Process Development and Scale Up:

III. Scale-up and scale-down of trickle bed processes

by

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Abstract

Trickle bed processes belong to the most widely used multiphase reactors and are applied on a large scale particularly for hydrotreatment of medium heavy and heavy oil fractions in the hydrocarbon processing industry. Laboratory scale reactors used in the development of new processes or in studies aimed at improving existing ones should therefore give accurate and meaningful test results which allow reliable upscaling. For reasons of efficiency in R&D, the size of the laboratory test units should be as small as possible without detracting from the meaningfulness of the data.

The present paper discusses scaling rules of laboratory trickle bed reactors and the influence of scale parameters on residence time distribution and catalyst contacting under conditions that are typical for hydrotreatment of oils. The main limiting factors for downsizing of laboratory trickle-bed reactors are the distortion of the packing in the vicinity

of the wall, axial dispersion and flow through the packing, and uneven catalyst irrigation. By dilution of a bed of catalyst particles with inert material of a much smaller particle size, it is possible to obtain kinetically representative data in very small laboratory reactors, viz., microflow reactors containing about 10 mL of catalyst.

Introduction

Among the various multiphase reactors, the trickle-bed reactor is probably the most widely used type of reactor. In this reactor, the catalyst is present as a fixed- or moving bed, while liquid "trickles" over the catalyst by gravity. The various possible configurations are shown in Figure 1.

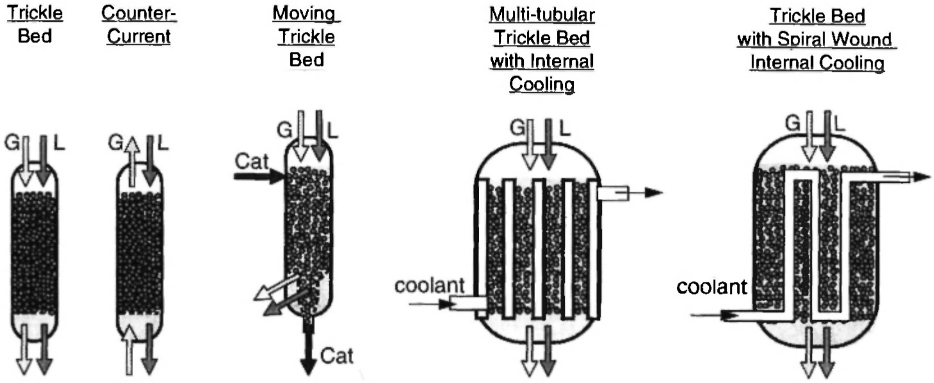


Figure 1. Three phase fixed/moving bed reactor configurations, with trickling liquid.

As can be seen, gas flows in a downward direction in most cases, i.e., in the same direction as the liquid. Upflow of gas whilst liquid trickles downward over the catalyst particles is in principle possible, but only at very low velocities or with very coarse packings. Therefore, nearly all commercial trickle-bed reactors operate with downward flow of liquid as well as gas, so that in practice trickle-flow is synonymous with cocurrent G/L downflow over a fixed or moving bed of catalyst. Trickle-bed reactors are used in many processes, in particular in the petroleum industry for hydroprocessing of medium heavy or heavy oil fractions. Table 1 lists some processes using trickle-bed reactors.

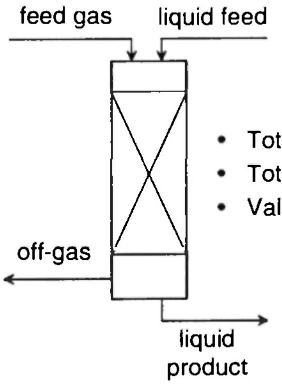
Application of trickle-flow is important as evidenced by not only the number and capacity of trickle-bed reactors installed but also the total investment and annual value of

Table 1. Examples of processes using trickle-bed reactors

- Hydrodesulfurization of gasoil, vacuum gasoil and residues
- Hydrodenitrogenation of gasoil and vacuum gasoil
- Hydrocracking of cat-cracked gasoil and vacuum gasoil
- FCC feed hydrotreating
- Hydrodemetallization of residual oil
- Hydrocracking of residual oil
- Hydrocracking/hydrofining of luboils
- Hydrogenation of aromatics in gasoil
- Catalytic dewaxing of gasoils and luboils
- Hydroprocessing of shale oils
- Paraffin synthesis by Fischer-Tropsch
- Oxidative treatment of waste water
- Synthesis of diols

products; see Figure 2.

In the present paper scale rules for trickle-bed reactors form the main subject of discussion. These scale rules are important in the scaling-up of a novel process investigated in the laboratory to a commercial process, and in the scaling-down of laboratory test equipment with the aim of increasing cost effectiveness of R & D as discussed in Sie and Krishna (1998a), whilst maintaining the meaningfulness of the data generated vis à vis commercial practice.



- Total installed capacity ≈ 10^9 t/y
- Total investment ≈ 2×10^{11} US $
- Value of products ≈ 3×10^{11} US $/y

Figure 2. Investment and financial outturn of trickle-flow processes.

Design of commercial trickle-bed reactors.

Hydrodynamics of trickle-flow.

The normal regime of trickle flow is mainly determined by the superficial velocities of liquid and gas. For cocurrent downward flow of liquid and gas through a bed of solid particles, the following regimes can be distinguished

- Trickle flow (gas continuous)
- Pulse flow (unstable regime with partly gas continuous and partly liquid continuous)
- Dispersed bubble flow (liquid continuous)
- Spray flow (gas continuous, highly dispersed liquid)

The boundaries between the different flow regimes are schematically shown in Figure 3.

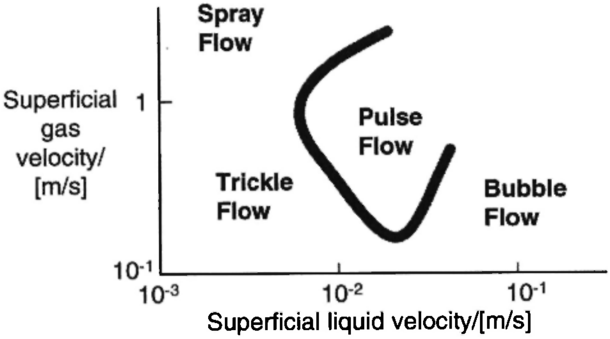


Figure 3. Co-current downflow regimes.

The precise location of the boundaries is dependent upon the properties of the fluids, which for a given set of gas and liquid depend on operating conditions. Figure 4 shows the shift in the boundary between the trickle-flow and pulse-flow regimes caused by increase of operating pressure, as determined in recent experiments (Wammes and Westerterp, 1990). It can be seen that the region of stable trickle-flow extends to higher velocities as the pressure (and thus the gas density) is increased.

