DON'T OVERLOOK STATIC-MIXER REACTORS

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Their simplicity belies their effectiveness

FIGURE 1. The heart of any static-mixing reactor, such as the one being assembled here, is its array of stationary guiding elements within the vessel

Static mixers are well established in the process industries for mixing, blending, and related tasks. However, relatively few engineers are aware of the growing use of these devices as reactors. They effectively handle a variety of difficult process situations, in a compact configuration that is environmentally attractive and safe.

A static mixing unit (Figure 1) consists of a series of stationary, motionless guiding elements placed lengthwise in a pipe, duct or column. Fluids are mixed by utilizing flow (pumping) energy [1].

This not only combines the fluids thoroughly but also enhances heat and mass transfer and provides a narrow residence-time distribution. All of these features are desirable in a reactor.

Static-mixer reactors are usually employed as continuous tubular reactors operating in plug-flow fashion (see table on p. 78, Row A). In this service, they offer many advantages over stirred tanks. The major ones are:

- Compactness and low capital cost
- Low energy consumption and other operating expense
- Negligible wear and no moving parts, which minimizes maintenance
- Lack of penetrating rotating shafts and seals, which provides closed-system operation
- Short mixing time, and well-defined mixing behavior
- Narrow residence-time distribution
- Performance independent of pressure and temperature

A static mixer is also useful in other configurations. It can serve as one or both components of a loop-reactor system, in which the reactants are fed to, and product withdrawn from, a stream of in-process material that circulates between two reactors (table, Row B). Such a system can operate in either the continuous or the batch mode. In the batch mode, the other vessel can be a stirred tank (table, Row C). The static mixer can also serve upstream of a continuous stirred-tank reactor (CSTR; table, Row E), thus enhancing the CSTR's inherent flexibility.

Setting the stage

Any reactor (static mixer or other) should be designed and operated for optimal conversion and selectivity. The basic requirements for this are the correct residence time for the reaction kinetics, and the correct mixing behavior. We can relate these parameters to static mixers by considering the concepts of mean residence time, mixing time, reaction time, and residence-time distribution

Except in the case of ideal plug flow conditions, fluid elements in different flow paths through a reactor have different residence times. At a mean velocity v_m, the mean residence time t_m is defined as follows:

$$t_m = L/v_m = V/U$$

To appreciate the significance of mixing time and reaction time, consider two competing and consecutive fast reactions:

$$A + B \rightarrow R$$
$$R + B \rightarrow S$$

The half-life times (time needed for the concentration of reactants to drop by 50%) for fast reactions range from milliseconds to seconds [2, 3]. So, it is vital that the components be molecularly mixed (micromixed) in the shortest possible time, and that all fluid particles have the same residence time.

If the desired product is R, the mixing time must be short compared with the reaction time for the second reaction. If the mixing time is too long or the reactor too big, B-rich zones will persist, where B can react with R. Not only will R be produced, but also a considerable amount of S. This is an instance of bad selectivity.

Reaction networks involving fast competing consecutive reactions of this type are likely to be highly exothermic. Due to the requirement for a small reactor, they can be carried out only in low-viscosity media where mixing by turbulence and cooling by dilution is possible. The same applies to a network of fast competing parallel reactions. Stirred tank reactors are unacceptable, and only a plug-flow reactor can be used. For either case, a static-mixing plug-flow reactor with intense radial mixing is ideally suited.

At the other extreme, reactions may take place very slowly, or in highly viscous media. For instance, the reaction time required for polycondensation of caprolactam into nylon 6 in a VK tube (a simple continuous reactor; see Figure 1) is 20 to 40 h [5]. Static-mixing elements can be applied in such situations to ensure radial mixing and a uniform residence time for all flow streams.

The ratio of reaction time to micromixing time is known as the Damköhler number, *Da*. When this is large, the influence of micromixing time on the product becomes negligible. Furthermore, simple reactions of the type A + B → C are not affected by micromixing time. Even so, the rate of mixing can be extremely important for product generation, due to the effect produced by concentration, temperature or shearing [4].

