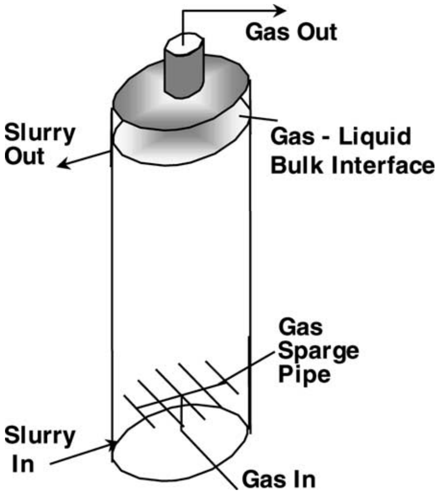


Fig. 8. Schematic diagram of a slurry bubble column reactor.

The slurry bubble column may be operated batchwise of continuously with regards to the liquid. While continuous operation is currently used for the slurry phase methanol process and Fischer Tropsch synthesis, current bubble columns installed for fat hardening duties are generally operated batchwise.

Vertical heat transfer tubes may provide heat transfer surface. These are in fact apparent in Fig. 9 as the small black circles. The high liquid rise and fall velocities in the two regions ensure high heat transfer coefficients and good heat transfer. The notable difference between the slurry bubble column and the stirred tank is that while internal coils in a stirred tank interrupt the natural flow patterns and are deleterious to mixing, in bubble columns, they have little or no effect on the overall hydrodynamics (depending on the tube spacing).

The bubble column may be operated at much higher catalyst loading then the stirred tank. Actual solids loadings of over 30 vol.% are known. Stirred tank values are rarely above 5%. This of course may lead to high attrition of catalyst is it is not robust. It does however allow much higher volumetric activities, or equally, allow economic deployment of low activity catalysts.

Overall, the bubble column appears a very attractive alternative to the stirred tank. It is flexible, efficient in terms of heat and mass transfer, and it allows high catalyst loadings. The simple internals facilitate easy cleaning and it is thus, suited to multiple product applications. The drawback is that the hydrodynamics are not yet well understood, and scale up is not straightforward. Thus, while in performance terms the bubble column looks a good alternate, the problem of difficult scale up remains and, in truth, may be exacerbated.

