Miniaturization of Hydroprocessing Catalyst Testing Systems: Theory and Practice

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Main factors limiting downscaling of fixed-bed integral reactors are discussed, which operate with a gas stream or with gas and liquid in trickle flow, as used in hydroprocessing of oil. Criteria developed for a sufficiently close approach to plug flow and for good contacting of the catalyst show that they can be met in very small reactors, both for processes with reactants in the gas phase and for trickle-flow processes, provided that the catalyst bed is diluted with fine inert material in the latter case. Experimental tests show that microreactors with typical catalyst volumes of 5–10 mL can be used to obtain representative results that can very well match data from industrial reactors. It appears to be feasible to miniaturize catalytic test reactors further to "nanoscale" reactors with as little as 0.2–0.4 mL of catalyst while maintaining the results to be meaningful. Even though there are advantages as well as limitations, miniaturization can enhance safety and reduce manpower.

Introduction

Miniaturization of equipment has many advantages and can in some cases even revolutionize fields of technology. Examples of dramatic impacts of miniaturization are in the field of biochemistry where the advent of microscale chromatographic separations (paper, thin layer, and capillary high-performance liquid chromatography (HPLC)) and other microscale analytical techniques have been crucial to progress in this field for the last decades, and in the field of electronic computing, where miniaturization is causing a revolution in information technology.

In the industrial chemical laboratory, too, reducing the scale of experimentation without detracting from the value of the results can be quite important, although the consequences of miniaturization may not be as spectacular as in the cases just cited. The incentives behind downscaling are manifold, and may include the ones below:

- Cheaper equipment to construct and install
- Fewer materials to consume, store, and dispose of
- Fewer demands on laboratory infrastructure, including lower utility requirements
- Intrinsically safer
- May promote better, more precise, working practices.

The present article deals with the topic of scale reduction in research on catalytic processes. Catalysis, being a molecular phenomenon, can in principle be studied on a very small scale. For example, a microgram sample of a compound having a molecular weight of 600 consists of as many as about 10^{15} molecules, which is more than sufficient for this sample to be truly representative. As a matter of fact, fundamental catalysis studies on single-crystal surfaces equivalent to one microgram of a practical catalyst often involve minute amounts of reactants, and these studies are made possible by the high sensitivity of modern analytical techniques such as mass spectrometry, gas chromatography, and spectroscopic techniques that are also based on molecular phenomena.

In contrast to these fundamental studies, research and development studies on industrial catalytic processes are not only concerned with understanding the basic chemistry of these processes but also with relating the information generated in the laboratory with industrial practice. Since the composition of practical feedstocks such as petroleum fractions may be very complex, and in view of the complicated reaction networks involved, a fundamental kinetic approach is only possible in a limited number of cases, notwithstanding the possibilities offered by modern analytical techniques and powerful computers. Therefore, there is a need for the ability to simulate the performance of an industrial reactor in the laboratory.

Traditionally, the laboratory equivalent of an industrial reactor as used in hydroprocesses (meters in width and tens of meters in height) was a pilot plant of much smaller dimensions but still very large according to laboratory standards (e.g., a catalyst bed a few centimeters wide and several meters high). The subject of the present article is the downscaling of this pilot plant to more convenient dimensions while retaining the validity of the results obtained. The article will focus on the downsizing of fixed-bed reactors, which are among the types of reactors most widely used in the petroleum industry. Fixed-bed reactors operated with a gaseous stream of reactant as well as with a combination of gas and liquid, namely, trickle-flow reactors, will be considered.

Downscaling Approach for Continuous-Flow Fixed-Bed Reactors

For a fixed-bed reactor operated under steady conditions, the important scaling factors are the dimensions of the catalyst bed and the catalyst particles. To simulate an industrial reactor generally operated as an integral reactor achieving practical levels of conversion of the reactant, the laboratory reactor must also be operated as an integral reactor giving the same conversion. The approach generally taken is to operate the laboratory reactor at the same space velocity as the industrial one. Since at a constant space velocity the linear velocity of the reactant stream is directly proportional to the bed length, a reduction of bed length will reduce the linear velocity and the Reynolds number accordingly ($Re = d_p * u/\eta$, in which d_p is the particle diameter, u the superficial velocity, and η the dynamic viscosity). In principle, this means that the hydrodynamics in the commercial reactor and the shorter laboratory reactor will be different.

Hydrodynamic factors play a crucial role in that they affect the reaction rates in an interactive way with the intrinsic chemical kinetics, so one cannot reduce the reactor length, or at least not by a large factor, without losing representativeness of the laboratory reactor. The only dimension that can be reduced is the reactor width, down to a size where the wall effect begins to affect results (to be discussed later). These considerations are more or less implied in the sizing of the traditional pilot plant for fixed-bed processes: reactor lengths of 5 to 10 m and reactor diameters of 4 to 10 cm.

Fortunately, however, in most fixed-bed processes of practical interest, in particular the widely applied fixed-bed processes in the petroleum industry, hydrodynamics play a less important role than chemical kinetics and intraparticle diffusion in determining conversions. In the general situation of slow or moderately fast reactions occurring over catalyst particles with effectiveness factors not much below one, the diffusion paths within the catalyst particle are of the order of the particle radius, while the effective film thicknesses outside the particle involved in gas–solid, liquid–solid, or gas–liquid mass transfer will be substantially smaller. This point is illustrated in Table 1, which gives the relative magnitude of the various mass-transfer resistances in a typical case of trickle-flow hydrotreating. Under these circumstances, hydrodynamics are only of importance insofar as they determine pressure drops, holdups in multiphase flow, and in certain cases distribution of fluids over the reactor cross section and heat-transport phenomena.

Table 1. Relative Mass-Transfer Resistances Estimated for a Typical Case of Gas Oil Hydrodesulfurization in Trickle Flow

Resistance	% of Total
From bulk gas to G/L interface	Negligible
From G/L interface to bulk liquid	2
From bulk liquid to ext. cat. surface	21
Intraparticle diffusion and reaction	77

When the desired function of the laboratory reactor does not include being representative on the last-mentioned points, but is restricted to representativeness in a chemical reaction sense only, considerable further downscaling is possible. As a starting point, one may assume that a well-designed industrial fixed-bed reactor is a close approximation of an ideal integral reactor that fulfills the following criteria:

1. All volume elements of the feed must spend the same time in the reactor so as to contribute equally to the overall conversion. In other words, the reactor should be a close approximation of a plug-flow reactor, which is the type of reactor to be selected for reactions of a positive order.
2. All parts of the catalyst bed must contribute maximally to the overall conversion, implying that all catalyst particles must be in good contact with the reactant stream.