For all reactions of greater than zero order, the reaction rate is highest when the concentration of reactants is the highest. The second column of the table (p. 78) shows the time behavior and attainable reactant final concentration for the γ-order reaction A + B → C, in various reactor arrangements having equal volume.

In the pure (idealized) plug-flow reactor (table, A) and batch reactor (table, C, D) the concentration of the

NOMENCLATURE

a	Mass transfer area, ft²/ft³
Bo	Bodenstein number
c	Concentration, mol/ft³
c_m	Mean concentration, mol/ft³
D	Reactor tube dia, ft
Da	Damköhler number
E_{ax}	Axial dispersion coefficient, ft²/s
Fr	Froude number 1
g	Gravitational acceleration, ft/s²
k_L	Mass transfer coefficient, ft/s
L	Reactor length, ft
Q	Heat transfer rate, Btu/h
Re	Reynolds number
T	Temperature, °F
t_M	Mixing time, s
t_R	Reaction time, s
t_m	Mean residence time, s
t_Z	Cycle time, s
U	Throughput, ft³/s
U_Z	Recirculation, ft³/s
v	Flow velocity, ft/s
v_m	Mean velocity, ft/s
V	Reactor volume, ft³
ϵ	Mass specific energy input, kW/kg
η	Viscosity, cP
ϕ	Phase ratio
ρ	Density, lb/ft³
γ	Reaction order

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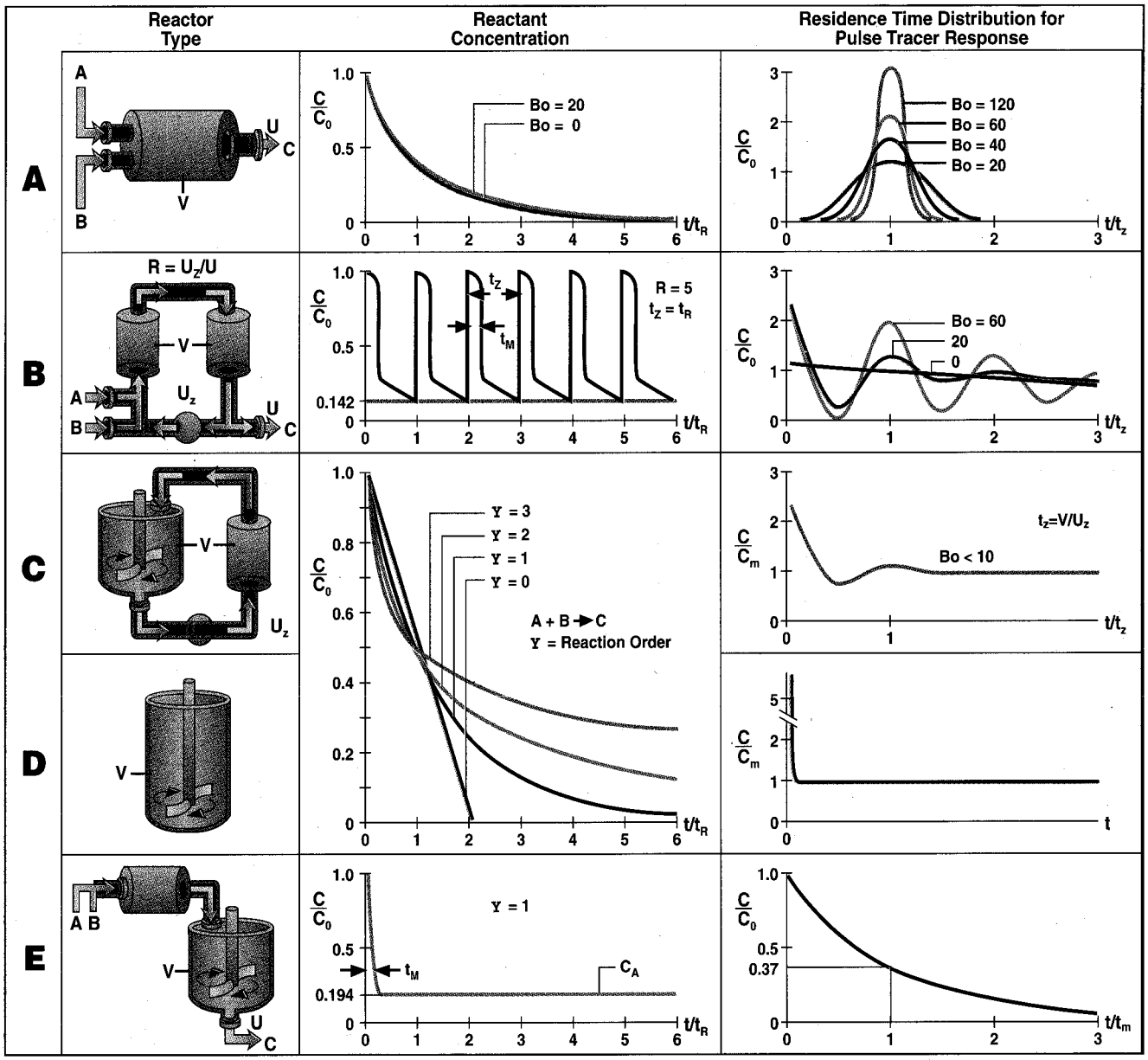