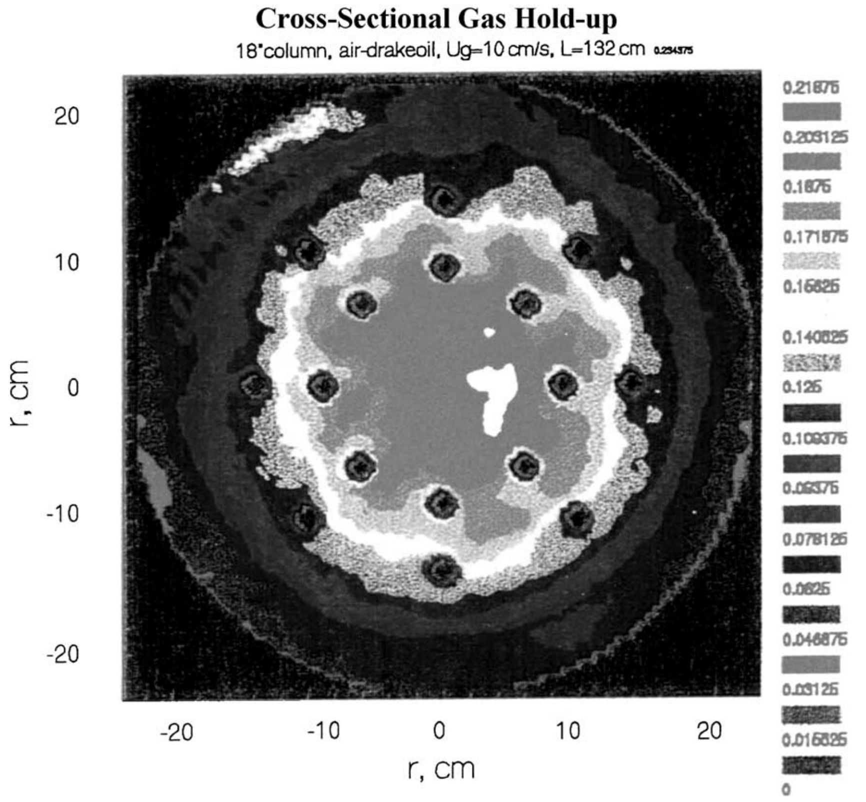


Fig. 9. Fractional gas phase hold up patterns in a bubble column measured by computer tomography.

6. Jet (or loop) reactors

In jet, or loop reactors, the gas liquid mixture is passed through a constriction, or eductor causing intimate mixing and break up of the gas phase into very small (<1 mm) bubbles. Rapid mass transfer equilibration of the gas and liquid occurs. The dispersion passes into the body of the reactor where sufficient time is allowed for reaction to occur. Mass transfer continues courtesy of the inlet velocity induced circulation and the intimate gas–liquid dispersion. The liquid from the reactor body is recirculated to the eductor, typically via a heat exchanger.

The best known and commercially most successful version of the reactor is the Buss loop reactor (Kvaerner Process Technologies). It is commercially proven for gas–liquid systems, with several hundred production scale installations. It uses venturi ejector to obtain mixing, Fig. 10, which is used also to pull a slight sub-pressure on the gas head space thus, naturally recycling the gas phase. Due to the “loop” design, the liquid is naturally fully backmixed, and the reactor can be operated in batch mode or in continuous mode with continuous addition to and withdrawal from the loop.

There are competitors to the Buss loop, although none are commercially as successful. It is hard to assess their performance and economics relative to more generic equipment types, because there are few independent assessments in the literature and it is difficult to assess the cost base from first principles.

An alternative design from academia is the co-current downflow contactor reactor (CDCR), Fig. 11. This design uses simple orifice type nozzle rather than the venturi and

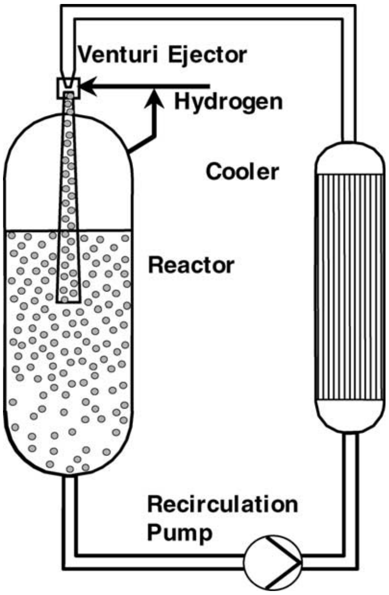


Fig. 10. Buss loop reactor.

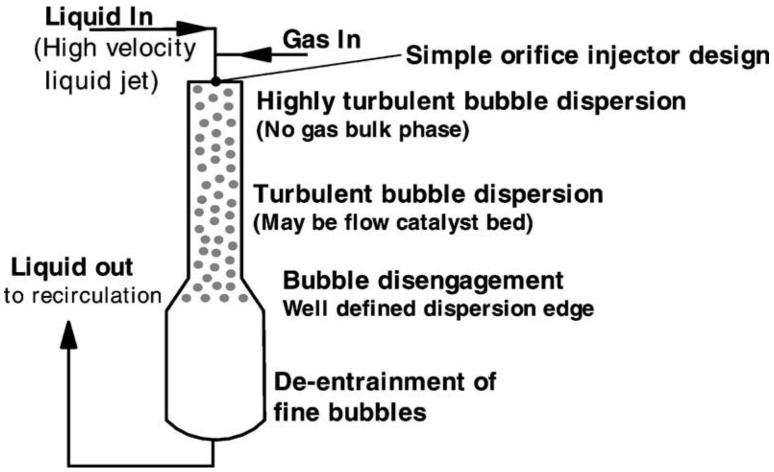


Fig. 11. Co-current downflow contactor reactor.

avoids bulk gas phase (which may be beneficial to safety in oxidation operations). Published data demonstrate the superior mass transfer performance relative to the stirred tank [15].

