Tiny reactors aim for big role


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Process intensification (PI) has promised many things but has it fulfilled its promises? When looking at reactor technology, the answer is a definite “Yes.”

The heart of chemical processing has always been the reactor, with the Continuous Stirred Tank Reactor (CSTR) long dominating continuous production. The CSTR was first used more than 300 years ago in the processing of gold ore, but maybe its time is up. PI is entering the scene in a big way; a number of new specialty reactors have appeared, bringing both technological advances and additional manufacturers into the market.

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The term “Process Intensification” was originally coined at Imperial Chemical Industries in the U.K. in the 1970s. Put simply, PI involves the miniaturization of unit operations. This miniaturization should bring:

- reduced energy use;
- decreased capital expenditure;
- lower plant profile (height);
- smaller plant footprint (area);
- environmental advantages; and
- safety benefits.

When building a new plant, process equipment typically represents approximately 20% of the capital costs, with structural steel, piping, conduit, wire and instrumentation accounting for much of the balance. Smaller unit operations made possible by PI translate into a more-compact plant, lower weight, and less structural steel, piping, conduit and wire. The reduced weight of the equipment may even allow savings on concrete foundations. Overall, PI means less-expensive plants with smaller footprints. In addition, many process-intensified plants are amenable to construction on skids, which can lower costs even further.

Decreased costs aren’t enough, though, to guarantee acceptance of units so different from conventional ones. With reactors typically considered the heart of the plant, companies also want increased reactor performance. Here, the new PI reactors provide a number of advantages. They cut residence times, boost reaction rates, minimize side reactions, and reduce energy-intensive downstream processing steps such as distillation and extraction. In addition, the units can dramatically decrease the volumes of explosive, hazardous or toxic compounds in the process.

With many reactions, heat-transfer, mass-transfer or mixing limitations control the reaction rate rather than the fundamental kinetics, explains Protensive, Newcastle upon Tyne, U.K., a developer of PI units. An exothermic reaction may require a couple of hours to carry out in a batch reactor not because of any kinetic constraint, but because of the time necessary to remove the heat of reaction, adds the company. PI reactors offer a way to overcome such limitations.

Now let’s look at five commercially available PI reaction systems to see how they work and the benefits they offer. We’ll also touch upon two established PI technologies — reactive distillation and static mixing.

Spinning tube
Kreido Laboratories, Camarillo, Calif., offers the Spinning Tube in a Tube (STT) reactor. This unit induces so-called Couette Flow by mixing reactants in a narrow annular gap between a stationary stator and a rapidly rotating, concentric, internal rotor (Figure 1) so that the reactants move as a coherent thin film in a high shear field, says the company.
This very high shear field extends over the total length of the tube. Flow through the annular space is actually in the laminar range. This unit is very compact (Figure 2) and can easily perform gas/liquid and liquid/liquid reactions.

The STT reactor accelerates the rates of chemical reactions by up to three orders of magnitude, increases conversions and yields, controls the quality of production in real-time, lowers costs, and dramatically decreases the time required for manufacturing scale-up, claims the company.

Some applications include: selective oxidation, selective hydrogenation, esterification, transesterification, saponification, hydroislylation, condensation reactions and preparation of ionic liquids.

The transesterification reaction of soybean oil and methanol for biodiesel production is being done at a residence time of 0.5 seconds. Kreido offers what it calls a complete pipe-to-pipe biodiesel production unit, the STT 30G.

Scaleup involves holding shear constant:

$$D1\nu1/d_1 = D2\nu2/d_2$$

where \(D\) is the diameter of the rotor in millimeters, \(\nu\) is the revolutions per second of the rotor, and \(d\) is the gap millimeters. If \(D1 = d2\) then, for any change in diameter, the new \(\nu\) can be calculated.

**Spinning disk**

Protensive makes the Spinning Disk Reactor (SDR), which provides plug flow and intense mixing while resisting fouling. The SDR relies on high centrifugal acceleration over a disk surface to overcome interfacial mass-transfer limitations that thwart conventional processes (Figure 3).
The generation of very thin films, typically fractions of a millimeter down to a few microns thick, through controlled flow rate and disc speed or RPM can deliver surface-to-volume ratios tailored to processing requirements, ranging from 1,000s of m2/m3 for high viscosity materials such as polymer melts, down to 100,000s m2/m3 for low viscosity systems typical of a wide range of chemical synthesis routes.

The SDR boasts an overall heat transfer coefficient typically five to 10 times greater than achieved by most heat-transfer devices, says the company, enabling small discs with low process fluid inventory to handle significant thermal duties. Figure 4 shows a laboratory unit.

