Shortcut Methods in Process Development

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Petrochemical process development has traditionally focused on creation of a fully integrated pilot plant, which serves as a mini scale model of the proposed commercial unit. Costs of piloting are generally considered high, relative to the earlier process-screening phase, albeit low, relative to the cost of commercial failure. All new construction is typically required, and staffing must safely accommodate around-the-clock operation. For a fully integrated pilot plant, the minimum allowable size of the most scale-sensitive unit operation may dictate the overall size of the entire pilot. Design is often driven to a relatively large footprint requiring handling of drum quantities of material, or greater. Risk is increased, especially where hazardous materials are involved, requiring added safeguarding via automated shutdowns and controls, or more expensive explosion-proof equipment. Typically, only one or two new unit operations are being tested, with a larger number of "known" steps included to separate products and close recycle loops. Extensive time and expense is often required however in making "known" operations work at the pilot scale with the high reliability needed to assess performance of the "new" unit operations.

In some cases, an alternate small-scale nonintegrated approach can be adopted, at a cost and timing that can be substantially less than that of a full pilot program. The following provides several examples of shortcut methods that have been deployed to speed process development or rapidly solve problems in commercialization.

A: Solid catalyzed liquid-phase reaction

A fixed-bed pilot plant reactor for a low-pressure liquid-phase reaction was constructed 3-meters tall by 25 millimeters diameter, driven by the minimum catalyst particle / tube diameter ratio (>10) needed to minimize channeling and axial dispersion. Required flowrate was set by minimum velocity to avoid a regime where exterior particle mass transfer resistance would dominate kinetics. Reactor height was then set by residence time needed for measurable conversion. Alternative shortcut batch reactors developed for rapid catalyst screening entailed 125-ml glass reaction flasks fitted with rubber stoppers, and vented via a syringe needle. A volatile reaction promoter was replaced via a higher molecular weight analog, with cross correlation of kinetic impact. Mixing was effected by shaker bath, to minimize catalyst attrition. The approach allowed multiple catalyst candidates to be screened in a short period of time in parallel, with sufficient accuracy that commercial kinetics could be obtained from shortcut method data. The pilot unit was run only as a final demonstration of concept. A comparison of cost and efficiency is given in Table 1.

B: High Pressure Gas-Liquid Reaction

Commercial gas-liquid reactions are often conducted in bubble column or jet loop reactors, or in some cases using a stirred tank with multiple impellers for gas redispersion. Laboratory studies often make use of the smaller scale and well defined contacting afforded by stirred reactors with hollow shaft impeller for gas redispersion, and rely on engineering correlations for direct prediction of gas-liquid transport and heat transfer for alternate commercial reactors. Lower cost laboratory reactors using magnetic stir bars or fins can also be employed for multi-throughput testing. Figure 1 depicts a microreactor of 25-ml total volume, typically loaded to a depth of 1 cm with liquid phase reactant, and either soluble, slurry, or fixed-bed catalyst. For the latter, reactions are often conducted without stirring, to examine catalyst particle size effects in the absence of attrition. Because the "film" of liquid phase is relatively thin, meaningful results can be obtained, especially in comparing kinetics or selectivities relative to a known catalyst or condition. Often, it is desirable to slow down the volumetric reaction rate relative to the intended commercial target, via decrease in catalyst concentration or reaction temperature, to accommodate slower gas-liquid transport. Table 1 again compares cost and productivity for several of these systems, relative to full pilot scale reactors that were used on similar process developments.

C: Continuous Fixed Bed Processes (Adsorption, Reaction)

Often, continuous contacting is required for testing of sustained performance of fixed-bed systems, to assess catalyst life or adsorption capacity under reactive conditions. In some cases, only small amounts of liquid product may be available for capacity or life assessment. In others, the need may exist to screen multiple materials for extended life performance testing, in a low cost, small footprint manner. Characteristically, these system designs are limited to 0.1 – 5 grams of solid catalyst or adsorbent, and must operate at a weight hourly space velocity (WHSV) of between 0.5 and 3 / hr.

Control of ultra low liquid flows (0.5 – 3 grams per hour) is problematic, due to plugging of small orifices in needle valves and small changes in driving force differential pressure. To solve this problem, a timer valve was employed on a pressurized feed reservoir for a number of the process studies, such that pressurized feed was supplied for a controlled number of seconds (typically 2 - 3) each minute. This allowed squeezing of a controlled number of drops of liquid (1 – 3) through a nozzle at a controlled frequency (verified by sight glass), and provided much improved hourly average flow control. Time constants for catalyst events are in general not sensitive to pulsing of liquid feed at this frequency, such that simulation of continuous fixed-bed operation for 1-gram of catalyst at WHSV of 1 – 3, could be achieved by 1 - 2 drops of liquid delivered each minute. If operated in downflow trickle bed mode, the liquid drops would simply fall through the bed under gravity flow and not achieve the desired residence time. Trickle bed performance was therefore simulated by running upflow as a fixed-bed bubble column[2], with continuous bubbling of a gas phase (e.g. H_2) in between slugs of liquid feed to a liquid-continuous reactor. Performance mimicked that achieved in larger trickle bed pilot plants. Due to low costs and small footprint, multiple units could be readily implemented in parallel, including a known catalyst, for relative performance testing. In one application, use of pressurized feed at small footprint improved overall reliability relative to previous larger-scale pilot testing, where pump mechanical failure ruined several life test runs, requiring additional instrumentation and staff monitoring.