A number of uncertainties do persist. The first is the mechanical attrition on a heterogeneous slurry catalyst by both the recirculation pump and through the dispersion orifice or throat. The absence of forced up draft in the body of the reactor also leads to problems in maintaining the catalyst in suspension. As an alternative, it has been proposed to used a fixed catalyst bed in the body of the reactor, and pass the pre-formed dispersion through a random packed bed of catalyst [16]

7. An alternative approach

A brief review of the gas/liquid/solid reactor options that may be applicable to intermediate scale and fine chemicals manufacture has indicated tat none are ideally suited. All have advantages and disadvantages, but suffer uniformly one major flaw; they are notoriously hard to scale up. The reason for this, as noted at the start of the paper, is that flow, bubble, mixing and kinetic lengths do not scale in proportion. This applies equally to slurry systems (stirred tank, bubble columns) and fixed bed systems (trickle bed), but for different reasons.

Existing reactor technologies, all scale from a small reactor in the laboratory to a single large one for manufacturing and do present scale up issues. Given that one of the objective questions set earlier was to derive designs to simplify scale up, is this approach logical, and is there an alternative?

7.1. A paradigm in process intensification

The route to process intensification lies in understanding the length-scales and time-scales involved in a typical reactor and plant design [17]. The envelopes for the various rate processes are shown approximately in Fig. 12. There is considerable overlap in these envelopes, and considerable variation in the time and length-scales of a given phenomenon from one process and reactor design to another. The overall message, however, is that a typical reactor tries perform and control processes at the sub-micron and sub-microsecond scales in a reactor that measures a metre or more in diameter and (for liquid phase based processing) a residence time of several minutes to several hours. This is illogical and almost unthinkable were it not for the inheritance of a fine chemicals industry almost wholly dependent on the stirred tank.

This representation emphasises the real issues in traditional scale up. While the molecular reaction processes are constant and micro-scale of turbulence (Kolmogorov lengths) may not change significantly, the distances over which the micro-scale turbulence must be carried does, and inevitably the macro-scale mixing time becomes extended with knock on effects for the rate of mass and heat transfer. A significant portion of the residence time in a large stirred tank is required simply for the time to fully mix the vessel contents and remix them in a dynamic process.

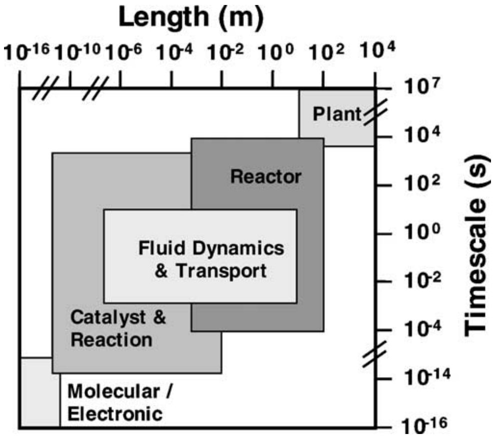


Fig. 12. Length-scales and time-scales in reaction engineering. Redrawn from [17].

Based on this diagram, the route to process intensification is through the minimisation of diffusional lengths and mixing volumes. Minimise macro-mixing lengths and the process will be faster as the mixing times are reduced towards those for molecular transport over short distances. A further benefit can be to improve control by dictating the fluid flow paths and reducing critical geometric lengths. Thinking is therefore, moving towards the use many small parallel reactor paths rather than one large one. Here lies the route to simple scale up; one channel to many channels. The challenge is that to do this without increasing the cost. This implies a structured reactor or catalyst within a single pressure shell in order to constrain plant costs.