Fast exothermic reactions can be conducted in the thin turbulent film on a spinning disc reactor using much higher temperatures than could be contemplated in stirred tanks. This is because the superior heat-transfer performance of the unit carefully controls temperatures, and completes reactions in a residence time of just 1-2 sec.

The reaction to produce CaCO3 via CO2 absorption is completed within 1 sec., says the company. The high surface-to-volume ratio can be used both to allow rapid transport between gas and liquids for simple operations such as stripping liquids of volatiles, scrubbing gases or for more-complex gas/liquid reactions.

For crystallization and precipitation, the vapor-stripping characteristics of the SDR, arising from the thin turbulent liquid film on the disk surface, combined with the reactor's plug flow characteristics, are said to allow excellent control over particle size selection and attainment of a relatively narrow particle-size distribution.

The reactor also reportedly can remove solvents or monomers left trapped in bundled polymer chains after polymer production to very low levels difficult to achieve in traditional equipment even with the use of vacuum and temperature.

**Controlled cavitation**

Hydro Dynamics, Inc., Rome, Ga., harnesses cavitation in its ShockWave Power Reactor (SPR) to provide increased mass transfer and scale-free heating. Basically, the shockwaves and resulting microscopic bubbles cause intense mixing as well as a cleaning action. Because heating takes place in the material, not by conduction through metal, there are no hot and cold spots.
The heart of the SPR technology is a specialized spinning rotor with cavities. The spinning action generates hydrodynamic cavitation within the cavities away from the metal surfaces. This cavitation is controlled by RPM — thus there is no damage to the equipment. Eight different parameters determine optimum hole location, depth, angle, layout, etc. The SPR looks like a pump from a casual observation (Figure 5); however, that is where the similarity ends.

**Figure 5.** Purposely generated cavitation enhances mass transfer and produces uniform heating.

To see a demonstration of the action of cavitation, including what happens after a small amount of gas has been added, go to [http://www.hydrodynamics.com/technology_review.htm](http://www.hydrodynamics.com/technology_review.htm).

The SPR can provide: reduced reaction time, uniform temperature with no solid scale build-up, fewer side reactions, and improved yield and quality.

The reactor suits both batch and continuous processes, and can provide up to 150-million-gal/yr processing capacity in a single unit. In addition, the unit can be easily retrofitted into existing operations.

The device already is used in numerous commercial applications, including the mixing of consumer products, food pasteurization/homogenization, gel and gum hydration, scale-free heating of chemicals, and concentration of solvents.

The unit also can serve as a superior gas/liquid mixer, handling gas-to-liquid volume ratios as high as 5 to 1, says the company.

**Microchannel reactors**

Velocys, Plain City, Ohio, uses microchannel technology to dramatically reduce heat and mass transport distances commonly found in conventional systems, thus increasing the rate of heat and mass transfer and, in turn, greatly accelerating reaction rates. Further, as the efficiency of converting feedstock material to products is strongly governed by the ability to control these chemical reactions — which depends upon the ability to control reaction temperature, which in turn is governed by the ability to move heat quickly — the technology often can increase product yield.

Velocys’ chemical processors feature parallel arrays of microchannels, with typical dimensions in the 0.010-in. to 0.200-in. range (Figure 6).
Figure 6. Microchannels permit use of much more active catalysts, which greatly boosts throughput.

This structure is said to allow use of much more active catalysts than conventional systems, greatly boosting the throughput per unit volume. A catalyst can be tethered to the reaction wall or coated inside the channels. Overall system volumes reportedly can be reduced by 10 to 100 fold compared to conventional hardware. Figure 7 shows a large-scale, prototype microchannel reactor that will begin operating in 2007.

Figure 7. Large-scale demonstration unit is slated for operation in the first quarter of 2007.

Some of the applications under development include:

- hydrogen production using steam methane reforming;
- high intensity oxidation and partial-oxidation reactions with improved process selectivity and yield;
- high-performance emulsification processes; and
- synthetic-fuel production and methanol synthesis in compact units suitable for land or offshore installation.

Steam reforming highlights the power of the approach. About 95% of the hydrogen produced today in the U.S. is made by reforming a methane source, such as natural gas using high-temperature (700°C to 1,000°C) steam. Refineries are major producers of hydrogen, using it primarily for their hydrocrackers and hydrotreaters. In the reforming process, methane endothermically reacts with steam under 3–25 bar pressure in the presence of a catalyst to produce hydrogen, carbon monoxide and a relatively small amount of carbon dioxide.