To be representative of an industrial reactor that comes close to this ideal, the laboratory reactor must also fulfill these requirements. Although improper design may give rise to industrial reactors that perform more poorly, it does not make much sense to try to mimic a malfunctioning reactor on a small scale. Therefore, compliance with the preceding requirements for an ideal reactor can be used as a guiding principle in downscaling of fixed-bed reactors, and in the following sections we will examine how far reactor dimensions can be reduced without violating these requirements.

Limits in Downsizing of Fixed-bed Reactors

Deviations from plug flow

Allowable Deviation from Plug Flow. The allowable deviation from ideal plug flow is determined by what is considered to be an acceptable difference in conversion rate achieved in the ideal and the real reactor, and is also a function of the order of the reaction and the degree of conversion. How much the residence time distribution in a practical reactor resembles that in an ideal reactor is generally expressed by the Péclet number ($Pé$), a dimensionless number that is numerically about twice the equivalent number of mixers in series. For a true plug-flow reactor both numbers are infinitely large.

Mears (1971) has derived a relation between $Pé$, the reaction order n, and the conversion X based on the criterion that a good practical reactor should require no more than 5% extra catalyst to achieve the same conversion as the ideal one. A similar relation has been proposed by Gierman (1988), which is based on the somewhat less stringent criterion that the temperature requirement for the same conversion should not be higher than theoretical by one degree Centigrade, which is considered to be the accuracy of temperature definition in practice. The latter relation, which will be used throughout this article, can be written as

$$Pé = L * u/D_{ax} > 8 * n * \ln\{1/(1-X)\}, \qquad (1)$$

in which L is the reactor length, u the superficial velocity, and D_{ax} the overall axial dispersion, which is made up from contributions from axial molecular diffusion, convective dispersion in the packing, and macroscopic velocity distributions in the reactor.

Axial Molecular Diffusion. This can be an important cause of spread in residence time in the reactor, particularly with gases of high diffusivity and at low linear velocities (low space velocities and shallow beds). For a rather demanding case, namely, hydrogen at ambient conditions at a gas hourly space velocity (GHSV) of 1,000, the minimum bed length needed to satisfy the criterion of Eq. 1 for a good reactor is shown in Figure 1. It follows that a microreactor with a bed length of 10 cm will in most cases be acceptable.

Axial Convective Dispersion. The statistical variations in width, length, and direction of individual channels within the packing result in a dispersion that is characterized by the dimensionless Bodenstein number ($Bo = d_p * u/D_{ax}$), which is analogous to the Péclet number but has the particle diameter d_p as characteristic dimension.

For axial dispersion in the packing, Eq. 1 can be written as

$$L/d_p > (8/Bo) * n * \ln\{1/(1-X)\}. \qquad (2)$$

For flow through packed beds Bo is a function of Re, and a global correlation between these dimensionless numbers has been established by Gierman on the basis of published data (Gierman, 1988). According to this correlation Bo decreases with decreasing Re until an approximately constant value of about 0.4 is obtained in the range of interest for small laboratory reactors. For the axial dispersion of the liquid in trickle flow, the constant value of Bo is an order of magnitude lower, or about 0.04. It is of interest to note that for trickle-flow processes as used in the petroleum industry the dispersion of the gas phase is generally unimportant, since the gas phase consists mostly of recycled hydrogen. Consequently, conversion of hydrogen per pass is relatively low and rather unimportant, so that only the dispersion of the liquid-oil phase needs to be considered.

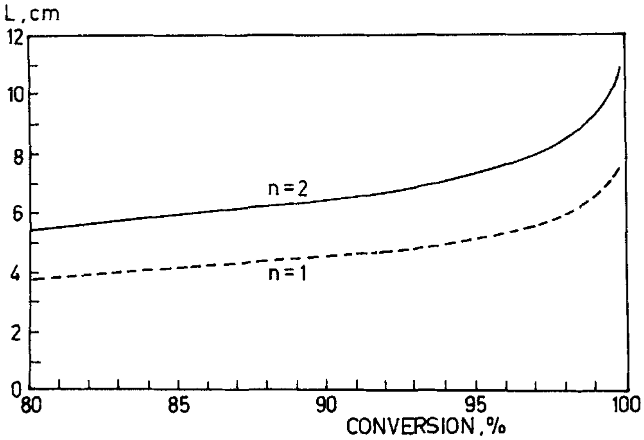

Figure 1. Minimum bed length as a function of conversion for a first- and second-order reactor, as determined by molecular diffusion in flowing gas.

Hydrogen at 1 bar and 25°C; GHSV = 1,000 nL/(L·h); ϵ = 0.4; τ = 2.

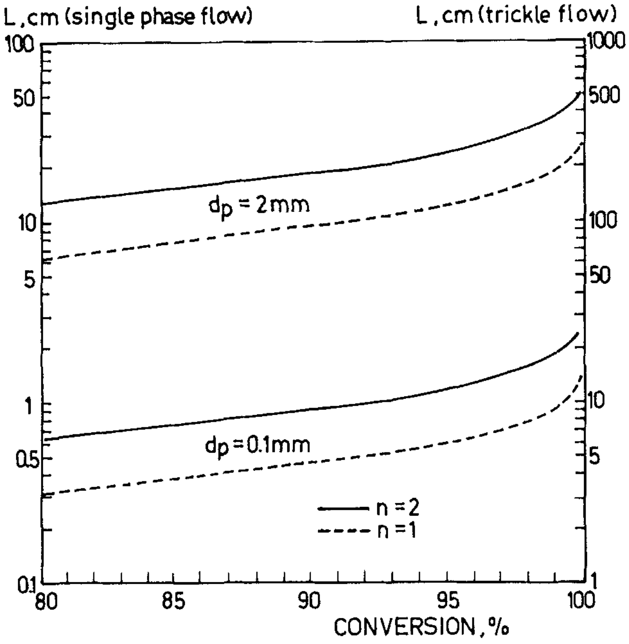

Figure 2. Minimum bed length as a function of conversion for a first- and second-order reaction, as determined by axial dispersion in the packing.

Figure 2 presents the minimum bed length calculated according to Eq. 2 with the values for Bo mentioned earlier, for beds of particles of 2 mm diameter (a typical size for fixed-bed catalysts). It can be seen that in the case of single-phase flow, for example, gas flow, a bed length of 20 cm as can be accommodated in a microreactor is adequate for not too demanding cases (conversions not exceeding 90%). However, for trickle-flow operation much longer beds are required. For instance, for 90% conversion in the case of a second-order reaction the minimum bed length of 2 m is required, which is in the range of pilot-plant reactors. Hence, microreactors are clearly unsuitable for testing catalysts of particle size in the millimeter range in trickle flow, and pilot-plant reactors seem indicated.

However, as can also be inferred from Figure 2, from the point of view of axial dispersion there should be little problem in testing particles of 0.1 mm diameter in a 20-cm-long bed in a microreactor even for trickle flow. This is one of the motives behind the catalyst dilution technique to be discussed later.