7.2. Micron-channel reactor concept

The logical end point of the argument in favour of small parallel paths is to move towards structures with micron-sized flow channels. Here the flow channels would be of a similar dimension to the scale of micro-mixing. This approach has been studied extensively over the last 10 years or so. Intricate devices can be made through a combination of micro-machining, lithography and micro-embossing [18]. An illustrative example is shown in Fig. 13a, which shows a typical plate with parallel 50 μm channels extending into the background, and the fluid entry region in the foreground [19]. These or similar plates may be stacked crosswise to build a heat exchange reactor with alternate plates carrying reactant(s) and heat transfer medium. The plates are then fitted with end caps providing entry and exit ports and diffusion bonded to produce a micro-heat exchange reactor, Fig. 13b [20]. The specific heat transfer surface of his micro-device in 20,000 m^2/m^3; compared to, typically, 500–1000 m^2/m^3 for a shell and tube heat exchanger.

This design concept meets all the criteria discussed in the previous section: small flow channels leading to process intensification, simplified scaling and hence shorter development times. There is considerable work now on trying to exploit this concept, particularly for heterogeneously catalysed gas phase reactions and controlled partial oxidation.

From the view point of the intermediate scale fine chemicals and manufacturer however, there are a few potential problems which relate primarily to robustness in operation. The key potential gremlin is fouling. Real process liquids do foul surfaces. Filtration is never perfect and 50 μm particles could easily be admitted to the reactor causing plugging. There is therefore, a natural reluctance to exploit this technology for this industry sector. Fig. 12, however, infers that any move towards the bottom left hand corner should be beneficial to scale up and rate, and the temptation is therefore, to question what benefits may be achieved through structuring a catalyst or reactor at a more comfortable dimension, say a millimetre of two.

7.3. Catalytic honeycomb monolith for multiphase reactions

The honeycomb monolith has been very successful in gas phase reactors and notably as the structured support form for the conversion of automobile exhausts. Attention for present purposes is focussed on its potential as a structured catalyst for multiphase processes in the intermediate and fine chemicals industry. The catalyst is fixed on the walls of the honeycomb in similar fashion to automobile applications. The honeycomb, with its regular channels, defines a plug flow of the mobile phases. Scale up is simply by increasing the monolith cross-section, keeping the channel size (“pores per inch”) constant. The issue is then scaling the liquid–gas feed system to the monolith. For present purposes, the gas and liquid flow is co-current and downwards.

The potential attraction of structured small channels lies in the intensification of the mixing and transport processes. Gas–liquid flow in small channels was studied over 40 years ago [21]. A number of clear flow regimes were defined, Fig. 14, ranging from small gas bubbles in a liquid continuum, through churn-turbulent bubbles that at their largest

