Reactor Scale-down for Pilot Plant, Bench Scale, and Multi-Throughput Units

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Cost-effective fast-track process development requires consideration of the minimum scale needed to obtain reliable data. Often, the optimal laboratory or pilot-plant reactor for reliably assessing kinetics and selectivities will look nothing like the ultimate commercial reactor. Several examples are discussed below.

A: Bubble Column Reactor Scale-Down

Where commercial-scale bubble column reactors are available for assessment of gas-liquid mass transfer characteristics in a similar liquid-gas system, the pilot reactor does not have to be a bubble column for successful process development and scale up. Bubble column reactors are typically characterized by two zones of operation: a highly backmixed near-distributor jet zone resembling a CSTR, where gas-liquid mass transfer rates are quite high, followed by a tubular flow zone away from the distributor.[1] Characteristics of the latter zone, which may comprise a majority of the reactor volume, is dependent on gas and liquid flowrates, column or tube diameter and length, presence of solids, and coalescence behavior of the dispersed gas phase, which may be a function of system pressure, as well as trace impurities which often dominate in fixing surface tensions and hence mean bubble diameter.[1-5]

Given the complexity of the problem, it is prudent to use idealized reactors with well defined contacting in pilot and laboratory studies, to determine intrinsic kinetics which can then be used with engineering correlations of bubble column performance, to predict scale-up performance. The stirred autoclave with hollow-shaft gas-inducing impeller is the workhorse of pilot plant and bench scale studies, due to ability to provide a fully backmixed, single stage.[6] Multiple backmixed reactors in series or similar configurations are then employed to simulate residence time distributions expected in commercial scale-up. For a recently completed sequence of pilot plants comprising four separate process development programs,[7] a 4-liter hollow-shaft gas-inducing impeller reactor (operated ½-full of liquid) was followed by two 1-inch diameter by 3-foot bubble columns in series, to simulate a single bubble column commercial reactor. This lineup provided residence time distributions (RTD) similar to that expected for commercial scale-up. Matching of RTD is critical, because residence time distributions can strongly impact byproduct chemistry. Failure to anticipate consequences of trace byproducts formed via undesired side reactions is one of the most frequently encountered problems in commercial scale-up, and is often implicated in failure to meet early targets for production or purity in new technology commercialization.

By operating pilot plants with residence time distributions approaching commercial designs via use of combinations of idealized, well-defined reactors, and by closing recycle loops in pilot plants, a steady state composition with representative trace

components can be obtained. Sampling and analysis then provides physical properties for use with engineering correlations for reactor and separations scale-up. Particularly important are interfacial or surface tensions, for use in multiphase reactor design, or multiphase separations (extraction). The pilot mixture also allows study of product purification with representative impurities, to determine the existence of possible difficult separations which may impact commercial design.

Scale down of bubble column reactors for pilot and bench-scale testing thus typically results in reactors that look nothing like the commercial bubble column, and most typically two sequences of scale down, one for the continuous pilot unit, and another for off-line reaction studies, as described below.

B. Multi-Throughput Lab Reactors simulating Multiphase Reactors

Further scale-down is often desirable in moving from pilot plant to bench-scale testing, where multiple parallel reactors can be employed to speed kinetics testing, or obtain side-by-side comparisons of reaction system performance. In some cases, direct sampling of steady state fluid compositions from the pilot unit can be used as the solvent and catalyst system for off-line side-by-side reaction studies, if the off-line reactors are sized 10-fold or more smaller in volume. This is advantageous because it is difficult and time consuming (minimum 2-weeks typical), to control all variables in a continuous pilot plant to reliably study a change in only one variable (e.g. temperature or catalyst component) via direct sequential comparison over several weeks of operation. Steady state compositions and performance are difficult to reproduce with high accuracy, during sequential weeks of operation. Design of a small-scale reactor for direct parallel testing with pilot fluid from a single sampling period, modified with one or more additives or variable changes (temperature, pressure), is highly advantageous in discerning underlying process phenomena. The mini-scale reactors are also useful in process screening mode, where multiple formulations or conditions are screened, side-by-side, to identify optimal catalysts and conditions.

Often, the smaller-scale reactors used for these studies may not provide the reactor performance desired for the pilot unit or commercial reactor. An example of this is in the scale-down of gas-liquid reactors with soluble catalyst, where hollow-shaft gas re-dispersion is not possible if reaction scale is limited to ca. 1 – 10 ml of liquid sample. In this case where only a small volume of liquid is available for reaction studies, a non-ideal reactor can be employed with adjustment of reaction conditions (catalyst concentration, temperature) so that a relative comparison of intrinsic liquid phase kinetics and selectivity is obtained. I.e. in absence of dispersed gas bubble formation via gas-inducing impeller, maximum gas-liquid mass transfer rates are slower than those which can be designed for pilot units or commercial reactors. Reaction conditions are thus adjusted so that the rate-determining step is the same as that in the pilot or commercial unit, even if absolute rates are not matched.[8]

A further problem exists with fixed-bed catalyst systems, where the workhorse mechanically-stirred reactor can readily attrit catalyst, leading to smaller particle sizes in the lab unit, for liquid phase systems where intraparticle transport resistances dominate the fixed-bed reactor performance. A small amount of catalyst fines can radically skew measured kinetics, where intraparticle resistance is large for the initial catalyst particles. Larger stirred reactors can avoid attrition via use of an annular catalyst basket.