Static-mixer reactors can be employed in various configurations (Rows A, B, C and E), including combinations with continuously stirred tank reactors (Rows C and E). Each produces particular reactant-concentration and residence-time-distribution patterns

SELECTING AND SPECIFYING

As the main text indicates, various static mixer arrangements are possible. The best choice for a given reaction depends on the required axial and radial mixing characteristics, residence time, heat transfer, and dispersion behavior, as well as the flow velocity range (Reynolds number).

Plug-flow reactors are the natural choice if there are no special reasons (p. 79) for using a loop reactor. For competing series or parallel reactions, plug-flow reactors are indispensable. For gas-liquid reactions, the choice of setup depends on the ratio of mass transfer rate to reaction rate (Hatta number) and the phase ratio. If the reaction is slow in the liquid phase, a bubble column or loop reactor is the correct choice. In the case of extremely fast liquid-phase reactions, in-line static mixers are installed after a liquid-atomization phase.

Once the configuration is set, the main criteria for designing the actual reactor are residence time, residence-time distribution, throughput, viscosity (and hence solvents and dilution), mass transfer, energy input, heat of reaction, pressure and temperature. These depend on the kinetics (including order of reaction), physical characteristics and heat of reaction, any or all of which are likely not to be known beforehand. As a basis for establishing such data, we highly recommend pilot tests in a stirred laboratory reactor.

The next step for scale-up is to transfer test results to a mini-pilot plant with static mixers of about 1 to 2 liters, or directly to a pilot plant with a capacity of 10 to 100 liters. However, because of the well defined structure of static mixers, scale-up factors of 1,000 or more in a single step are not unusual.

Finally, bear in mind that static mixers are essentially continuous-operation devices. Although existing batch processes can be converted to continuous operations with static mixers, the switchover is not easy. It normally requires intensive collaboration between the chemical-process firm and the reactor manufacturer. ❐

reactant falls continuously from the initial value c_0 to the final value, c_A. In this type of equipment, reactions always take place at the maximum possible reactant concentration. Both of these types of reactors require the same minimal reaction time for a given conversion. In the example shown, for a first-order reaction ($\gamma = 1$), a conversion of 98.4% is attained in six half-life times.