Figure 5 presents a generalized diagram in which the transition between the different types of flow is shown for loadings of liquids and gases which differ from water and air, the

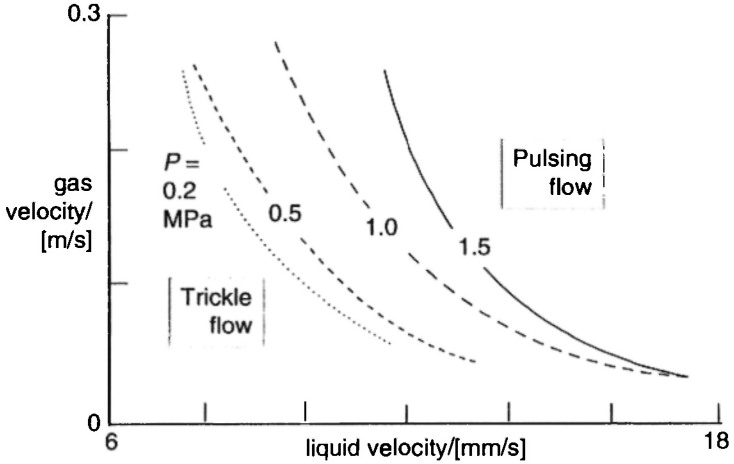


Figure 4. Effect of pressure on the transition between trickle flow and pulse flow. Adapted form Wammes (1990).

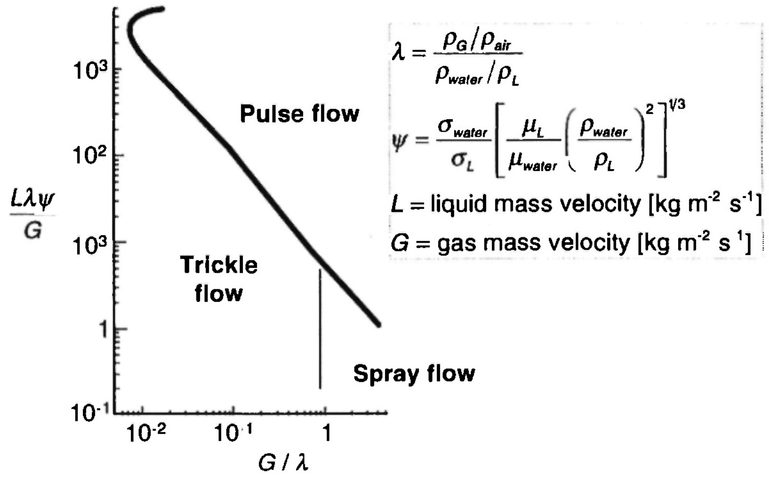


Figure 5. Generalized flow pattern diagram for non-foaming liquids. After Charpentier and Favier (1975).

fluids for which most experimental data are available. This diagram, which is valid for non-foaming liquids, shows that surface tension, viscosity and density are the important parameters for the liquid, and density for the gas.

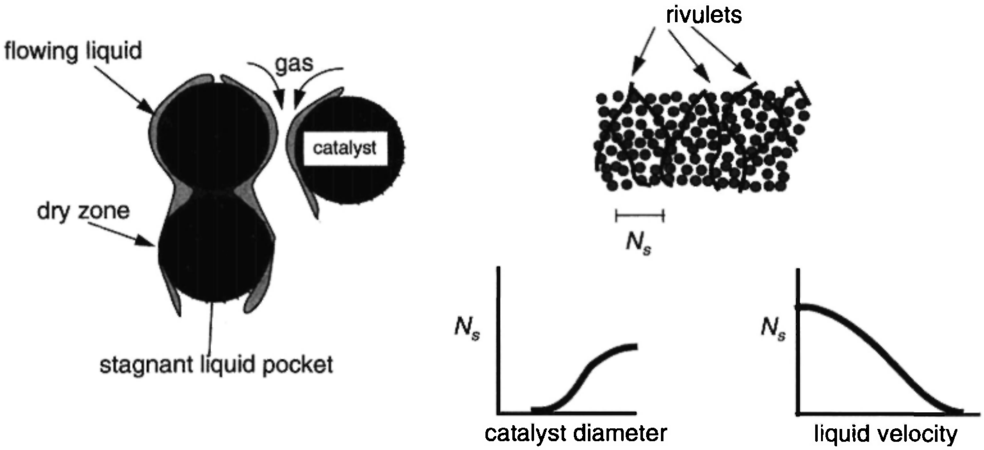


Figure. 6. Gas and liquid flow patterns at the scale of the catalyst and on the scale of the bed. Adapted from Koros (1976).

Figure 6 shows the gas and liquid flow pattern on the scale of a particle under typical trickle-flow conditions. The catalyst particle tends to be covered by a film of flowing liquid of variable thickness, while gas tends to flow through the interstitial space which is not occupied by liquid. The figure also shows that at the contact points between adjacent catalyst particles there are pockets of liquid which are stagnant. Mass transfer between these stagnant pockets and the flowing liquid has to occur by diffusion.

On a somewhat larger scale, inhomogeneities in liquid flow can be distinguished in that, particularly at low liquid velocities and with large catalyst particles, the liquid passes through the bed not as a flowing film around every particle, but as small streams which follow distinctive paths through the bed, so-called rivulets. The characteristic distance between adjacent rivulets is a function of catalyst particle diameter and liquid velocity as indicated in Figure 6. This tendency of the liquid to bypass parts of the bed and thus to exclude catalyst particles from direct contact with flowing liquid is detrimental to reactor performance, and this non-ideal situation is known as incomplete wetting of the catalyst.