Wall Effect and Other Causes of Transverse Macroscopic Velocity Profiles. In addition to the axial dispersion discussed earlier, which is an intrinsic characteristic of the packing and which finds its origin in the more or less random variation of velocity vectors on the scale of the particle diameter, more systematic differences in velocities may occur in the flow through the bed. A lateral velocity profile over the reactor diameter may be caused by nonuniform packing (uneven compaction or segregation of particles in the case of a catalyst with a spread in particle size).

Although the preceding lateral velocity profile may be avoided by careful filling of the reactor, there is another, more inherent cause of systematic velocity differences, namely, the wall effect. The packing of particles cannot be the same very close to the wall of the reactor as the unperturbed packing farther away from it. Generally, there is a much greater voidage in the wall region than the average voidage in the interior of the reactor, as found both experimentally (Benati and Brosilow, 1982) and in computer-simulated packings (Zimmerman and Ng, 1986). The greater permeability in the wall zone, which tends to enhance the flow in combination with the flow retardation by the reactor wall, results in a radial velocity profile with a maximum located one to a few particle diameters away from the wall (Fahien and Stankovic, 1979; Vortmeyer and Schuster, 1983).

The wall effect gives rise to an appreciable spread in residence time of the reactant. However, as the ratio between bed diameter and particle diameter increases, the flow through the wall zone will carry less weight, and at a sufficiently large ratio its effect becomes acceptably small. At a ratio higher than about 25 the wall effect no longer has a noticeable effect on the average properties of the bed, for example, average porosity and average permeability (Chu and Ng, 1989).

Figure 3 shows the relation between the minimum reactor diameter and the particle diameter with a value of 25 as a criterion for an acceptably small wall effect. This figure can also be read as the maximum particle diameter that can be applied in a reactor of a given diameter. According to this figure, a fixed-bed catalyst of a practical size in the millimeter range can only be tested in reactors of several centimeters width if the effect of the wall is to be minimal. Hence, for testing catalysts of such a practical size, a pilot-plant reactor with a diameter of at least 4 cm seems indicated, and a microreactor with a diameter of 1 cm or less is clearly unsuitable. However, with respect to the wall effect there should be no problem in such a microreactor with much smaller particles, for example, 0.1 mm diameter, and this is a further reason for applying the catalyst-bed dilution technique to be discussed later.

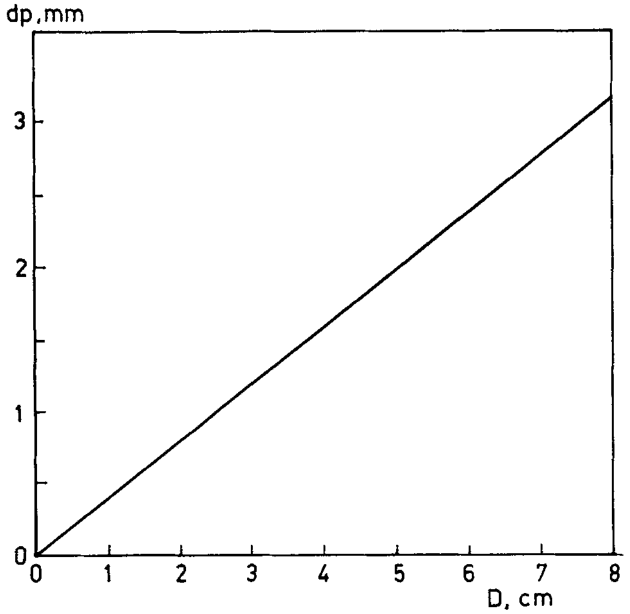

Figure 3. Maximum particle size for a given bed diameter, as dictated by the criterion for negligible wall effect.

Reducing the Effect of Lateral Flow Profiles by Lateral Diffusion. The preceding criterion for negligible wall effect is unduly stringent in the specific case that there is a sufficiently fast exchange of mass between regions of low and high forward velocities. This applies specifically to fixed-bed reactors operated with gases, which have a relatively high molecular diffusivity. Fast lateral mass exchange reduces the spread in residence time caused by the lateral velocity profile, and the interaction between axial velocity differences and lateral exchange results in a dispersion that can be described by an axial diffusivity known as the Taylor diffusivity.

The length equivalent to one mixing stage associated with the Taylor diffusivity can be written as

$$2L/P\acute{e} = 2\kappa * R^2 * v/D_{\mathrm{rad}}, \tag{3}$$

in which v is the average interstitial velocity, R the bed radius, D_{rad} the diffusivity in the radial direction; κ is a dimensionless number that characterizes the flow profile. Combining Eqs. 1 and 3, one obtains

$$L * D_{\mathrm{rad}}/(R^2 * u) > 8(\kappa/\epsilon) * n * \ln\{1/(1-X)\}, \tag{4}$$

in which ϵ is the bed voidage.

The axial dispersion in packings caused by the combined effects of lateral flow profiles and radial diffusion has been the subject of many studies in chromatography. Information obtained in these studies is relevant to the present problem since the requirements of an ideal packed chromatographic column, namely, minimal band broadening and adequate contacting of the solid phase, are identical to those of an ideal fixed-bed reactor. In studies with packed chromatographic columns it has been found that for columns with a low ratio of tube diameter over particle diameter ($D/d_p < 5$) the value of κ is about 0.04, which is about twice the value of 1/48 for the parabolic Poiseuille profile of laminar flow in a tube (Sie and Rijnders, 1967). Using the value of 0.04 and assuming the mechanism of radial diffusion to be molecular diffusion through the bed, we have calculated the maximum bed diameters for which radial diffusion is effective in wiping out the effect of the wall. (Note that there is a *maximum* limit on the bed diameter, whereas in the absence of fast radial diffusion, there is a *minimum* diameter for a negligible wall effect.) From results presented in Figure 4 it can be seen that with gas as flowing medium there should be no problem in testing catalyst particles of a practical size in a microreactor of 1 cm diameter, notwithstanding the fact that the diameter ratio may be smaller than 5. On the other hand, the diffusivity in liquids is too low to rely on lateral exchange for effective counteraction of the wall effect in microreactors, since the maximum bed diameter for this to happen is in the millimeter range (Figure 4).

Measurement of residence-time distribution in microreactors operated with gas have confirmed that as a consequence of fast radial diffusion the contribution of the wall effect to the residence-time distribution is a relatively minor one. Data shown in Table 2 show that this contribution is negligible as compared to axial molecular diffusion.