In contrast to this, the reactant concentration in an idealized CSTR is consistently the same as at the outlet (Table, E). Despite having the same mean residence time as a batch and plug-flow reactor, reactant conversion in a CSTR is only 80.6% after six half-life times.

As for the residence-time distribution, its significance can be emphasized by considering a hypothetical tubular reactor that is equipped with no internals, through which the process material is passing in laminar flow. The residence-time distribution for such flow is extremely wide.

The fastest flow path is in the center of the tube, with twice the average velocity. This center core material thus gets processed for only half of the mean residence time. On the other hand, the 5% of material that is flowing near the tube wall has four to five times the residence time experienced by the center core material.

Residence-time distribution is often quantified by the Bodenstein number (Bo)*, a measure of the width of residence-time distribution according to the dispersion model

$$Bo = vL/E_{ax}$$

where E_{ax}, the axial dispersion coefficient, serves as a measure of the degree of radial or backmixing. For an idealized single CSTR reactor, Bo = 0; for an idealized plug-flow tubular reactor, Bo = ∞; and for a cascade of j continuously stirred tanks in series, Bo = 2 j [6].

Their wide residence-time distribution makes plain tubular reactors unsuitable for carrying out laminar-flow reactions. And the problem is compounded if the reaction is highly exothermic or endothermic, because there may be a significant temperature difference between the center and the inside tube wall, leading to undesired reactions, lack of product uniformity, and discoloration.

This wide residence-time distribution and unfavorable time-temperature distribution in a tubular reactor can be reduced by using static mixers. They enhance radial mixing, and simultaneously increase heat transfer four to ten times due to forced radial convection. It has been shown that the favorable residence-time behavior of a 1-m-long tubular reactor with static mixers is equivalent to that of 25-50 CSTR reactors in series.

Residence-time disturbance

The residence-time distribution may change during the course of a reaction. During many polymerization reactions, for instance, the viscosity rises from about 1 mPas to over 1,000 Pas, a millionfold rise.

Such viscosity increases cannot be handled by an empty tube reactor. Low-viscosity monomer at the core will tend to pass unreacted through the vessel in a fraction of the mean residence time. Conversely, the portion near the wall will remain far too long, and almost fill the reactor with highly viscous dead zones.

On the other hand, in tubular reactors equipped with static mixers, the viscosity in the vessel can increase more than 100-fold within short reactor sections without having effect on the residence time distribution. In the VK tube reactor that was previously mentioned, the static-mixing elements assure practically ideal plug flow conditions, in spite of extremely low velocity and the effect of small amounts of rising vapor bubbles from the polycondensation process.

Admittedly, this performance is possible only because the reaction takes place in a very viscous medium. In aqueous liquids under otherwise comparable conditions, a quite different residence-time-distribution problem would arise: The reactor would be so badly affected by buoyancy forces and resultant free convection that it would behave almost like a single stirred tank (Bo = 0).

The degree of such disturbance by convection under laminar flow conditions is quantified by the ratio of the Froude Number 1, *Fr* (a measure of the relative prevalence of inertial and gravitational forces) to the Reynolds number *Re*:

$$Fr/Re = \eta v/gD^2\Delta\rho$$

(Note that the "delta" term in the denominator pertains to density, not pressure.) The severity of free convection increases with large tube diameter *D*, low viscosity η, and low flow velocity *v*, (i. e., at low values of *Fr/Re*). Even slight differences in temperature, concentration, density or pressure drop are enough to initiate free convection.

For vertical and horizontal reactors, *Fr/Re* ratios less than 1 can lead to critical free-convection operating problems. In the case of horizontal reactors, values that are lower than this can bring on slow sedimentation of reaction products.

Such conditions do not arise if the flow velocity is increased. But such an increase often raises the pressure drop or makes the reactor excessively long.*

A recent approach to minimizing free-convection problems in low-viscosity plug flow reactors employs a proprietary combination of static mixer and sieve tray for reactor columns. The optimal combination of static-mixer packing with dual-flow sieve trays gives Bo numbers of 5-7 per meter of packing at only 2 mm/s flow velocity, even with aqueous media and strong free-convection interference at 5% gasification. These columns are suitable for hydrolysis, esterification, transesterification and other slow reactions.