Figure 7 shows a correlation between the wetting efficiency and the liquid load for typical liquids as used in practice and for catalysts of normal dimensions (1-5 mm diameter). It can be seen that at Reynolds numbers above 10, the wetting efficiency can be close to 1. This corresponds to the liquid velocities that are typically used in industrial rectors. The

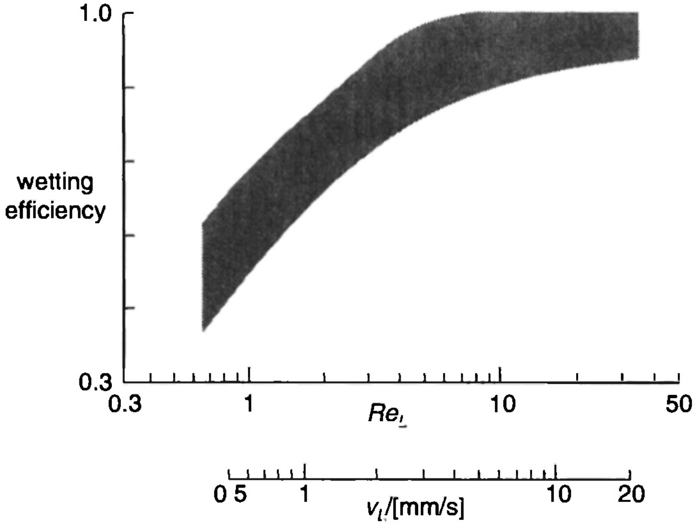


Figure 7. Wetting efficiency as a function of liquid load for catalyst particles of typical size. Adapted from Westerterp and Wammes (1992).

figure also shows that in the region of much lower Reynolds number the wetting efficiency decreases appreciably with decreasing Re. This incomplete wetting is a factor of particular importance for trickle-flow experiments on a small scale in the laboratory. It will be treated in more detail later when discussing the possibilities and limitations of downscaling of laboratory equipment.

Chemical engineering aspects of importance for design of commercial trickle-bed reactors.

Some important aspects for the design of trickle-bed reactors which have received much attention in chemical engineering investigations are listed in Table 2. These aspects are dealt with in reviews of trickle-bed reactors and in books on multiphase catalytic reactors, e.g., by Satterfield (1975), Shah (1979) , Ramachandran and Chaudhari (1983), Tarhan (1983), Gianetto and Specchia (1992) and Burghardt et al. (1995).

Table 2. Some important chemical engineering aspects for design of commercial trickle-bed reactors

- Pressure drop
- Liquid and gas hold-ups
- Catalyst contacting (wetting)
- Axial and radial dispersion
- Mass transfer
- Heat transfer
- Thermal stability

Advantages and disadvantages of trickle-bed reactors

The advantages and disadvantages of trickle-bed reactors, as generally experienced in practice and as rationalized by the above-mentioned chemical engineering studies are listed in Tables 3 and 4.

A relatively large minimum particle size, as dictated by pressure drop considerations, may not always be detrimental. As discussed in Sie and Krishna (1998b), intraparticle diffusion limitation may be turned to advantage to enhance selectivity or to improve catalyst tolerance for poisons by proper catalyst particle design.

Table 3. Main advantages of trickle bed reactors

- Close to plug flow of gas and liquid phases
- Small liquid phase hold-up compared to e.g., slurry or ebulliating-bed reactors; thus suitable for minimizing homogeneous liquid phase reactions
- Because of co-current flow of gas and liquid there is no problem of flooding as is possible in counter-current flow operation
- Generally simple construction and easy operation with fixed adiabatic beds; in case of exothermic reactions gas quenches and liquid and /or gas recycle limit temperature rises

Table 4. Main disadvantages of trickle-bed reactors.

- Radial dispersion of heat and mass is a problem with highly exothermic (or endothermic) reactions; less easy constructions as multi-tubular or internally cooled fixed beds necessary for (near) isothermal reactor operation
- At low liquid velocities maldistribution, channeling and incomplete catalyst wetting occurs
- Particle diameter cannot usually be smaller than 1 mm because of pressure drop considerations; intraparticle diffusion may be limiting activity and affect selectivity adversely
- Counter-current operation is usually the preferred mode for deep conversions, e.g., in equilibrium limited hydrogenations, but not possible at practical velocities of gas and liquid because of danger of flooding

Scale-up and design of industrial trickle-bed reactors.

In the case of a trickle-flow process with a fixed catalyst bed the scaling-up from a properly functioning laboratory size reactor to a full-scale industrial size reactor is generally not a difficult matter. With the available chemical engineering know-how embodied in correlations and models a large scale difference can generally be bridged: design of the industrial unit is often possible on the basis of data from process development units without the need for larger intermediate scale units such as demonstration units or semi-commercial plants. This is, of course, not always the case: when dealing with moving catalyst beds or with systems subject to fouling by mechanical deposition of solids within the bed such intermediate scale units may be necessary, unless the problem is a purely physical/mechanical one which may be adequately investigated in cold flow models of representative size (see Sie and Krishna (1998a)).

A large scaling-up factor is possible in the case of reactors for hydroprocessing of oil, which represent the largest application of trickle-bed reactors. This is to a large part due to the fact that flow-related mass-transfer limitations do not play a very important and certainly not an overriding role in this application. Moreover, flow-related dispersions do not play a great role either: in properly designed laboratory and industrial trickle-bed reactors gas and liquid flows are close to plug flow, as mentioned in Table 3.

The mass transfer resistances involved in the transport of molecules from the gas phase to the active surface of the catalyst are shown in Figure 8. Estimates of the relative magnitude of the mass transfer resistances can be made by calculations basis available chemical engineering correlations. The relative importance of the various mass transfer resistances thus estimated for a typical case of hydrotreating is shown by the figures listed in Table 5; these figures illustrate the predominance of intraparticle diffusion.

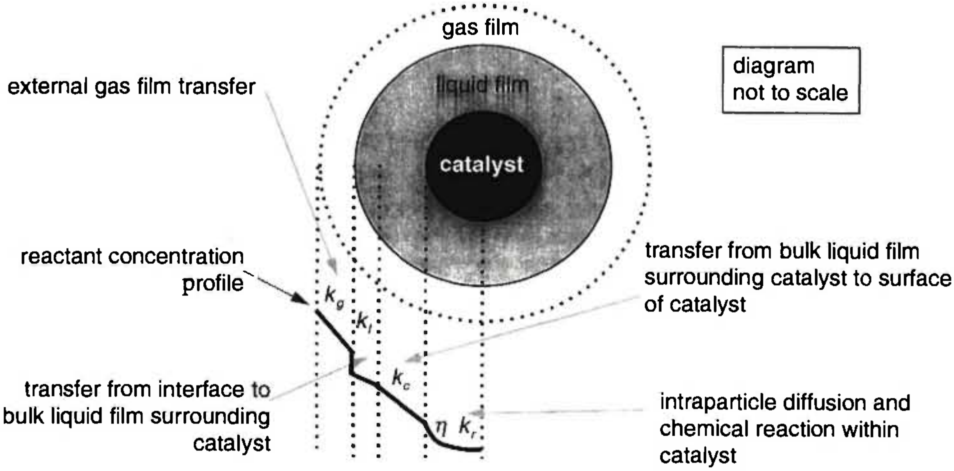


Figure 8. Mass transfer resistances in a trickle-bed.