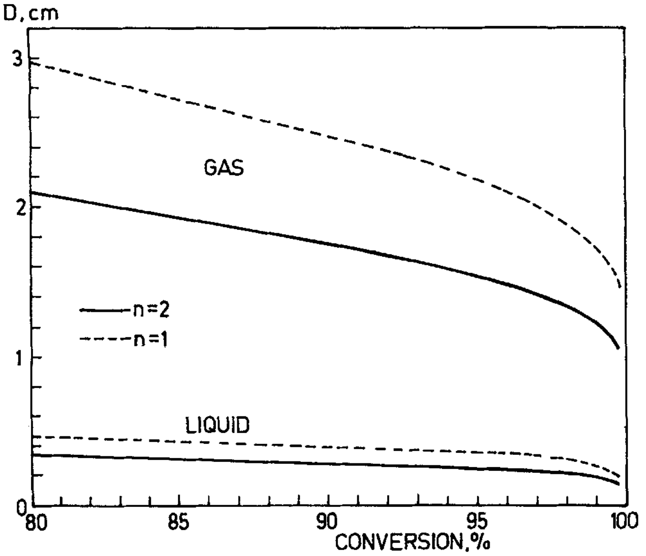

Figure 4. Maximum bed diameters for effective counteraction of radial flow profiles by radial diffusion.

Beds with $D/d_p < 5$. Gas: Hydrogen, $P = 1$ bar; $T = 25°C$; GHSV = 1,000 nL/(L·h). Liquid: n-Eicosane. $T = 300°C$; WHSV (weight hourly space velocity) = 1 kg/(kg·h). $\epsilon = 0.4$, $\tau = 2$.

Catalyst contacting

The second requirement of an ideal reactor, namely, that all catalyst particles are in good contact with the reactant stream, will in most cases of a single fluid phase be fulfilled if the first criterion of a sharp residence time distribution is met. However, in the case of two flowing phases a sharp residence-time distribution is no guarantee for adequate contacting. In a trickle-bed reactor a situation may prevail where liquid flows preferentially through a certain part of the bed, while gas flows mainly through the other part. Such macroscopic maldistribution of liquid can be observed in experiments with colored liquids, but can also be simulated with computer models (Zimmerman and Ng, 1986). This maldistribution, often referred to as incomplete wetting, may be sustained if the force of gravity responsible for the downflow of liquid is much larger than the frictional forces. If the latter forces predominate, the high pressure drop will force liquid to flow through every available interstitial channel, and consequently catalyst contacting will be good.

Table 2. Measured Axial Dispersion in a Microflow Reactor with Gas Flow*

Packing	Pe	No. of Mixers	D_{ax} (cm^2/s)	$\epsilon D_{mol}/\tau$ (cm^2/s)
Spheres $d_p = 1.5$ mm, $\epsilon = 0.40$	105	53	0.132	0.137
Cylinders $d = 1.5$ mm, $L = 3$ mm, $\epsilon = 0.44$	97	49	0.143	0.151

*$L = 10.2$ cm, $D = 0.8$ cm, $V = 5$ mL. Nitrogen, $P = 1$ bar, $T = 25°C$, GHSV = 450 nL/(L·h). Tracer: He. Binary diffusion coefficient of He in $N_2 = 0.678$ cm^2/s, $\tau = 2$ (assumed).

A criterion for adequate wetting or even irrigation of catalyst is the following one proposed by Gierman and Harmsen (Gierman, 1988)

$$W = \eta_L * u_L / \left(\rho_L * d_p^2 * g \right) > 5 \times 10^{-6}, \qquad (5)$$

in which η_L is the dynamic viscosity of the liquid, ρ_L the liquid density, and g the gravity constant. The dimensionless constant W is the wetting number that compares frictional and gravitational forces. The numerical value in the preceding equation has been determined on the basis of a large volume of experimental data, and its order of magnitude can be rationalized by simple considerations (Sie, 1991).

Figure 5 shows the minimum bed length as a function of particle diameter required to meet the wetting criterion just given. The figure may also be read as the maximum particle diameter that can be applied in a bed of a given length. It can be seen that, for liquid viscosities in the range typical for petroleum fractions under hydroprocessing conditions, a minimum length of several meters is required with particles having a diameter of 2 mm and larger. Hence, for testing of such catalysts under trickle-flow conditions, a relatively large pilot plant reactor is required and a microreactor can be ruled out. However, the figure also shows that with much smaller particles, for example, 0.2-mm diameter and smaller, the required bed length for good wetting of the catalyst is less than 20 cm. Hence, with such small particles microflow reactors become eligible for testing catalyst for trickle-flow processes. This constitutes a third argument for the catalyst dilution technique to be discussed below.

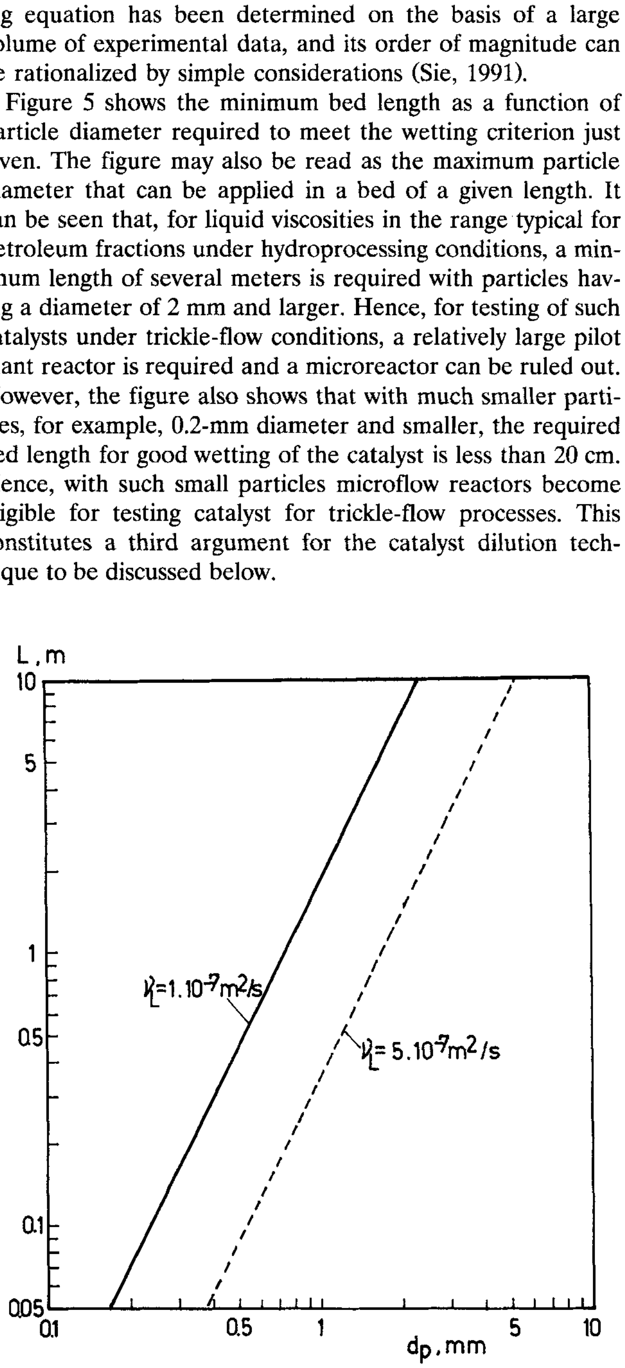

Figure 5. Minimum bed length for particles of varying size, as dictated by criterion for even irrigation.