Another low pressure application sought to use ^{13}C isotope tracing to deduce polymer degradation mechanisms. The continuous contacting experiment was conducted directly in an NMR tube using the timer-control liquid feed system described above. A

1/16-inch dip tube extended to the bottom of the NMR tube for injection of feed, allowed the contacting experiment to be conducted upflow in sealed tubes housed in water or oil bath. The reactor tube was isolated and detached from the flow manifold for periodic (biweekly) NMR analysis. Alternate modifications where NMR analyses were not required used high pressure glassware (7 bar) for visual inspection of solid integrity as a function of exposure time.

D: Fixed-Bed Catalyst Mechanical Strength Testing

Several process developments and commercializations involved streaming of downflow fixed-bed catalysts with questionable mechanical strength. In one case, a pilot unit was designed, but not constructed, for downflow testing of a deformable solid catalyst. The pilot was designed on the premise of matching the commercial height (7 meters) and linear velocity, using a smaller cross section (25 mm). The unit was to encompass 3 stories of a pilot plant facility, requiring 3 - 6 months construction.

The pilot scale-up concept was however flawed. Theory can show[1] that unless the coefficient of friction is zero, wall effects would dominate in the pilot unit, such that actual stress on the solid catalyst at the bottom of the reactor in the commercial unit would be only a small fraction of the stress obtained in the pilot test, despite matching linear velocity and bed height. It would be theoretically impossible to match the commercial stress in a flow pilot, unless the pilot was built at full commercial scale.

The problem was solved by use of 10-ml of solid catalyst packed in a 50-ml glass syringe, housed in a tray on an electronic balance. The plunger was replaced by a smaller-bore version, to apply pressure on a wire screen without wall contact. By applying known loads to the plunger and reading the weight measured on the balance, the mechanical loading on the bed could be assessed. With the syringe tip plugged, water was added to fill the syringe barrel well above the top of the solid catalyst bed. The stopper was removed, and time required to drain a volume of water (until interface just reached the top of the bed) was measured via stopwatch to assess bed permeability. From this data of permeability vs. applied stress, a model was fitted to Darcy's law with nozzle correction, and adjustment of fluid density and viscosity to match process conditions. Apparatus assembly and data collection required only 1 day, and provided data representative of commercial operation, which would have been completely impossible with the larger-scale pilot it replaced.

The approach was adapted to additional process developments via an improved apparatus using free weights to load a 25-mm diameter acrylic column free of nozzle effects, to facilitate calculation and apply more consistent stress relative to operator pressure.

E: Crystallization

Crystallization pilots typically are sized at 4-liters or above in volume, basis scale-up criterion for liquid-solid systems. Smaller-scale approaches have however been successfully employed. Given high surface / volume ratio for laboratory scale equipment, Teflon or glassware washed via an EPA-certified procedure is preferred for trace chemistry studies. A multi-throughput device for crystallization study at the 1 – 10 gram scale was assembled from EPA-certified glass septum vials, and a block heater. Side-by-side comparison of known vs. test sample studies enabled relative performance to be assessed, despite poorer separation factors (5 – 10) obtained in the small scale units relative to the larger pilot designs (10 – 1000). Ability to conduct 6 – 12 crystallizations in parallel within 2 hours enabled throughput to be increased more than 10-fold, to elucidate trace chemistry issues.

F: Liquid Extraction

Liquid extraction is another unit operation that can be simulated on a very small scale (glass vials, 1 – 20 gram samples, or separatory funnels (25 – 500 ml). A protocol of shaking the vial to mix phases for 5 minutes assures approach to equilibrium. GC analysis of upper and lower phases allows partition coefficients to be assessed. Re-extraction with pure upper or lower phase solvent (cross current extraction[3]) enables the concentration dependence of liquid-liquid equilibria to be assessed. Where volatile components are encountered, use of stirred laboratory reactors with phase separation in a pressurized sight glass can be employed.

G: Distillation and Stripping

Product degradation caused by trace chemistry during short contact time steam stripping was in one case simulated by heating in Teflon vials for 2 – 5 hours. Use of Teflon provided an inert surface so that trace chemistry impacts could be discerned above background noise, with appropriate mathematical modeling. Sizing of distillation columns for separation of trace impurities has also been done using laboratory batch fractionation columns (Oldershaw or protruded metal packed column). While it is not possible to demonstrate commercial separation using short lab-scale columns, doping of components of know relative volatility can be used to correlate separation factors for unknown components present in the same distillation. Large-scale pilot distillation may thus be avoided, in some cases.