Loop reactors with static mixers

Ordinary plug-flow reactors are subject to a further difficulty: High reactant concentrations may cause reactions to go out of control. Among the problems this can cause are these:

- Uncontrollable temperature rise
- Uncontrollable viscosity rise
- Undesirable byproducts
- Wide molecular-weight distribution due to chain fracture
- Inadequate energy dissipation in multiphase reactions

(*Continues*)

*Strictly speaking, the Bodenstein number has been derived for tubular reactors. Even so, it is also relevant in this broader context.

*Nevertheless, at some installations, plug-flow reactors are in fact extremely long—for example, some high-pressure reactors for polyethylene production have a tube length of 2 km.

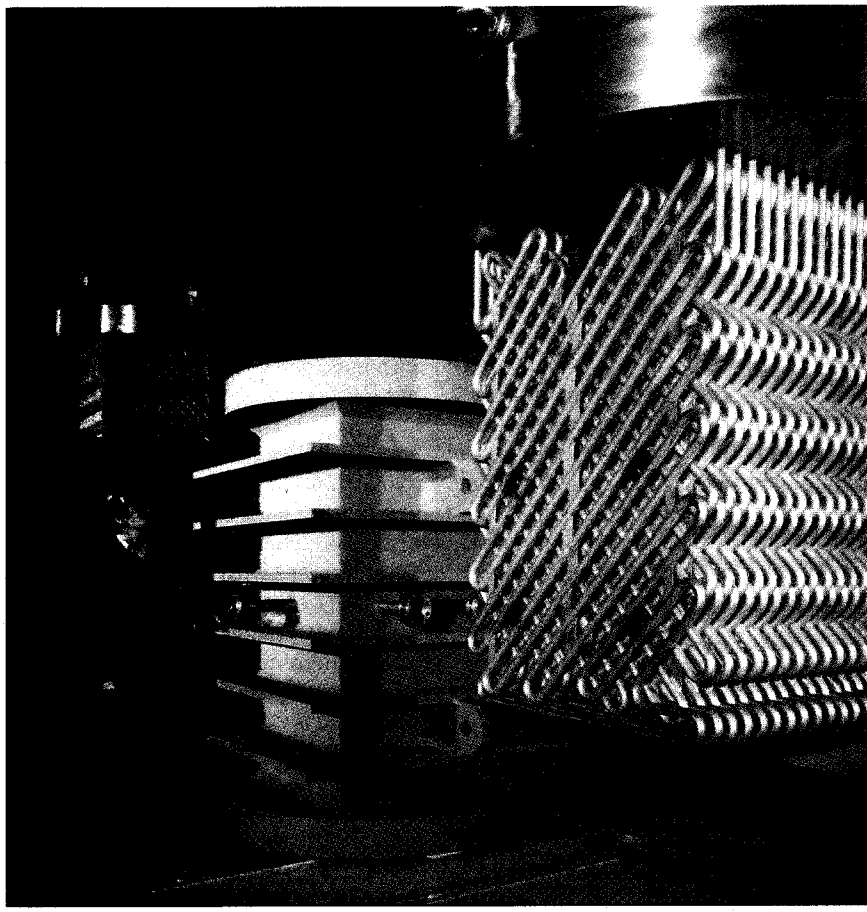

FIGURE 2. Proprietary design of this static-mixer reactor features mixing elements (right) that are not plates, but instead hollow tubes through which a heat-transfer fluid flows. One advantage is the heat removal offered for highly exothermic reactions

- Excessive mixing time
- Inadequate shear rate

An attractive solution in such cases is to link a pair of static mixers as a loop reactor (table, B). The residence-time, mixing and heat-transfer behavior of this type of reactor can be adjusted practically without limit by varying the number of mixing elements, their length-to-diameter ratios, the number of feed points and the recirculation rate. This approach is also another solution to the aforementioned problems involving low flow velocity or inordinate reactor lengths.