LHSV (liquid hourly space velocity) = 1 L/(L·h).

Catalyst Bed Dilution with Fine Particles of Inert Material

From the foregoing discussion it transpired that for fixed-bed processes operated with gas flow, reactors as small as microreactors (about 1-cm diameter, 5 to 20-cm bed length) can be used for testing catalysts of realistic size (1- to 3-mm diameter). In contrast herewith, relatively large pilot-plant reactors (several meters high, several centimeters diameter) are required for testing such catalysts for trickle-flow processes.

In principle, one has the option of crushing the industrial catalyst and testing it in the form of fine particles in small reactors. However, aside from the danger of affecting catalyst properties by the crushing and sieving operations, the data obtained with crushed catalyst may not be representative for industrial practice. If pore-diffusion limitation occurs with the practical catalyst, the crushed sample will exhibit a higher activity. But even when the main reaction is not or is only slightly limited by intraparticle diffusion, other reactions in complex reaction networks involving a multitude of different feed molecules may be more seriously limited by pore diffusion. Hence, changing the catalyst particle size can affect not only the apparent activity of the catalyst, but selectivity and deactivation behavior as well.

The dilemma of wanting to test relatively large industrial catalyst particles and needing fine particles in small beds for the hydrodynamic reasons discussed earlier can be solved by surrounding the catalyst particles with small granules (0.05–0.2-mm diameter) of an inert material. Thus, the hydrodynamics of the flowing fluids will be mainly dictated by the packing of small inert particles, whereas the catalytic conversion behavior is that of the catalyst in the actual size. The improvement in plug-flow approach of laboratory trickle-flow reactors by adopting this catalyst-bed dilution technique has been demonstrated in experiments with isotopically labeled oils under typical hydroprocessing conditions (Van Klinken and van Dongen, 1980). Another beneficial effect of catalyst-bed dilution is that temperature homogeneity in the bed is improved and that the chances of temperature runaway are diminished in the case of strongly exothermic reactions, especially when using inert diluents with high thermal conductivity, such as silicon carbide or alundum.

The technique of catalyst-bed dilution opens the way to testing of industrial fixed-bed catalysts in very small laboratory reactors, even for trickle-flow processes. This is supported by the results of bed-length reduction in gas-oil hydrotreating experiments, shown in Figures 6 and 7. From the data for an *undiluted* bed shown in Figure 6, it can be inferred that shortening of a pilot-plant reactor from 4.8-m length by a factor of 3 is accompanied by a significant deterioration of the apparent catalyst performance. This can be understood from the previous discussion, since the length of the shorter reactor (1.6 m) is below the minimal lengths dictated by acceptable axial dispersion and by catalyst wetting (cf. Figures 2 and 5). By contrast, reduction of the length of a *diluted* catalyst bed by a factor of 2, namely, from 40 cm to 20 cm, does not noticeably affect the test results, as can be inferred from Figure 7. In addition to supporting the earlier thesis that extraparticle mass-transfer effects play a minor role only, these results indicate that testing of diluted catalysts for trickle-flow processes is feasible in microreactors, since the

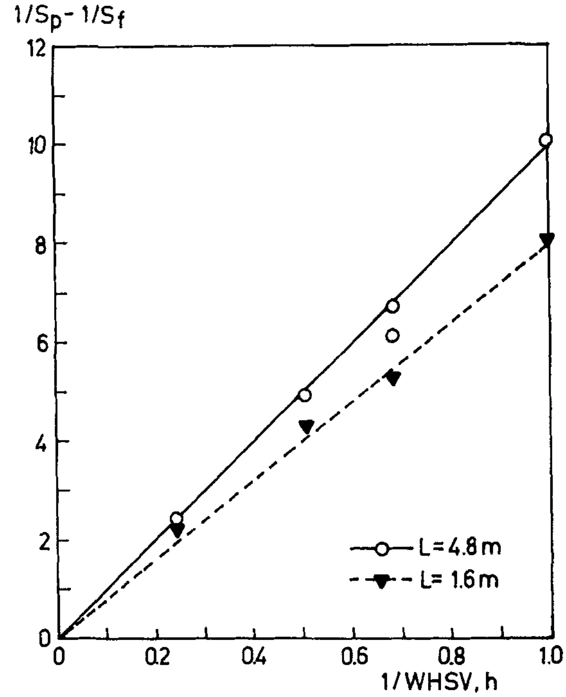

Figure 6. Second-order plot for hydrodesulfurization of a light gas oil in trickle flow over undiluted beds of different lengths.

$D = 8$ cm. Catalyst: Co/Mo/Alumina, 3-mm pellets.

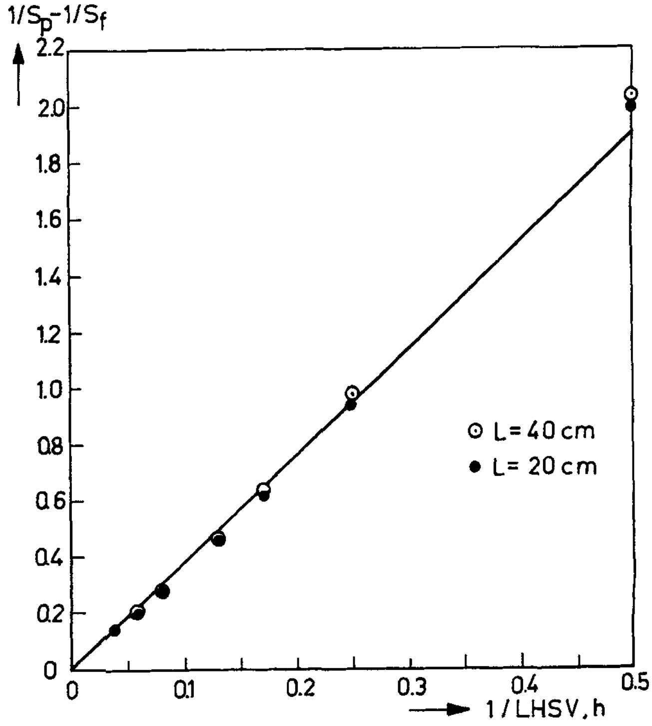

Figure 7. Second-order plot for hydrodesulfurization of a gas oil in trickle flow over diluted beds of different lengths.