With the microchannel technology, hot combustion gases push the reaction forward, with the hot gases flowing in channel layers alternating with the reactor channel layers. The hydrogen is then purified in a pressure swing adsorption unit. Plant size is reduced by 90% compared to conventional reformers, and the approach boasts a 30% savings in capital cost, higher thermal efficiency and lower emissions, according to the company.

Scale-up is easily accomplished by adding more layers of channels. Once a plant is in operation, its capacity can be increased simply by installing additional layers of channels.
Oscillating flow
Cambridge Reactor Design, Cottenham, U.K., offers the Oscillating Flow Reactor, which takes advantage of the company’s Oscillating Flow Mixing (OFM) technology (Figure 8).

![Typical configuration](image)

**Figure 8.** Baffle geometry coupled with intensity of oscillation produced by pistons control mixing behavior.

OFM combines fluid oscillations with baffle inserts to provide highly effective mixing in tube reactors. Mixing behavior is controlled dynamically by oscillation intensity or geometrically by baffle design. While the technology can be applied to batch operations, it is said to be particularly suited to continuous processing.

The standard reactor consists of an oscillator base and a reactor tube top section (Figure 9). A nutating cam mechanism driven by an electric motor and linear actuator controls the amplitude and frequency of operation. A pair of pistons driven off the two cams provides oscillations in an inverted “U” arrangement of reactor tubes. All of the variations are achieved by electronic control of the motors.

![Standard design](image)

**Figure 9.** Standard design includes an oscillator base and a reactor tube top section.

Process tubes are added via top plate extensions, each of which takes two reactor tubes. In this manner, the unit can be operated as four-pass, six-pass, etc., as required to increase reactor volume or residence time.

Typical applications include biodiesel, suspension polymerizations and liquid/liquid dispersions.

**Reactive distillation**
PI doesn’t necessarily have to involve cutting-edge mechanical developments. Another, long-established form of PI is reactive distillation, which combines a reactor and distillation column. The technique typically is used with reversible, liquid-phase reactions. For many such reactions — including esterifications, transesterifications, hydrolyses, acetalizations and aminations — byproduct formation limits the amount of product made. Reactive distillation allows removal of the byproduct, thus shifting reaction equilibrium and leading to more product. Other types of reactions that could benefit from reactive distillation include: alkylation/transalkylation/dealkylation, isomerization and chlorination.

Reaction components are fed countercurrent into a distillation column. Then, the product and byproduct can be separated by distillation. Some reactions require placement of catalysts inside the column — e.g., via structured packing coated with the appropriate catalyst, trays containing pillows filled with catalyst particles or pillows filled with catalyst particles rolled into bales.
Figure 10 shows an esterification reaction for a high-boiling carboxylic acid being added at the top of the reactive distillation column and a lower-boiling point alcohol being added at the bottom. Byproduct water comes off the top of the column and the product ester comes off the bottom.

Figure 10. This unit produces an ester as bottoms product, while byproduct water goes overhead.

We expect installations using reactive distillation to continue to grow at a moderate pace in this decade.

Static mixers
Another traditional form of PI also garnering increasing interest relies on the use of so-called static or motionless mixers as reactors either as single units or in bundles with a jacket.

Chemical reactions in the laminar fluid-flow range (below a Reynolds number of 2,000) are possible with a Continuously Fluid Reactor (CFR) developed by R. C. Costello & Associates (Figure 11).

Figure 11. Internal elements fold streams billions of times, providing intense mixing.

The Model CFR-T consists of a 3/8-in.-diameter Type-316 stainless steel tube with mixing elements that divide the flow at the beginning of each element. Subsequent stretching and folding produces a radial motion of the high-velocity core regions outward toward the wall of the reactor, which has an inside diameter of about 0.20 in. Without the elements, flow clearly would be laminar but with them intense mixing occurs, enabling liquid/liquid and gas/liquid reactions to occur.

A bench-scale device is offered with 34 mixing elements, which means the liquid contents is split and folded 234 (or more than 17 billion) times after passing through the CFR.

For multiple units in series, BMR Group, Cranfield, U.K., offers the FlexReactor, which looks similar to a heat exchanger with static mixers in each tube. The unit can be re-piped with simple U-tube connections to have multiple passes in series or parallel operation. Heating or cooling is easily achieved with the FlexReactor.

A small revolution
The unrelenting pressure for less expensive plants and better process performance favors the increasing use of PI reactors. Prospects for acceptance are improving as the technologies prove themselves more widely in commercial applications and more vendors promote the PI approach. So, it’s clear that these small units promise to have a big impact.

Rocky Costello is president of R. C. Costello & Associates, Inc., Redondo Beach, Calif. E-mail him at rcc@rccostello.com.

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