When operating at less than design throughput, loop reactors are easily controlled by adjusting the recirculation rate. And unlike plug-flow reactors, loop reactors can also be conveniently operated on an intermittent basis.

The reactant concentration at all points in the loop reactor is slightly higher than in a CSTR, but much lower than in a plug-flow reactor. The conversion of the loop reactor shown in the table in Row B is 5% higher than that of the corresponding CSTR with the same reactor volume (table, Row E).

The third column of the table shows the residence-time-distribution characteristics of a loop reactor in batch (Row C) or continuous (Row B) operation as function of Bo number in the loop. The loop residence-time distribution at low Bo number (i.e., a short loop) or short cycle time t_Z is practically the same as in a CSTR. The concentrations throughout the reactor are immediately balanced.

At high Bo number (a long loop with static mixers), the loop behaves like a series of ideal plug-flow reactors, with individual response functions. This can be a disadvantage with extremely fast reactions, because axial temperature or concentration differences build up in the loop and take a long time to disperse. In such cases, the reactants should be fed at several points along the loop. The combination with a stirred tank, shown in Row E of the table, offers the high flexibility of a stirred tank as well as the advantages of a static mixer.

Exothermic-heat transfer

Reactors that are assigned to carry out exothermic reactions under isothermal operating conditions must be capable of very good heat transfer through the vessel wall per unit of vessel volume. Unfortunately, this capability becomes more and more difficult to realize as reactor size increases.

Thus, small diameter plug-flow reactors used in pilot plants in most cases do not incur heat-transfer problems. However, the heat-transfer surface per unit reactor volume and the heat transfer coefficient both decrease with increasing diameter. So, the heat-transfer capacity of most reactors falls off rapidly with increasing volume). The resulting problem is especially acute under laminar flow conditions with viscous substances.

A frequent strategy with highly exothermic reactions is to employ multitube heat exchangers, thus obtaining large surface-to-volume ratios. But the flow must be suitably divided among the parallel tubes (often a large number of them).

In some cases, this multitube approach is feasible. In other situations, the likelihood of flow-distribution problems (some of these subject to aggravation by the ongoing reaction itself) make the use of multitube reactors difficult, risky or dangerous [11]. Among these situations are:

- Gas-liquid reactions
- Polymerizations
- Reactions with phase or viscosity changes

To deal with such cases, a patented static-mixer reactor has been developed (Figure 2). Its flow-guiding elements are arranged in the same way as the crossbars of the static mixer shown in Figure 1. However, instead of being constructed with solid plates, its mixing elements consist of tubes through which a heat transfer fluid flows.

As a result, there are hardly any temperature or radial concentration differences. The heat-transfer capacity is very high, and is nearly constant regardless of reactor diameter.

Heterogeneous reactions

In heterogeneous reactions (gas-liquid, liquid-liquid, liquid-solid or gas-solid), the mass transfer rate between phases is often more critical than the reaction rate itself. Mass transfer is determined not only by the reactants characteristics, but also by the mass-specific energy input ϵ, flow velocity and pressure drop.

According to turbulence theory,

changes in drop or bubble size are proportionate to $\epsilon^{-0.4}$. The specific mass transfer area a depends on the bubble size and on the dispersed phase ratio ϕ. At the same time, the mass transfer coefficient k_L increases with increasing energy input.

Liquid-liquid and gas-liquid systems are governed by the relationship $k_L a/\phi \approx \epsilon^{0.8}$ [14]. With low energy consumption (natural circulation), $k_L a$ values of 0.1–1 s^{-1} are attainable, whereas forced circulation using in-line mixers can achieve values of 10–100 s^{-1}, in aqueous media.