$D = 2$ cm. Catalyst: Co/Mo/Alumina, 1.5-mm cylindrical extrudates. Diluent: 0.2 mm SiC.

length of the shorter catalyst bed is in the range covered by microreactors. Further evidence for this conclusion will be presented below.

Representativeness of Catalyst Testing in Microflow Reactors

Fixed-bed processes with reactants in the gas phase

From the previous discussion on the limiting dimensions of laboratory fixed-bed reactors it followed that for these processes microreactors with a bed diameter of about 1 cm and a bed length between 5 and 20 cm should give results that come close to those of an ideal reactor, except for the most demanding cases (conversions very close to 100%). Such results should therefore be representative for an industrial process, assuming that the latter is carried out in a well-designed reactor.

Evidence to support this statement is presented in Table 3, which compares microflow test results on light paraffin isomerization (a process with reactants in the gas phase) with data on the same catalyst and feedstock from a commercial unit. It can be seen that there is a quite satisfactory agreement between the two sets of data. It is of interest to note that the catalyst in the form of extrudates of 1.5-mm diameter has not been diluted.

Trickle-flow processes

The suitability of microflow reactors with diluted catalyst beds for testing of industrial catalysts used in trickle-flow processes such as hydroprocessing of petroleum fractions is demonstrated by the data of Table 4, which is a direct comparison between microflow test results and commercial operating data on hydrodesulfurization of the same gas oil over the same catalyst under comparable conditions. In the microflow test the catalyst bed of 1.2-mm extrudates was diluted with 0.05-mm particles of silicon carbide. The close correspondence between the two sets of data implies that the data generated in the microreactor test can be considered to be meaningful for industrial practice.

Miniaturization of Catalyst Testing below the Scale of Microreactors

From the analysis of the limiting geometric factors, presented in the earlier part of this article, it can be concluded that the microreactor scale is not necessarily the smallest scale for representative testing of fixed-bed catalysts. As follows from the earlier analysis, it is in principle possible to reduce the reactor diameter of about 1 cm (typical for a microreactor) down to a few millimeters, while keeping the bed length about the same. The lower limit is in fact determined by the requirement that the catalyst particles have to be accommodated in the reactor, for example, for 1.5-mm-dia extrudates the minimum inner diameter of the reactor may be about 2 mm. This implies a reduction in reactor and catalyst volume by a factor of about 25, that is, instead of a typical catalyst volume of 5–10 mL in microflow reactors, the catalyst volume in the submicro- or "nanoflow" reactor amounts to as little as 0.2 to 0.4 mL.

Table 3. Comparison of Microflow and Commercial Results for Isomerization of Light Naphtha over a Pt/Mordenite Catalyst (1.5-mm Extrudates)

Reactor	Microflow	Commercial
Catalyst charge	2.1 g	15.9 t
Isopentane in product, % of total C_5	64.2	63.3
Isohexanes in product, % of total C_6	81.9	84.8
2,2 diMeButane in product, % of total C_6	17.4	19.8
C_{5+} yield, wt. %	97.8	97.2
RON-0 of product (calc.)	79.6	79.7

Table 4. Comparison of Microflow and Commercial Results for Trickle-Flow Hydrodesulfurization of Gas Oil*

Reactor	Microflow	Commercial
Catalyst volume	20 mL (diluted)	122 m^3
Sulfur in product, wt. %	0.075	0.082
% Desulfurization	95.4	95.0
Second-order rate constant	23.5	20.9

*Catalyst: Co/Mo/Alumina, 1.2-mm trilobe extrudates. Diluent: 0.05 mm SiC. Feed: Middle East heavy gas oil, 1.64 wt. % S. Operating conditions (WHSV, WABT (weighted average bed temperature), hydrogen/oil, partial pressures of hydrogen and hydrogen sulfide at reactor inlet) same in both cases.

Even on the latter small scale, meaningful test results can be obtained, as will be demonstrated below.

Fixed-bed processes with reactants in the gas phase

Table 5 presents comparative test data obtained in microflow and nanoflow reactors for the isomerization of light paraffins over a catalyst shaped as extrudates of 1.5-mm diameter. The nanoflow test data match the microflow test data quite well. The latter test data have been shown to be representative for catalyst performance under industrial conditions, and by implication this should also be true for the nanoflow test results.

Figures 8 and 9 compare microflow and nanoflow test results on the hydrodesulfurization of the same gas oil over a catalyst shaped as 1.5-mm extrudates, diluted with 0.05-mm particles of silicon carbide. It can be seen that there is a good match between the data obtained with the two types of reactors, both with respect to desulfurization rate (Figure 8) and the effect of temperature on desulfurization (Figure 9).

Table 5. Comparison of Microflow and Nanoflow Test Results for Pentane/Hexane Isomerization*

Reactor	Microflow	Nanoflow
Catalyst charge, g	5	0.2
Isopentane in product, % of total pentanes	58.3	59.5
Isohexanes in product, % of total hexanes	80.7	80.2
2,2 diMeButane in product, % of total hexanes	16.4	16.5
C_{5+} yield, wt. %	99.0	98.9
RON-0 of product (calc.)	77.8	77.9

*Catalyst: Pt/Mordenite, 1.5-mm extrudates (undiluted). Feed: *n*-pentane/*n*-hexane/CycloC_6 61/34/5 (wt. %). $T = 260°C$; $P = 25$ bar; hydrogen/feed = 1.25 molar; WHSV = 1.70.

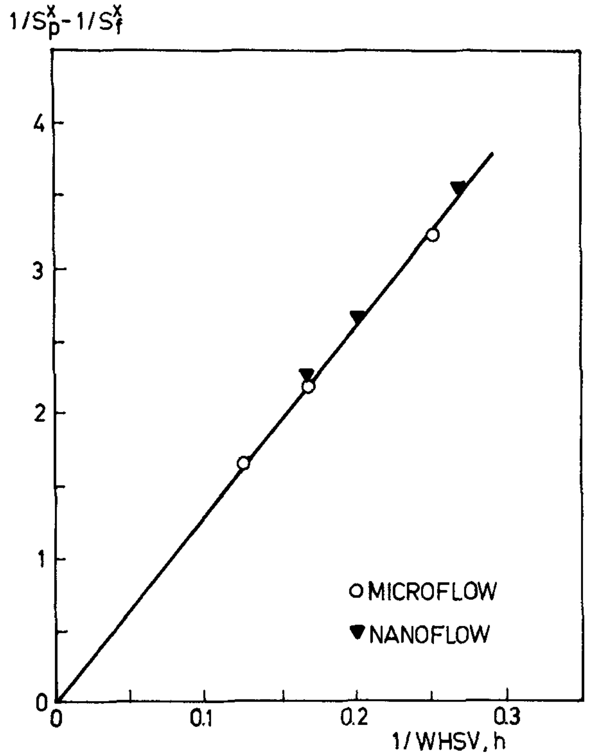

Figure 8. Microflow vs. nanoflow test results for hydrodesulfurization of gas oil in trickle flow; effect of space velocity.