Discussion

Shortcut methods have in many cases supplemented or replaced traditional pilot plants in both troubleshooting commercial processes, and developing new processes. Primary advantages include low cost, shorter startup time, small footprint, reduced risk of safety incidents, rapid implementation, higher throughput, and rapid adaptability to changing design concept. Disadvantages include limited process integration, additional modeling required for interpretation, potentially reduced accuracy of data or experimental simulation, and the need to anticipate trace chemistry and steady state impacts, vs. finding these impacts empirically in a fully scaled continuous unit.

An underlying benefit of attempting to devise low cost, shortcut methods for a given process study is that underlying physicochemical mechanisms must generally be considered more explicitly, in order to design a representative test. One cannot rely on the often false paradigm that if the pilot equipment visibly resembles a mini-scale version of the proposed commercial unit, the process can be directly scaled up from the pilot unit design.

Table 1 compares approximate costs and throughput for a number of traditional fully continuous pilot operations, vs. a shortcut method providing similar or in some cases identical data. A fully integrated pilot unit with multiple unit operations at the 1 – 4 liter scale can range in cost from $200,000 to more than $1 million. Shortcut methods can often provide a useful and cost effective approach for deciding between competing process options, or in a better initial design for a traditional pilot facility. Costs are typically less than one-tenth the cost of a traditional pilot. In some cases where process and commercial risk is tolerable, shortcut methods may eliminate the need for a traditional full pilot demonstration altogether. More commonly, they may be employed to shorten the cost and duration of process development and fully integrated pilot testing, as a complementary tool.

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References

1. W. L. McCabe and J. C. Smith, *Unit Operations of Chemical Engineering*, McGraw-Hill, NY (1976).
2. Y.T. Shaw, *Gas–Liquid–Solid Reactor Design*, McGraw-Hill, New York, 1979.
3. R. E. Treybal, *Mass Transfer Operations*, McGraw-Hill, NY (1980).

Figure 1: Tube-Film Gas-Liquid-(optional)Solid Reactor
25 ml total volume

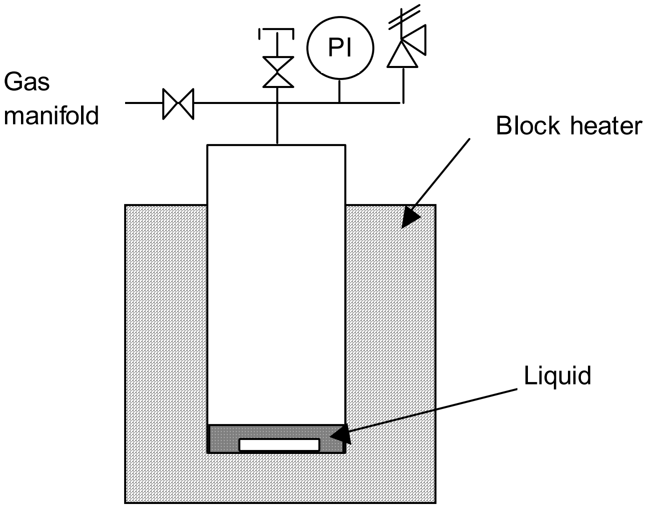

Table 1: Approximate Installed Costs of Unit Operation for Full Pilot vs. Shortcut Method

#	Unit Operation	Pilot Scale	Typical Pilot Capex	Pilot construct months	Shortcut scale	Shortcut cost	Shortcut construct	Shortcut Tests / day	Shortcut throughput gain
A	Liquid-solid reactor	3-meter x 25 mm; L/hr	$250,000	6 - 9 mo.	5-g	$2,000	1-day	12	2700
B	Gas-Liquid reactor	5-liter, L/hr	$250,000	6- 9 mo	100-g	$55,000	3-mo	2	8
B	Gas-Liquid reactor	5-liter, L/hr	$250,000	6- 9 mo	40-g	$25,000	1-mo	6	45
B	Gas-Liquid reactor	5-liter, L/hr	$250,000	6- 9 mo	6-g	$7,000	2-wks	6	96
C	Fixed-bed life / capacity test	0.5-meter x 10mm	$125,000	3- mo	1-g	$10,000	1-mo	2	6
D	Fixed bed stress test	7-meter x 25 mm; L/hr	$200,000	3- 6 mo	10-g	$100	1-day	8	infinite
E	Crystallization	4-liter, L/hr	$125,000	3- 6 mo	5-g	$500	1-day	12	1620
F	Liquid extraction	1-meter x 50 mm; L/hr	$75,000	3- mo.	100-g	$12,500	2-wks	2	13
F	Liquid extraction	1-meter x 50 mm; L/hr	$75,000	3- mo.	3-g	$5	1-day	10	900
G	Steam Stripper	1-meter x 50-mm	$100,000	3- 6 mo	1-g	$250	1-day	12	1620
H	Distillation	7-m, 75 mm diameter	$200,000	3-6 mo	0.67-m	$1,000	2-days	1	68

Pilots = 1 test / day

Throughput gain = (Co/C)*(T/To)*N where C = construction time, T = throughput, N = shortcut test/day, and "o" denotes traditional pilot