However, this is not readily achieved via multi-throughput micro reactors of 1- to 10-ml liquid volume, as required for scale-down.

An alternate approach is to simply layer the catalyst over the bottom of a reactor heated by block heater or other means, with no stirring, maintaining only a small (1-cm) liquid film over the catalyst pellets (Figure 1a). This has proven successful in diagnosing relative catalyst performance under conditions where intraparticle transport resistance dominates overall kinetics, as shown for hydrogenations over nickel catalyst pellets in Figure 1b. Again, comparisons are best made at reduced temperature or reduced reactant concentrations, such that gas-liquid transport is not rate limiting, despite use of stagnant films for gas-liquid transport.

C: Fixed-Bed Reactor with Resin Catalyst

Ion exchange resin catalysts are also subject to attrition, but have improved intraparticle transport relative to metal-oxide supported catalysts, such that transition from exterior-particle vs. intraparticle control of mass transfer is less definitive.[9] An approach to reactor scale-down for these systems that was successfully employed to test alternate catalyst formulations in parallel, entailed use of septum-capped Erlenmeyer flasks in a shaker bath. An existing pilot plant reactor entailing 3-meter tall x 25 mm reactor was used to establish a tie point for kinetics, which were subsequently adapted to a less active, higher molecular weight co-catalyst which could be implemented in the shaker flask experiment. Use of the known catalyst system in side-by-side testing with new catalyst formulations in the shaker-bath assembly, allowed the bulk of catalyst development to be done in parallel, via shaker-bath flask reaction kinetics and selectivity assessment. Optimal candidates were then tested in the pilot reactor, to demonstrate viability, prior to successful commercial implementation. Once again, the reactor used for process development (Erlenmeyer flask in shaker bath) looked nothing like the commercial reactor or pilot plant (liquid tubular reactor with fixed-bed solid resin catalyst). Shaking provided just enough agitation to enhance exterior particle transport, without attriting catalyst, simulating exterior-particle conditions found in liquid-solid flow reactors.

Stresses and pressure drop were not simulated, however, as wall effects can be shown to dominate any laboratory or pilot reactor developed for downflow fixed-bed resin catalyst testing. A separate cold flow apparatus was developed, using water as solvent and mechanically applied weights to simulate pressure drops across the bed that would be realized commercially. Results were correlkalted to the commercial system via development of a mathematical model to correlate fluid properties.[8] This apparatus dramatically showed that some resin catalyst formulations would lead to complete plugging in commercial operation (Figure 2).

Scale down of the commercial reactor thus entailed a combination of experimental methods to evaluate individual phenomenon (inherent kinetics and selectivity in intraparticle transport-control regime), and downflow permeability or pressure drop. No one laboratory reactor or unit could represent the commercial unit.

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C. Trickle-Bed Reactors

Trickle-bed reactors provide challenges in scale down, as gravity forces control liquid velocities for a conventional fixed bed, and wall effects are substantial[10] if the ratio of tube / catalyst particle mean diameter is less than 10. Fine inerts can be used for small-scale downflow study under some circumstances, if performance can be established via comparison with a known, larger-scale system. An alternate approach is to move to an upflow fixed-bed bubble column, where the flow regime is now liquid continuous, with dispersed gas bubbles. Figure 3 describes a simple system with pressure feeds of liquid and gas via small bore (1/8-inch tubing) operated in the slug-flow regime. A wider diameter reactor (3/8-inch diameter minimum) provides for gas bubble nucleation and establishment of a liquid-continuous phase, whose upflow residence time in the reactor is readily controlled. Residence times can be varied at will by liquid flow control, despite use of microscale reactors as small as two inches in height, containing as little as fractions of a gram of catalyst.

Again, the reactor does not directly resemble the commercial unit or pilot-scale test, and it may be necessary to slow intrinsic kinetics via control of reactant concentrations or temperature, such that volumetric reaction rates do not exceed the poorer gas-liquid transport obtained in a fixed-bed bubble column. Comparisons of catalyst life (kinetics and selectivity vs. time) can be made, however, especially via side-by-side testing of a known catalyst and operating condition.

Summary

Scale-down of reactors is an important concept in process development. Pilot plant reactors should generally not attempt to reproduce commercial units, unless one wants to engage in a large-scale, costly, and time-consuming effort where scale is sufficiently large such that conditions in the pilot reactor approximate those in the commercial unit, for all parameters associated with the scale up. The latter is often almost impossible to achieve, unless the pilot plant reactor is indeed the same size as the commercial unit. Attempts to forgo detailed analysis and evaluate of individual scaling phenomenon by building an “arbitrarily big” pilot reactor often result in disaster: costly and slow pilot programs that fail to give scale-up information needed for commercial implementation (e.g. Figure 2).