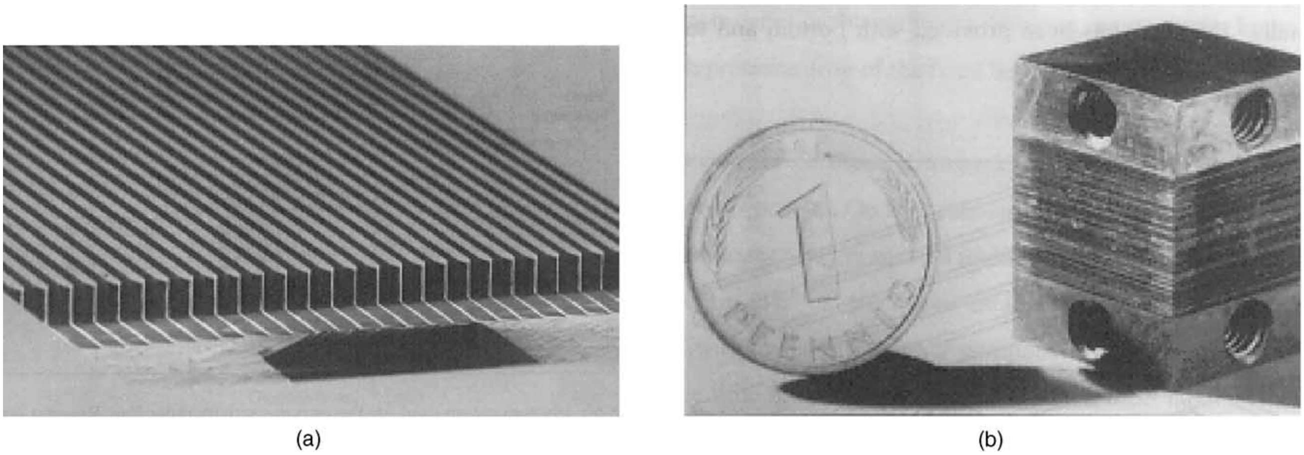


Fig. 13. Micro-machined heat exchange reactors: (a) plate with 50 μm channels [19] and (b) assembled micro-reactor [20].

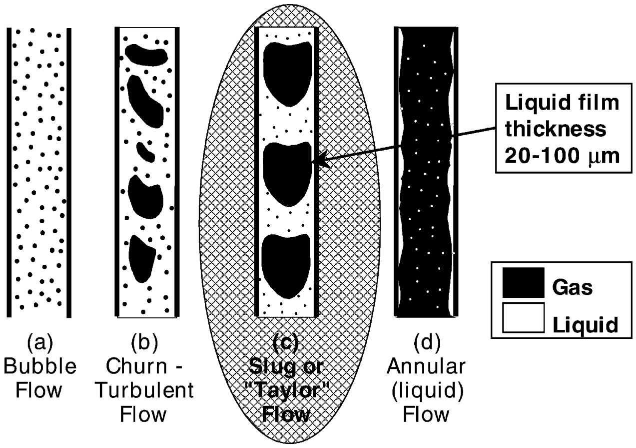


Fig. 14. Gas–liquid flow regimes in small channels, shown for downwards co-current flow. Redrawn from [25].

are constrained by the channel walls, to axial flow of gas through an annular liquid flow. The most interesting of these is the third, where the size of the discrete bubbles is constrained by the channel walls; referred to as slug or Taylor flow. The interest in the current context lies in the thin film separating the gas bubble from the catalytic wall, variously estimated at 20–150 μm in thickness.

By using a structured flow diffusional distances in the micron range can be achieved. Fig. 15 shows the benefit in overall reaction rate by using a monolith rather than a slurry reactor [22], with this data set showing a 30× increase in rate. "Greater than order of magnitude" increases in rate have been corroborated more recently in other laboratories [23,24]. Volumetric rate benefits over trickle bed reactors have also been shown [25].

7.4. A flexible multi-product monolith reactor concept

Based on this evidence, the tenets of the arguments for process intensification inferred from Fig. 12 appear to be valid. This format does not, however, immediately appear to satisfy the requirements for process and product flexibility inherent in the intermediate and fine chemicals industry.

One concept is to install monoliths as a pump around from a storage tank or receiver vessel [24,26]. By using small diameter tubes (e.g. 150 mm) and connecting these in parallel into a recirculation loop from a storage tank, Fig. 16, significant flexibility may be achieved [27]. The recirculation flow, with of without gas co-feed, may pass through one or more of these tubes at a time. The reactor legs may be therefore, used in parallel or in series. The tubes may be loaded with different monolith catalysts and thus,