High viscosity is often linked with high mass concentration, which strongly reduces gas solubility. With increasing viscosity η, mass transfer decreases rapidly as a function of $\eta^{-0.7}$ [15]. This resistance to mass transfer must be overcome through high energy input or dilution.

One way to supply energy effectively is via a loop reactor outfitted with static mixers. In one such application commercialized a few years ago, a proprietary organic liquid is contacted with oxygen in a closed loop system (no venting of gas) involving high viscosities around 60 cP. The strongly exothermic reaction must take place isothermally, at 9°C. This process yields an intermediate product important for pharmaceutical use.

For safety reasons, the amount of reactants and hence the reactor volume must be small. In addition, the reactor must be able to absorb the entire heat of reaction (until the reaction is completed) if the cooling or reactor recirculation systems fails. The residence time required for this mass-transfer-limited reaction must be reduced to less than 60 min by high energy input.

A forced-circulation loop with the aforementioned patented mixer reactors and static mixer-dispersers provides the necessary mixing time and the mass and heat transfer capacities. This reaction was first carried out successfully in a mini-pilot plant, using a reactor of nominal 80 mm dia. The subsequent full-scale plant with 450-mm-dia reactors has been operating troublefree since 1991 [16].

Similar loop reactors are in service as fermenters for viscoelastic biopolymer solutions. In such biological processes, the heat of reaction is generally slight and mixing elements without internal cooling can be used. Biological systems often employ solid-liquid fluidized bed reactors with immobilized enzymes. Installing static mixer packings in these fluidized beds can significantly increase the space-time yield. In one situation involving the hydrolysis of lactose, it rose by a factor of 2.7 [17].

Heterogeneous reactions also arise during chemical or petrochemical process-gas treatment, such as the selective absorption of hydrogen sulfide from natural gas. Acid gases and liquors react rapidly in static mixers, with residence times much under 1 s.

In these cases, the gas is the continuous phase while the liquid is atomized. Installation of a static mixer after the atomizing stage allows more-intensive contact between the phases, as well as high turbulence and high relative velocity.

The static mixers generate a liquid film on their surface, as well as a flow of fine droplets. The reaction takes place in the liquid film on the static mixing elements and in the droplets.

Static mixers are also in widespread service as plug-flow or loop reactors, or gas-liquid contactors, in processes involving oxidation, chlorination, hydrogenation, alkylation or phosgenation. In these cases, the gas is the dispersed phase.

A very recent innovation is the use of static mixing elements as the support structure for heterogeneous catalysis of gases (for removal of NOx, and for production of phthalic anhydride) or liquids (bubble columns for hydration and for reactive distillation). The combination of mixer structure and catalyst-combines the advantages of static mixers with the effect of conventional catalysts. Compared with dumped packings, the pressure drop is low and the radial mixing effect high. Compared with parallel channel structures, the mass transfer values are four to five times larger [19]. ■

Edited by Nicholas P. Chopey

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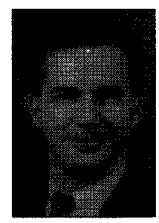

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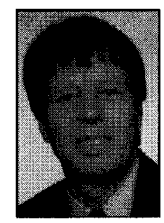