Table 5. Relative magnitude of mass transfer resistances in a typical case of hydroprocessing

Resistance	% of total
From bulk gas to G/L interface	negligible
From G/L interface to bulk liquid	2
From bulk liquid to external catalyst surface	21
Intraparticle diffusion and reaction	77

On the basis of reliable data obtained with actual feeds and catalysts in properly dimensioned laboratory process development units, design of the industrial trickle-bed process is relatively straightforward. The desired capacity and conversion required determines total catalyst volume. Taking into account the total amount of heat generated and the specific heats of the process streams as well as the maximum allowed temperature rise per bed, the number of beds, the distribution of catalyst over the beds and the quench gas flows are determined. Given the total reactor volume the total bed height and reactor diameter can be chosen. The linear flow rates are established and pressure drops can be calculated according to available correlations for the catalyst of the size and shape considered.

In the design of industrial reactors for processes operating under elevated pressure, such as hydroprocessing of oil, relatively high reactors are generally preferred over short ones of larger diameter within the constraint set by permissible pressure drop. Taller and narrower reactors are generally cheaper to fabricate and also require less area to install. The tall reactors give rise to high fluid velocities which may be close to the limits set by the transition to pulse flow and consequently ensure good wetting of the catalyst is obtained (cf. Figure 7). The typical liquid and gas loads of commercial trickle-bed reactors in hydroprocessing of oils are shown in Figure 9, which also shows the loads in typical process development units. The

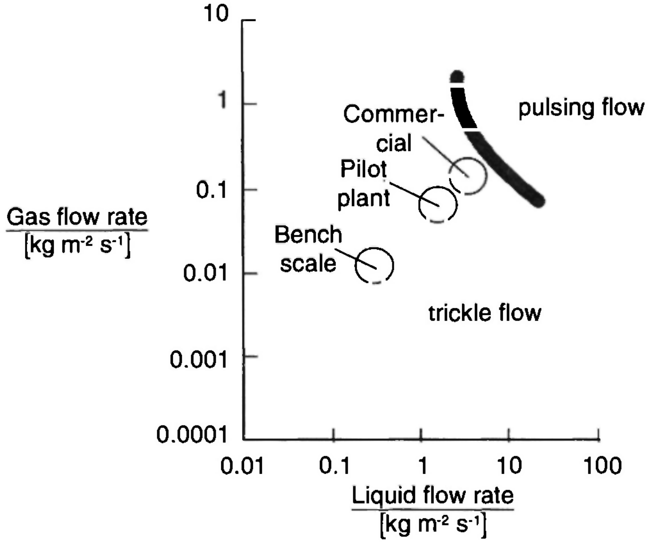


Figure 9. Liquid and gas loads in typical trickle-bed reactors for hydroprocessing of oils.

main characteristics of commercial trickle-bed reactors for hydroprocessing are summarized in Figure 10.

- Gas and liquid velocities are high
- wetting is good
- k_Ga, k_La and k_ca_p are usually high and not limiting
- Hydrogen is usually present in excess and its concentration is virtually unchanged
- The reaction rate of the liquid phase reactant B is therefore

$$R_B = \eta k_r C_B$$

where k_r is the reaction rate constant, m³/(kg cat)/s. The conversion χ is

$$\ln\left(\frac{1}{1-\chi}\right) = \frac{\eta k_r}{WHSV}$$

Figure 10. Characteristics of commercial trickle-bed reactors for hydroprocessing.

The mechanical engineering design of trickle bed reactors involves choice of material, determination of wall thickness, location and size of pipe connections and manholes and details of internals such as distributor trays, catalyst support grids, bed supporting beams, etc.

Distributor trays are particularly important for good performance of the reactor, since the limited rate of lateral mixing does not easily correct initial maldistribution of liquid flow. In particular with large diameter reactors, design and construction of distributor trays require attention, e.g., when the local flow of liquid is determined by the liquid height above the tray, accurate horizontal positioning is needed for large diameter trays.

The effect of improper liquid distribution on the performance of commercial hydrotreaters is shown in Figure 11. It can be seen that the degree of hydrodesulfurization obtained in two commercial reactors is less than that obtained in a large pilot plant, even at the higher liquid velocities in the commercial reactors. However, when a correction is made for the degree of utilization of the catalyst bed (determined from liquid hold-ups), a closer correspondence is obtained between the results obtained in the different reactors, as shown in Figure 12.

A simplified drawing of an industrial trickle-bed reactor as used for hydroprocessing of an oil feed is shown in Figure 13. Figure 14 shows a picture of the reactor section of a

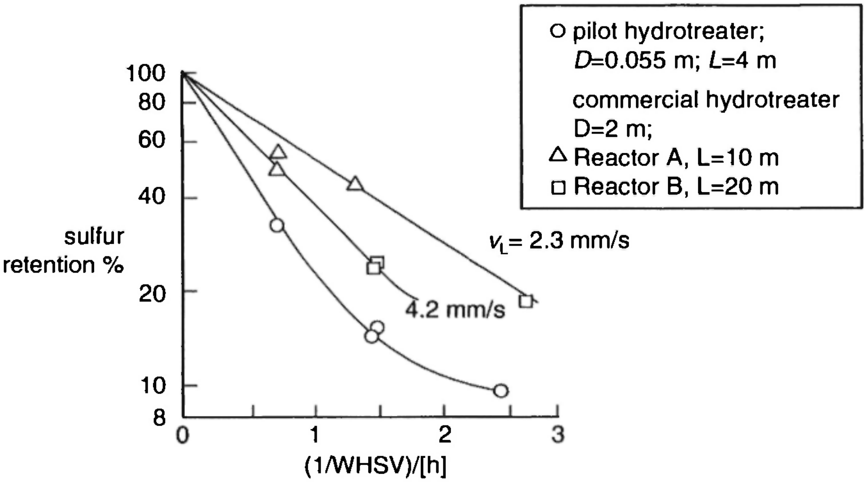


Figure 11. Sulphur removal in commercial and pilot hydrotreaters (Ross, 1965).