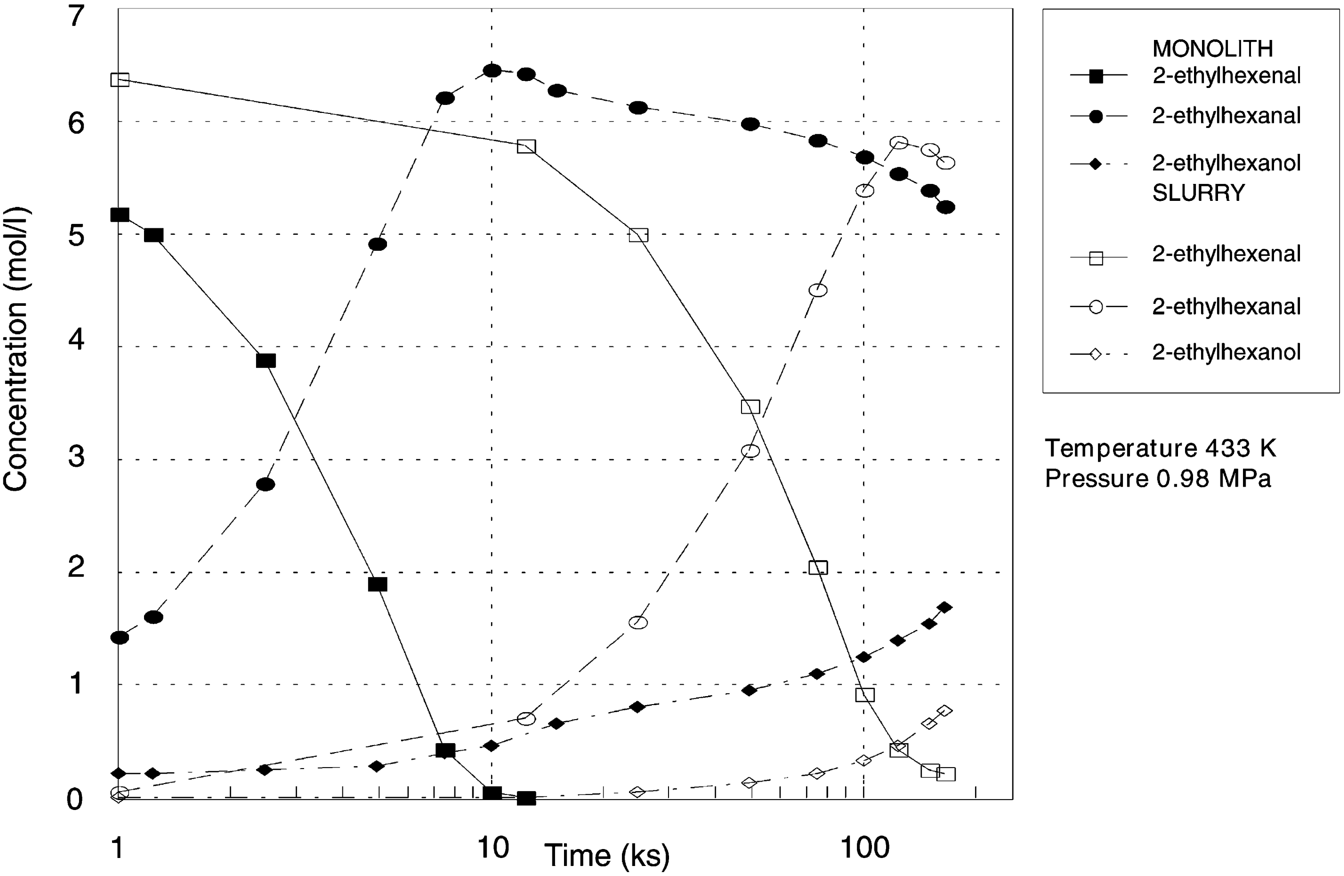


Fig. 15. Comparative data in a stirred tank and a monolith reactor for the hydrogenation of 2-ethyl hexenal. Redrawn from [22].