Catalyst: Co/Mo/Alumina, 1.5-mm cylindrical extrudates. Diluent: 0.05 mm SiC. $x = 0.84$.

Since it has been shown that microflow test data can be representative for industrial operation, it follows from the preceding comparison that nanoflow test data, too, can be meaningful for industrial practice. This statement is substantiated by Table 6, where such test data on hydrodesulfurization of a gas oil over a catalyst shaped as 1.5-mm extrudates are directly compared with data from a commercial hydrodesulfurization unit.

Potential errors in catalyst sampling

Proper sampling from a catalyst batch composed of nonidentical catalyst particles is obviously important for obtaining meaningful results. To obtain representative samples of such an inhomogeneous catalyst batch for testing in laboratory reactors ranging from pilot plants to microreactors, the well-known procedures for sampling of solid granular material have to be adhered to. However, with a catalyst sample as small as that to be tested in nanoflow reactors, an additional problem may arise due to the small number of particles.

A catalyst sample of 0.3 g, consisting of 1.5-mm-dia. and 4-mm-long extrudates will typically consist of about 40 particles, and at this small number the law of statistics has to be considered. Figure 10 presents the calculated standard deviations for a random sampling from a mixture of two catalysts (A and B) that differ in activity by a factor k_A/k_B. Assuming that a standard deviation below 5% is acceptable, it can be seen that there is no problem when the sample size consists of 10,000 particles, as long as the sampling is nonselective. However, at a sample size corresponding with 20 particles, the standard deviation may be above 5% when the activity ratio is larger than about 1.5 and when the less active catalyst constitutes a major proportion of the mixture. If the less active catalyst is a minor component of the mix, for example, 10%, the standard deviation remains below the set limit of 5%, even at a very large activity ratio.

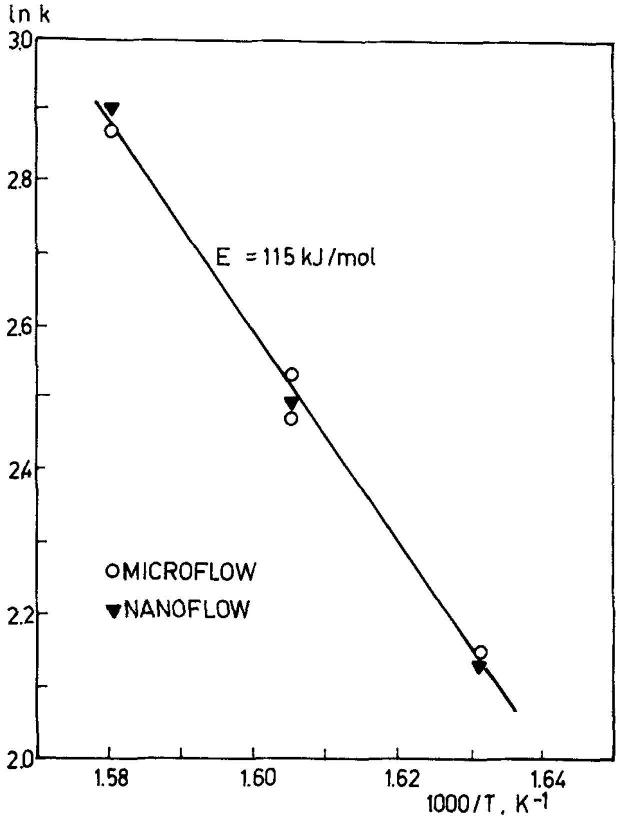

Figure 9. Microflow vs. nanoflow test results for hydrodesulfurization of gas oil in trickle flow; effect of temperature.

Catalyst and diluent as stated under Figure 8.

The latter situation may occur in practice because a batch of catalyst can be contaminated with a small amount of less active or even inert material. In such a situation, the limited number of particles in the test sample does not necessarily pose a problem, as long as the sampling is done in a nonselective manner.

Table 6. Comparison of Nanoflow Test Results with Data of Commercial Operation on Hydrodesulfurization of Gas Oil*

Reactor	Nanoflow	Commercial
Catalyst charge	0.228 g (+ diluent)	33.5 t
Sulfur in product, wt. %	0.155	0.144
% Desulfurization	80.5	81.9
2.1-Order rate constant	22	24

*Catalyst: Co/Mo/Alumina, 1.5-mm trilobe extrudates. Diluent: 0.05 mm SiC. Feed: Gas oil 162–415°C, 0.794 wt. % S. Conditions (WHSV, WABT, hydrogen/oil and partial pressures of hydrogen and hydrogen sulfide at reactor inlet) same for the two cases.

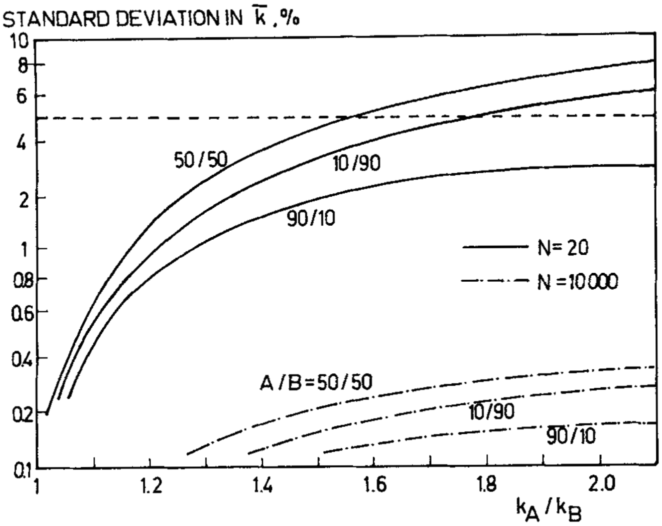

Figure 10. Sampling errors from a catalyst mixture composed of two components having different activities, for samples consisting of *N* particles.

However, when there is a large activity difference and when the less active material is abundant the statistical error may be unacceptably large for small samples. Fortunately, this is not a situation of much practical interest since such an inhomogeneous catalyst is obviously not an optimal one and there is hardly a reason to try and assess the performance of such a poor batch of catalyst with great accuracy.