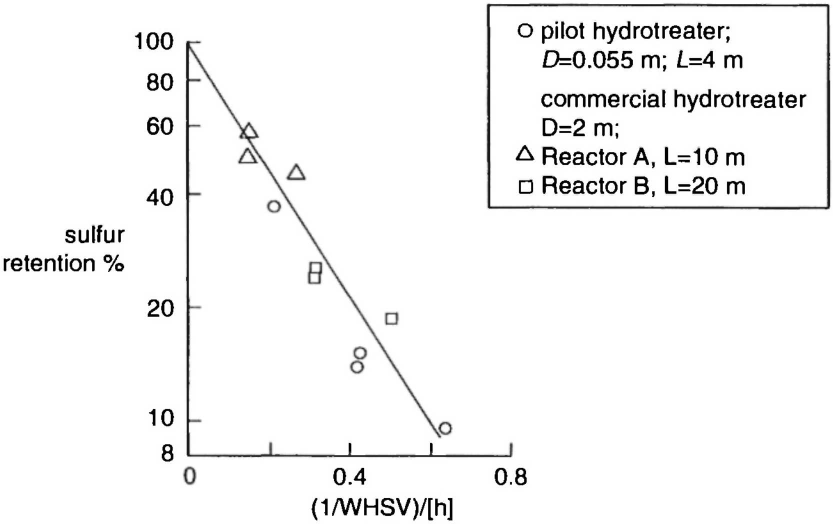


Figure 12. Sulfur removal in commercial and pilot hydrotreaters corrected for degree of catalyst bed utilization (Ross, 1965).

commercial fixed-bed trickle-flow hydrodesulfurizer for a residual oil, as designed by Shell and installed at a refinery in Japan.

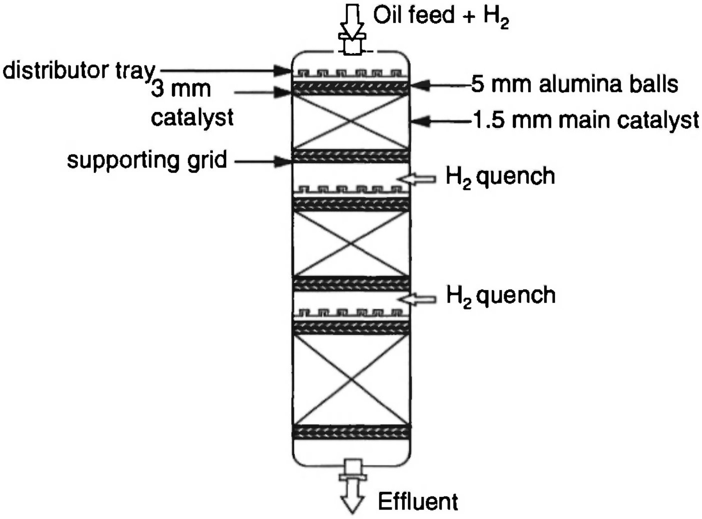


Figure 13. Simplified drawing of an industrial trickle-bed reactor for hydroprocessing of oil.

Figure 14. Photograph of the reactor section of a trickle-flow residue hydrodesulfurizer of 7000 t/day design capacity.

Process development units for study of trickle-flow processes: possibilities and limitations in downscaling

Fixed-bed trickle-flow processes belong to the category of processes where the mechanical and physical engineering aspects of industrial-scale reactors are reasonably well established so that the development of a new process based on the application of a novel catalyst, a new feedstock, or a different process line-up can be largely focused on the more chemical aspects of the process. As stated above, reliable information on process performance and optimal process conditions obtained in laboratory process development units can in many cases be a sufficient basis for scaling-up the process to commercial scale. Hence, in the case of a fixed-bed trickle-flow process such as applied in hydrotreating, the problem is in fact to provide information on the effects of new catalysts, alternative feedstocks, operating conditions on product yields and properties that are valid for the commercial plant to be built or for an existing commercial unit in which the new or adapted process is to be carried out.

In the latter light, process development can not only be seen as a scaling-up activity, but also as a scaling-down exercise, i.e., the scaling-down of an industrial reactor to a laboratory process development unit that is equivalent as far as the above-mentioned chemical kinetic aspects are concerned. This is in line with the cyclic character of process development as discussed in Sie and Krishna (1998a)

Scaling-down is also important with respect of reducing the scale of the process development units themselves so as to enhance the cost effectiveness of R & D, as discussed in Sie and Krishna(1998a). In this scaling-down, the problem is how to reduce the size of the process development units without detracting from the accuracy and the meaningfulness of the process data which can be obtained from these units.

Alternative ways of downscaling of a commercial reactor.

In principle there are a number of alternative ways to scale down an industrial trickle-bed reactor as shown in Figure 15. These ways are further discussed below.

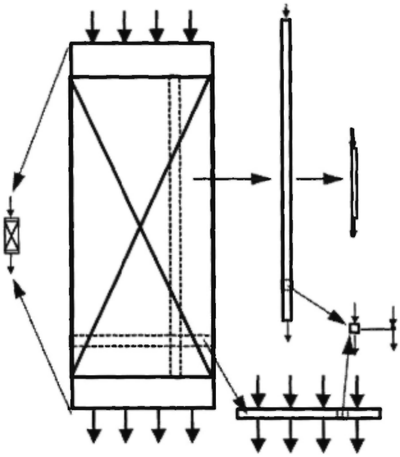


Figure 15. Downscaling of a fixed trickle bed: alternative ways of size reduction.

Downscaling according to geometric similarity

This approach, in which the main dimensions of the bed, viz., bed height and bed diameter are reduced by the same factor, leads to relatively short and relatively wide laboratory reactors, as can be seen from the data in Table 6.

The short length of the laboratory reactors leads to much lower liquid velocities than in the industrial reactor when operating at the same liquid hourly space velocity (at equal LHSV the superficial linear velocity of the liquid is directly proportional to bed height). These differences in velocities and particle Reynolds numbers (i.e., Reynolds numbers with particle diameter as characteristic dimension) lead to differences in hydrodynamics which have an effect on the results. E.g., at the low Reynolds number, catalyst wetting is likely to be incomplete, see Figure 7. The relatively large diameters of the pilot plant and bench-scale reactors may give rise to undesired radial temperature profiles if the reactor is not operated as a true adiabatic one. Apart from the visual alikeness, there is no merit in scaling-down according to the principle of geometric similarity, and this approach is therefore not advisable.

Table 6. Scaling down according to geometric similarity

	Commercial	Pilot Plant	Bench Scale	Micro-flow
Volume/ [m^3]	100	0.010	0.00015	0.000008
Reduction factor	1	1×10^4	7×10^5	1.3×10^7
Diameter/ [mm]	2500	120	30	10
Length/ [mm]	20000	900	200	90
Liquid velocity/ [mm/s]	11	0.5	0.1	0.05
Particle Reynolds Number	55	2.5	0.55	0.25

LHSV=2 m^3/ m^3/h; $\nu = 3 \times 10^{7}$ m^2/s; d_p = 1.5 mm

Commercial reactor represented by differential reactors

If bed height and bed diameter are not reduced by the same factor but changed independently, one may choose between two basic possibilities. Taking a commercial-size reactor as starting point, one may arrive at a small laboratory reactor in two different ways, viz.

(a) keeping the fluid velocities the same but accepting a reduction in average residence time of the reactant by increasing the space velocity with decreasing bed height, and

(b) keeping the average residence time of the reactants the same (i.e., identical space velocity) without necessarily keeping the fluid velocities identical.