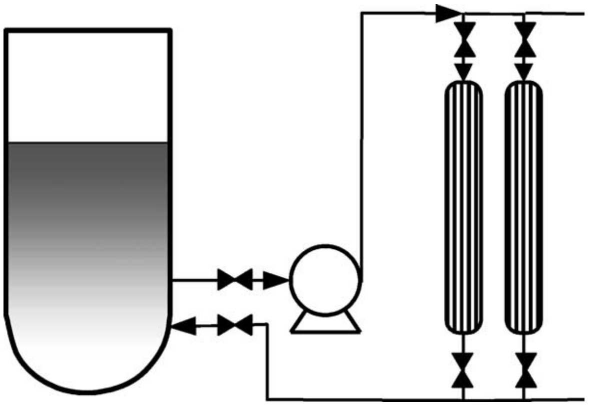


Fig. 16. Monolith pumparound reactor concept for operating flexibility.

flexibility and multi-product capability is achieved simply by switching the flow from one (or more) tube to another. The catalyst containing tubes may be thought of as reactor modules, and may be added, replaced and removed to fit in with the requirements of the production schedule.

The installation is, in principle, simple and thus low cost, especially if done as a retrofit to existing storage facilities. Cooling and/or heating may be provided either by a heat exchanger in the recirculation loop or via coils in the receiver vessel. Flow through the catalyst containing tube may be gas–liquid or liquid only. The loop is of course low pressure drop, and the pressurisation is essentially liquid only and thus, energy costs should be low.

This "in-loop" design offers the potential for a fixed-catalyst reactor that inherently possesses a multi-step and multi-product capability. It offers as much flexibility, and may be more, than the stirred tank, with the benefit of the increased efficiency and control offered by the structured nature of the catalyst and flow channels.

7.5. *Other approaches to structured reactors*

The above is not intended as an open endorsement of monoliths for multiphase reactors. This work is however, an example available in the public domain of what may be achieved using structured catalysts and reactors with controlled flow in small channels. Other examples in the public domain potentially relevant to the intermediate and fine scale chemicals industry include:

- Micro-engineered catalysts [28] are being proposed, where the structure of the catalyst is used to dictate flow paths for gas liquid mixtures. The driver for the development has been reactive distillation, but application in other gas liquid reactions can be envisaged.
- Composite structured packing is a simple approach to a semi-structured catalyst [29] where the small catalyst particles are loaded into an inert honeycomb monolith type structure. The packing has a low "tube"/particle diameter ratio, 1 or 2 is cited, and may be simple spheres, cylinders or more complex shapes.
- Katapak (Sulzer ChemTech) was originally developed also for reactive distillation. With its parallel, corrugated channels, it is a commercially available option for a structured catalyst that is, however, now starting to be considered for other multiphase reactions [30].
- Fibrous structured catalytic packing elements [31], have been proposed, disposed in similar fashion to sieve plates, in bubble columns or vertically for trickle operation. Laboratory studies with this type of catalyst in a stirred autoclave indicate very high activity.
- Sandwich cross-flow catalytic packing [32]: catalyst particles are supported between two meshes aligned perpendicular to the direction of flow to present a static mixer type array of flow channels between the catalyst particles. Using this approach, it is possible to achieve kinetic control under flow conditions that in a random bed would be mass transfer limited.
- Compact heat exchange reactors, with convoluted flow channels for the process fluids have been developed by Chart Heat Exchangers Ltd. (UK) and tested for liquid–liquid reactions for a homogeneously catalysed reaction, demonstrating greater than order of magnitude increases in rate [33].

There are many more examples in the literature, and it can be assumed that this is only the tip of the iceberg that is the industrial effort in this area.

8. Conclusion

Intermediate scale and fine chemicals reactors have historically dominated by the stirred tank. This reactor is however, not efficient as a mixer, is hard to scale up for multiphase processes and shows significant losses of efficiency at larger scale. There are many proprietary improvements to the basic design, especially regarding impellers, but the stirred tank remains fundamentally flawed as a large-scale mixing and reaction device. Multiphase reactor designs from larger scale and non-catalytic processes are now being considered. These include trickle beds, bubble columns, and jet or loop reactors. Increasing efficiency and design confidence is leading to improved economics. Structured reactors and catalysts are an exciting development that may offer the potential for high efficiency reactors with the flexibility required in the batch chemicals manufacturing industry.

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