Implementation and Consequences of Small-Scale Catalyst Testing

The increased possibilities of catalyst testing on a smaller scale than considered feasible in the past, and the advantages attached to experiments on a small scale, have led to a gradual replacement of the traditional large pilot plants by smaller units. This can be seen from Table 7, which compares the distributions of reactor units of varying size in an oil-process R & D laboratory in 1970 and 1987. It can be seen that during the intervening period bench-scale and microflow units have taken over many of the tasks formerly reserved for larger pilot plants. In more recent years, microflow tests are being widely applied, not only in exploratory studies where in the screening of new catalysts and unconventional feedstocks the small sample sizes are very important, but also in the process research and development studies on more established processes. In addition to the previously cited processes, namely, paraffin isomerization and hydrotreating of distillates, microflow reactors play an important role in research and development on most hydrocarbon-conversion processes, including catalytic reforming (Sie and Blauwhoff, 1991), hydrocracking (Van Dijk et al., 1991), and even hydrodemetallization and hydroconversion of residual oils (Oelderik et al., 1989). The use of microflow reactors is not restricted to simple once-through experiments in isothermally operated reactors, since on this scale accurate simulation of adiabatic operation has proven feasible (Sie and Blauwhoff, 1991), as well as simulation of a hydrocracker with on-line fractionation and recycle of fractionator bottoms (Van Dijk et al., 1991).

Table 7. Distribution of Number of Reactor Units*

Year	1970	1987
Microflow (≅ 0.01 L)	13	50
Bench Scale (≅ 0.1 L)	20	38
Pilot Plant (> 1 L)	67	12
Unattended units	13	94

*At the oil process R & D Department of the Koninklijke/Shell Laboratorium, Amsterdam (in % of total).

Driving forces behind this trend have been the improved research and development efficiency resulting from savings in costs, materials, and personnel, as well as the enhancement of safety and environmental friendliness of the operation. The savings in materials in moving from pilot plant to microreactor testing can be illustrated by comparing the feed requirements of these two reactor units for a typical case of gas-oil hydrotreating: whereas the pilot plant consumes monthly amounts of oil and hydrogen gas that have to be supplied on a periodic basis by tank cars and tube trailers, the microflow needs in a similar period can be covered by a jerry can of oil and a few gas bottles. In the pilot-plant case, the storage and disposal of the large amount of unused products may also constitute a logistic problem with environmental aspects.

The enhanced intrinsic safety resulting from miniaturization may be illustrated by the maximum hazards of a nanoflow reactor. When working with flammable gases or liquids, flow rates are so small that they can only sustain a flame comparable in size to that of a small candle. Working with synthesis gas, the small flow rate may give rise to an emission of toxic carbon monoxide that is of the order of that from a burning cigarette. The maximum release of compressed gas from the reactor inventory upon mechanical failure would be less than from a punctured bicycle tire and if this gas is explosive, its detonating power can be compared with that of a small firecracker. Hence, many of the safety systems mandatory in the case of larger reactors (fire detectors, flammable and toxic-gas detectors, special ventilation, etc.) can be simplified or even dispensed with.

The higher intrinsic safety of smaller reactor units makes it easier to automate these units and to allow them to operate around the clock without human attention. The increase in automation, which has accompanied the size reduction of the reactor units in the period 1970–1987, is clearly shown in Table 7, where the percentage of unattended units is seen to increase from 13 to 94.

The increase in research productivity resulting from catalyst testing on a smaller scale is illustrated by Figure 11. It can be inferred that the more modern, automated microreactor unit operating without human attention requires an order of magnitude less manpower than the traditional large pilot plant it has replaced.

Concluding Remarks

It has been shown that microflow and even smaller reactors can be used not only in fundamental kinetic studies with powdered catalysts, but also for testing practical fixed-bed hydroprocessing catalysts under industrially relevant conditions, that is, with catalysts in their actual shape and size,

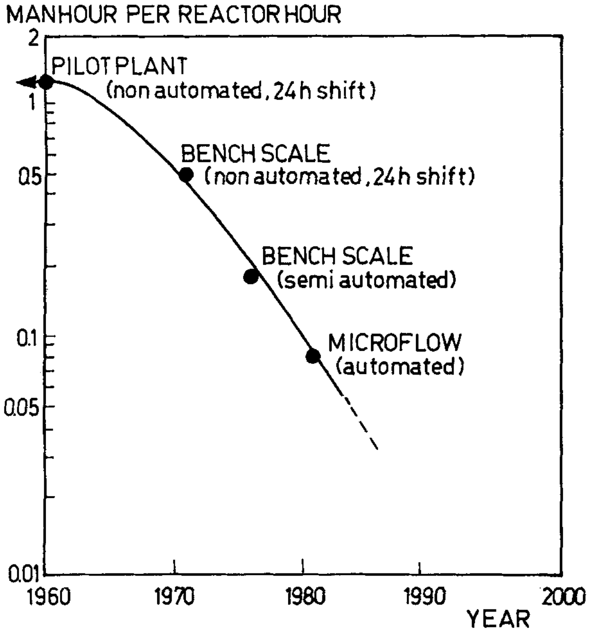

Figure 11. Manpower needs of different reactor units as a function of the approximate introduction year for general use in oil process research.

with practical feedstocks, and at conditions of space velocity, temperature, and pressure that are comparable to those in practice, yielding data that can match those of commercial operation. This applies not only to fixed beds operated with a stream of gas, but equally to fixed beds operated with liquid and gas as trickle-bed reactors, provided the catalyst bed is diluted with fine inert material. This experimentally verified conclusion is supported by a theoretical analysis of the factors that limit the downscaling possibility of fixed-bed reactors.

These small reactors can now be used for generating catalytic performance data that some 25 years ago had to be done in large fixed-bed pilot plants, at only a fraction of the costs, materials usage, and personnel need associated with the operation of the large pilot plants. Hence, for many catalytic process studies there is no need for the traditional large pilot plant any more. Nevertheless, cases will remain where experiments on a large scale cannot be avoided, for example, when large quantities of a new product are needed for market development in anticipation of commercial production. A large pilot plant is also needed when hydrodynamic factors play a crucial role in determining the chemical conversions of a catalytic process or when mechanical/physical features, such as fouling of the bed by particulate matter, are important. Another reason for a large and complex integrated pilot plant is when the process configuration is complex and involves separation steps and recycles of streams that cannot be miniaturized in a representative way.

For the evolution in catalyst testing systems, where miniaturization is increasingly offering capabilities at lower costs but cannot make large pilot plants totally redundant, an analogy can be drawn with the evolution in computing: while microcomputers are finding an ever increasing role, it is still necessary to make use of mainframe and even supercomputers in special applications.

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Notation

D_{mol} = molecular diffusivity, $m^2 \cdot s^{-1}$ or $cm^2 \cdot s^{-1}$
E = activation energy, $kJ \cdot mol^{-1}$
k = reaction-rate constant
P = pressure, bar
S_f = sulfur content in feed, wt. %
S_p = sulfur content in product, wt. %
T = temperature, degrees Centigrade
V = catalyst bed volume, m^3 or L
ν = kinematic viscosity, $m^2 \cdot s^{-1}$
τ = tortuosity factor

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