The first option has the advantage that the hydrodynamics in the laboratory reactor are the same as in the commercial one, but conversions will be lower. In the extreme case of a very short reactor this implies that one is working with a differential reactor rather than an integral one. If the reactor is fed with the same feed as the commercial one, the conversion in the very short laboratory reactor represents that obtained in a topmost layer of the industrial catalyst bed.

This approach implies that one studies the behaviour of a horizontal shallow layer of the vertical catalyst bed, as indicated by the horizontal slice in Figure 15. Recognizing the fact that different volume elements of the bed should be identical in lateral direction, it will be clear that it is not necessary to study the whole cross section of the commercial reactor, but that one may look at only a small part of it, i.e., one may reduce the diameter considerably.

For such a differential-type reactor there are hardly any demands from the point of view of axial dispersion of the fluid, and therefore such a reactor can very easily be further reduced in size. In the end, one may arrive at a single-pellet reactor as a representative differential reactor.

A draw-back of this approach is that it will be necessary to study partial conversions at different conversion levels. To predict the integral conversion in a commercial reactor from a series of differential conversion experiments with feedstocks representing various degrees of conversion of the primary feed, a substantial experimental effort and a kinetic process model is needed. The parameters to be used in this model are in principle dependent upon both feedstock and catalyst and have therefore to be determined for each individual case. Particularly when studying conversions of the relatively heavy oil feeds of trickle-flow processes of the oil industry, the molecular compositions of feeds and products and the reaction networks are usually very complex so that the demands on analytical and computational power may be very high. Therefore, although this approach is basically sound it may not be practical in most cases.

Commercial reactor represented by an integral laboratory reactor

The other possibility for downscaling mentioned above is to keep the space velocity in a laboratory reactor the same as in the industrial one, i.e., the laboratory reactor should simulate the industrial integral reactor with respect to conversions and selectivities.

If fluid dynamics and reaction kinetics are so closely interlinked that their effects on the chemical reactions are inseparable, the only way to scale down a commercial reactor to a representative integral laboratory reactor is to reduce diameter while keeping length the same. As long as the diameter is not reduced beyond the limit set by wall effects (to be discussed later) the particle Reynolds number and fluid dynamics are identical with those in the reactor of commercial size.

This approach is in principle based on the notion that in a well-designed commercial reactor the situation in a horizontal plane within the bed is the same everywhere. Thus, the pilot plant reactor is a hypothetical narrow vertical column cut out of the industrial catalyst bed, as indicated in Figure 15. The minimum size of a truly representative pilot plant reactor is therefore determined by a diameter which is determined by the catalyst particle diameter, as will be discussed below, and a length which should be the same or not much smaller than that of the industrial reactor.

A comparison of results obtained in a pilot plant of this category and a commercial unit for hydrotreating heavy gasoil is presented in Table 7. It can be seen that the results of the pilot plant reactor corresponds well with those obtained in commercial practice. Evidently, the pilot plant reactor is sufficiently long, although its length (3.9 m) is smaller than that of the commercial reactor (12.2 m).

Table 7. Comparison of pilot plant and commercial unit for hydrodesulfurization of heavy gasoil over 5 mm Co/Mo/Alumina pellets (Le Nobel and Choufour, 1959).

	Pilot Plant	Commercial Unit
Height/[m]	3.9	12.2
Diameter/[mm]	80	1700
Volume/[m^3]	0.020	26.1
WHSV/[kg/m^3/h]	2300	2350
T_{inlet}-T_{outlet}/ [°C]	360-375	363-379
Pressure/[bar]	57	57
Gas rate/[m^3/kg]	0.120	0.121
H_2 concentration/ %v	> 99	97.0
Density/[°API]	35.5	35.3
S in product, %w	0.37	0.39
2nd order k for HDS	4.80	4.35
ASTM dist/[°C]		
5 %v	263	261
10 %v	263	261
50 %v	319	318
90 %v	368	369

Downscaling of laboratory trickle-bed reactors: basic requirements for an ideal integral fixed-bed reactor

The pilot plant reactor as described above can be considered to be a good small-scale replica of the commercial reactor and should yield meaningful data on integral conversions, selectivities, catalyst stability, and so on. It is still a large pilot plant, however, according to laboratory standards and will be expensive to construct and operate.

Further reduction of such a pilot plant reactor is possible if the effects of fluid dynamics can be decoupled from reaction kinetics proper. Fortunately, this separation is permissible in most cases of trickle-flow hydroprocessing of oils. This is because fluid-flow dependent factors such as gas/liquid mass transfer and liquid hold-up (important for homogeneous non-catalytic reactions) generally play a minor role only (cf. Table 5). In this case, further downscaling of laboratory reactors for the study of trickle-flow processes is possible provided the laboratory reactor has to be representative in a reaction kinetic sense only. Study of flow-related phenomena such as pressure drop, liquid hold-up, mass and heat transfer, etc., may be carried out separately in cold-flow models of representative size, as discussed in Sie and Krishna(1998a).

A starting point for the downscaling of laboratory pilot plant reactor is the assumption that an industrial trickle-bed reactor of good design is, or at least should be, close to an ideal integral reactor as will be defined below. There is little point in trying to simulate the imperfectness of a poorly performing commercial reactor which suffers from a faulty design (cf. Figure 11). Hence, a representative laboratory reactor should be sufficiently close to an ideal reactor, too, even if the hydrodynamic situation differs from that in the commercial reactor. Hydrodynamics in the laboratory reactor are only important inasmuch as they affect compliance with the following requirements of an ideal integral reactor:

(1) All volume elements of the feed must spend the same time in the bed. In other words, the reactant must pass through the bed in plug flow, which implies that its residence time distribution must be the same as that in a large number of mixers in series

(2) All parts of the bed must maximally take part in the overall conversion, which implies that

all catalyst particles must be adequately contacted with the reactant.

In the following part it will be discussed how the reactor dimensions can be reduced without violating the above conditions for an ideal integral reactor. The main dimensions that have to be considered in the downscaling of trickle-bed reactors are the bed length, the bed diameter, and the particle diameter, as shown in Figure 16. The role of these dimensions in downscaling of laboratory trickle-bed reactors will be discussed below.