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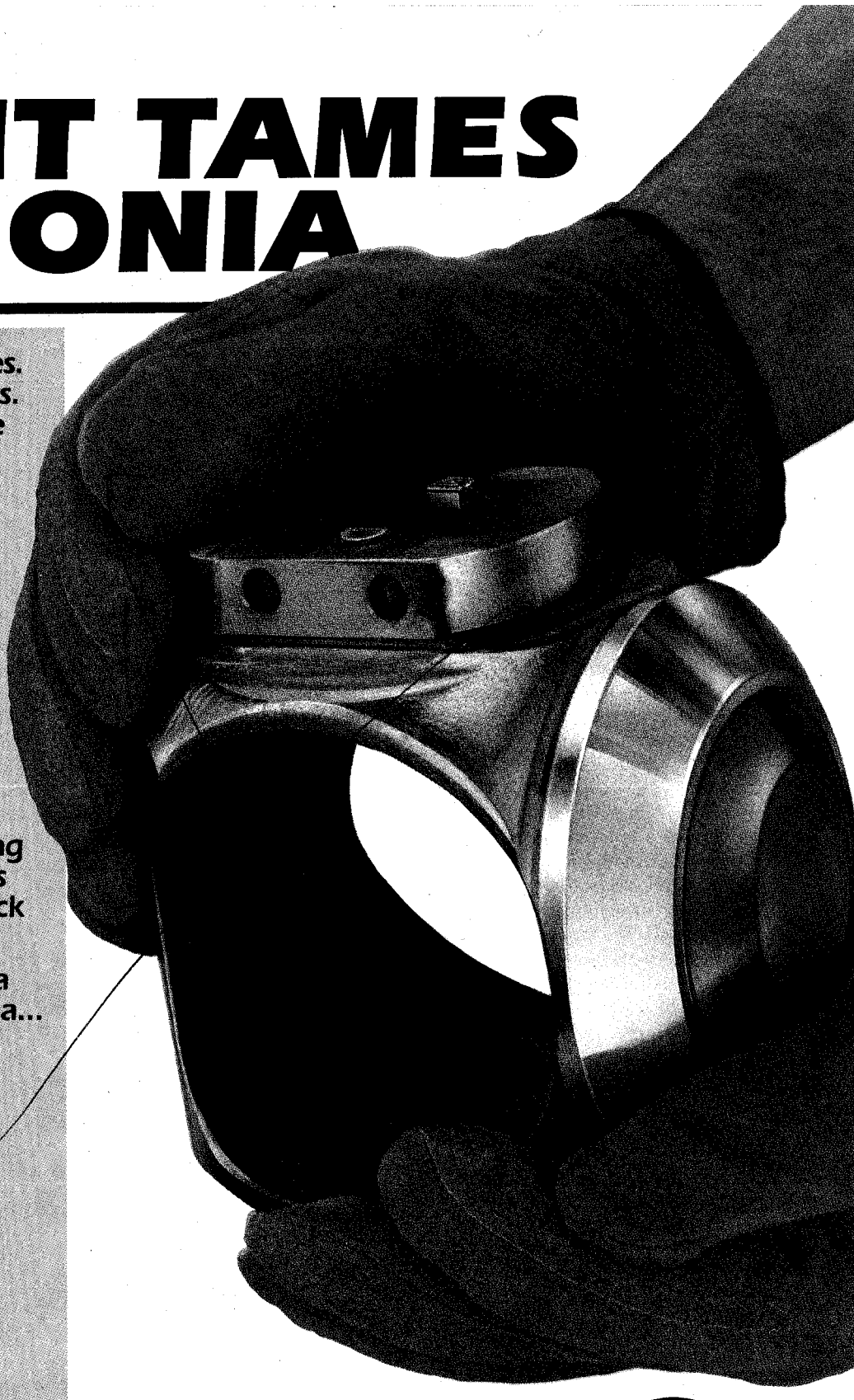

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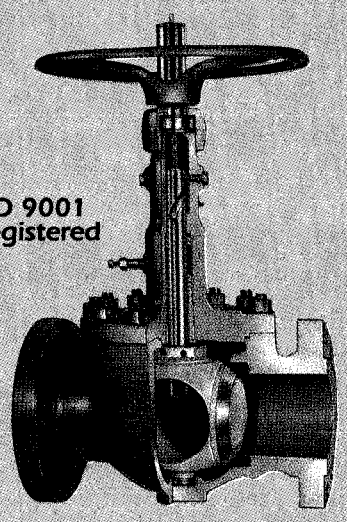

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