Scale down from known commercial performance may also entail several steps for an optimized process development program. Pilot reactors are typically best chosen to operate under idealized conditions, such that reliable kinetics and residence time distributions can be employed to simulate what the commercial reactor would achieve. Multi-throughput screening reactors are then desirable at an even smaller scale, to conduct side-by-side testing of pilot plant compositions, and to screen catalyst systems for optimal candidates prior to pilot testing. Often, these operate under sub-optimal reactor conditions not representative of intended commercial operation, but can be scaled to provide key comparative information by direct side-by-testing with a known, for which a tie-point with commercial or pilot design has been established.

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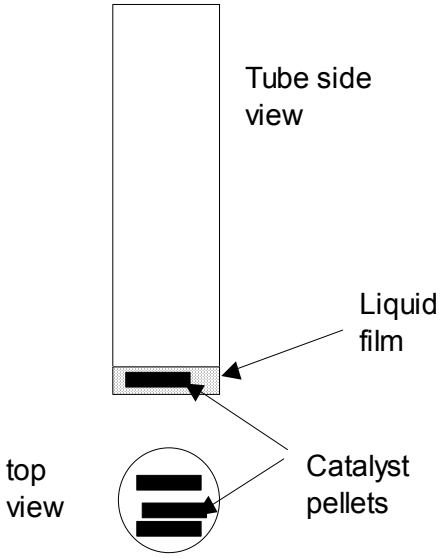
Figure 1: Static Micro Tube Reactor to Assess Relative Activity of Catalyst Pellets

a) Illustration of reactor



b) Rate data vs. catalyst particle size

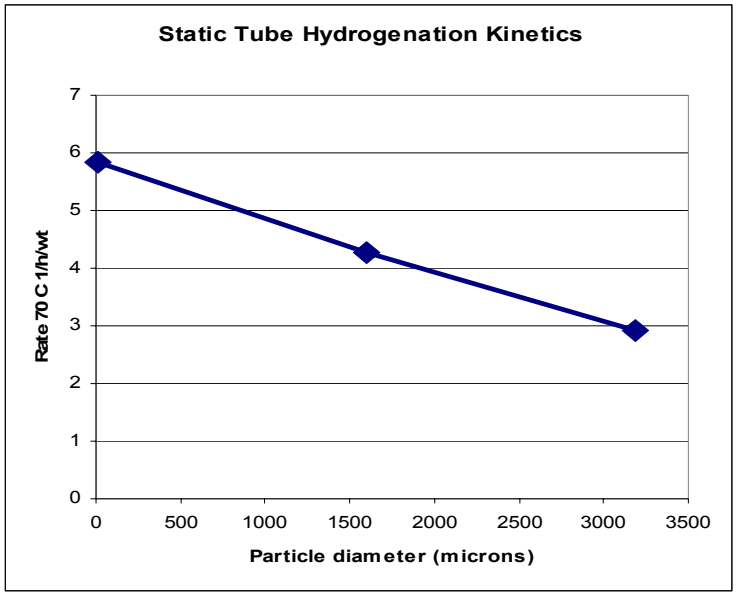


Figure 2: Pressure Drop Across Ion Exchange Resin Catalysts.

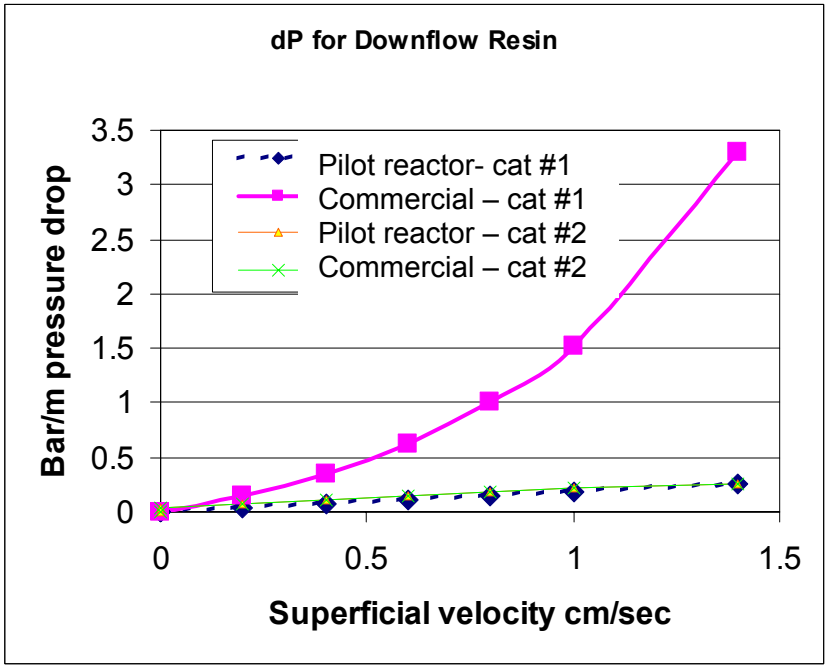


Figure 3: Upflow fixed-bed bubble column reactor simulating trickle bed