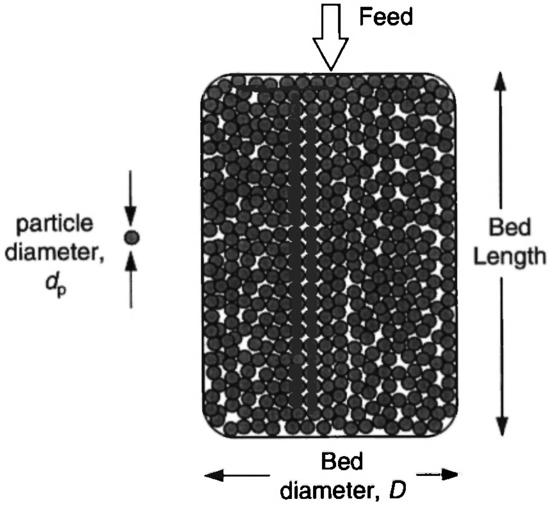


Figure 16. Important dimensions in a trickle-bed reactor.

Effect of reactor dimensions on residence time distribution of reactants

In most hydroprocesses hydrogen gas is fed to the reactor well in excess over the amount consumed in the reaction, to maintain hydrogen partial pressure and to cope with the exothermic heat of the reaction. The degree of conversion of hydrogen is therefore relatively low and the residence time distribution of the gas is relatively unimportant. Hence, only the residence time distribution of the oil has to be considered.

Effect of reactor diameter; influence of the wall

Very close to the wall the packing of particles is different from that in the interior. As the reactor diameter is reduced, this wall effect gains importance so that the overall characteristics of the packing can no longer be considered to be the same as those of the unperturbed packing.

The change in voidage near the wall has been the subject of many experimental and theoretical investigations. Experimental techniques for studying radial voidage variations include those in which particles are embedded in solidifying wax or resin followed by examination of individual cuts, and experiments in which levels of dosed volumes of liquid are determined while spinning the packing in a centrifuge. As an example, Figure 17 shows some experimental results compared with a mathematical description of these voidage variations.

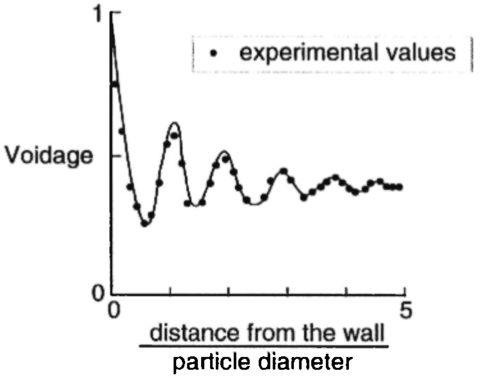


Figure 17. Voidage variations in radial direction (Govindarao and Froment, 1986; Benati and Brosilow, 1962).

With the advent of computers of increased computing power, the effect of the wall can be studied for hypothetical, "computer generated" packings. These packings are generated by allowing particles to drop randomly in a bin of specified dimensions and to seek stable positions, see Figure 18. For such computer-generated packings, it is easy to calculate the local bed porosities and specific areas, i.e., the outer surface area of the particles per unit volume of bed. Figure 19 shows a thus calculated bed porosity profile across the diameter of

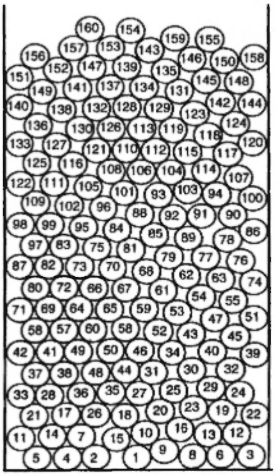


Figure 18 . Computer generated packing (Zimmermann and Ng, 1986). Numbers indicate the order by which they were dropped into the bin.

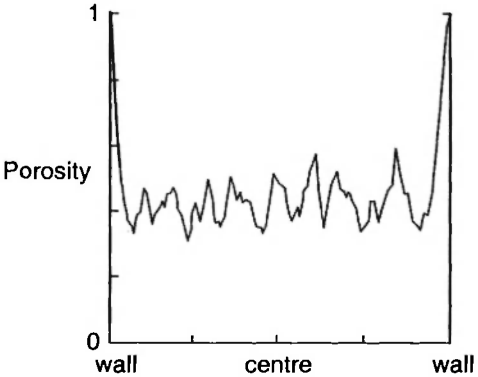


Figure 19. Porosity profile for a computer generated three dimensional column packed with uniform spheres (Zimmermann and Ng, 1986).

a computer generated packing of uniform spheres. It can be seen that there is an extraordinarily high voidage near the wall whereas further away from the wall the porosity fluctuates around a constant average value.

The variation in radial direction of the specific area is shown in the left part of Figure 20. As a consequence of the increased voidage near the wall, the specific area attributable to the outer surface area of the particles is also below average in the region close to the wall.

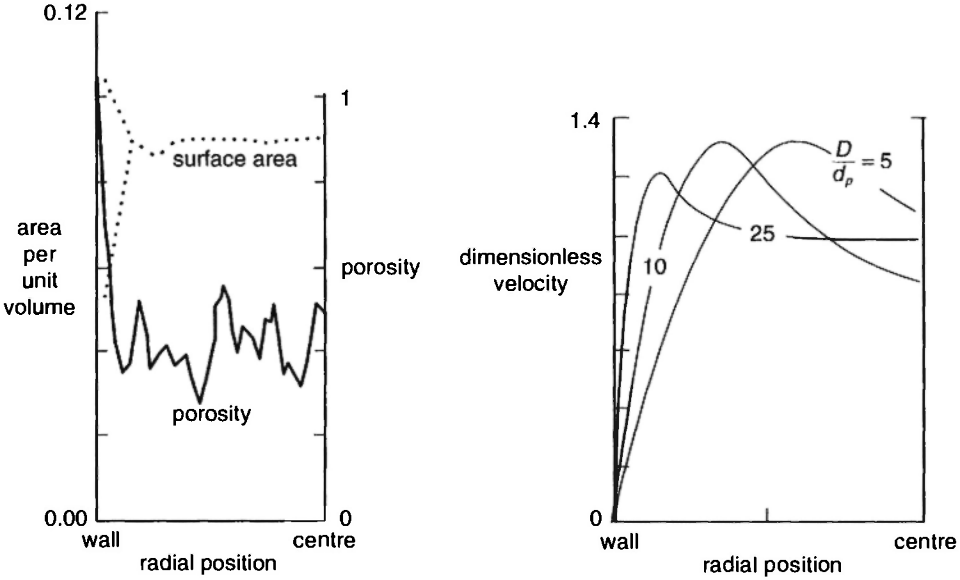


Figure 20. Porosity, surface area and velocity as a function of radial direction. Left: porosity and specific area (Chu and Ng, 1989). The upper broken line is the specific area including the wall. (b) Velocity (Fahien and Stankovic, 1979).

However, when one includes the wall surface, the specific area is higher than average close to the wall.

Both bed voidage and specific area influence local fluid velocity and thereby contribute to deviations from ideal plug flow. In the region very close to the wall, the higher voidage tend to give rise to a higher velocity, whereas the higher specific area (including the wall surface) tends to retard the flow. As a consequence of these effects, the local velocity passes through a maximum a few particle diameters away from the reactor wall, as is demonstrated by the velocity profiles measured by Fahien and Stankovic (1979) shown in the right hand part of Figure 20. Similar profiles have been found earlier by Morales et al. (1951) and by Schwartz and Schmitz (1953) as well as in more recent studies by Vortmeyer and Schuster (1983).

From the radial flow profiles shown in Figure 20 it can be inferred that flow is very uneven at a low value of the ratio between reactor diameter D and particle diameter d_p, e.g., $D/d_p = 5$. At a larger ratio, e.g., 25 there is a reasonably large inner part of the bed where flow is even. To avoid a significant contribution of flow in the wall region to the overall flow, the D/d_p ratio should therefore not be below this value. This can also be seen from Figure 21,

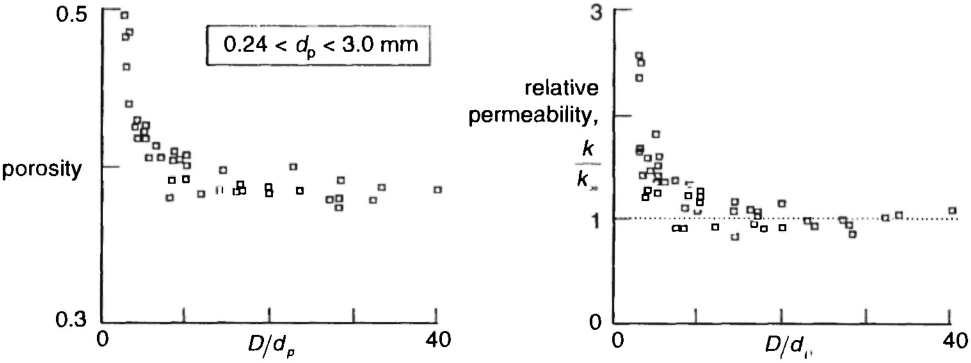


Figure 21. Dependence of overall bed porosity and permeability on the ratio between bed and particle diameters. (Chu and Ng, 1989).

which show the average porosity and permeability of packed beds as a function of the ratio between bed and particle diameters. At a D/d_p value above about 20, the wall effect ceases to be important. It is of interest to note that experimental results obtained with particles of widely differing size can be correlated on the basis of the dimensionless parameter D/d_p.

The pronounced velocity profiles which are present in beds of low D/d_p ratio lead to a spread in residence time of the reactant. The effect of a velocity profile might be diminished if diffusion in a lateral direction would be sufficiently fast. Whilst this generally the case with gases flowing at the usual rates through packed beds of up to a few centimeters diameter, diffusivities of liquids are too low for wiping out the effect of radial flow profiles. Since in the case of trickle-bed reactors for hydrotreating the flow profiles and residence time distributions of the liquid phase rather than the gas phase are decisive for reactor performance, one cannot count on a beneficial effect of radial diffusion.

To keep the role of the wall effect below an acceptable minimum in fixed beds operated with liquid or with liquid and gas in trickle flow, it is therefore advisable to use as criterion a D/d_p ratio larger than 20.

Effect of bed length

Reduction of bed length is likely to cause a greater deviation from plug flow than a reduction in bed diameter. If the height equivalent to mixing stage in the bed would remain the same, a decrease in bed length would mean a lower number of mixers in series, and hence a wider residence time distribution. However, at constant liquid velocity a shorter bed implies a lower fluid velocity which may also be a factor for a greater deviation from plug flow.

The limitation on shortening of the bed is clearly demonstrated by Figure 22. It can be seen that results obtained on hydrodesulfurization of a gasoil in a pilot plant reactor of 4.8 m length are in satisfactory agreement with those obtained in a commercial reactor (less than 10% difference in reaction rate constant). This is in line with the previously discussed comparison between a pilot plant reactor of similar size and another commercial unit (See Table 7). Figure 22 also shows that further reduction of the bed length to 1.6 m leads to significantly deviating results: the rate constant found with this shorter pilot plant is some 25% lower than the rate constants found with either the commercial reactor or the 4.6 m pilot plant reactor. Such a deviation is considered unacceptable.

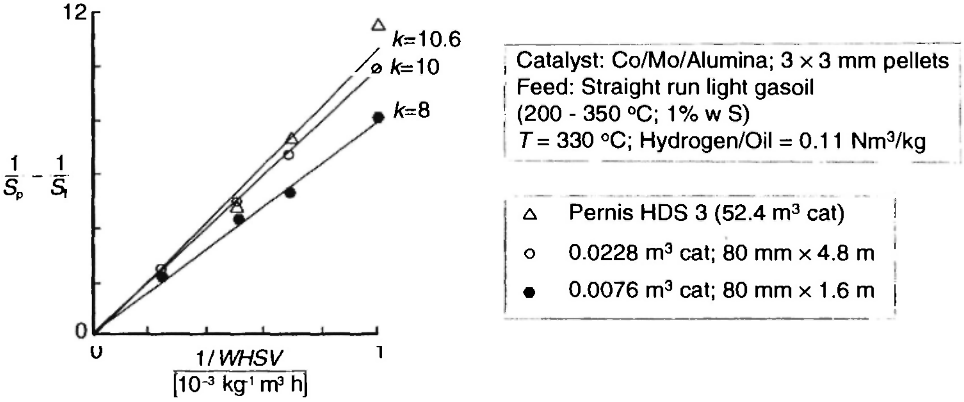


Figure 22. Comparison of pilot plant and commercial reactors for hydrodesulphurization of gasoil. Effect of pilot plant reactor length.

It is of interest to note that the diameter of these pilot plant reactors ($D = 80$ mm) is sufficiently large to meet the previously discussed criterion for the wall effect with the catalyst particles used ($d_p = 3$ mm; $D/d_p = 27$). The deviating results obtained with the shorter pilot plant reactor have to be, at least partly, ascribed to axial dispersion in the main part of the packed bed.

The axial dispersion of the reactant in a fixed bed can be described by the equivalent number of mixers in series (N) or the dimensionless Péclet number (Pe) with the bed length L as characteristic dimension. To describe the axial dispersion as a characteristic of the packing the particle diameter rather than bed length may be used as characteristic dimension, yielding the dimensionless Bodenstein number (Bo).

For a sufficiently close approach to an ideal plug flow reactor, N or Pe should exceed a minimum value which depends on the degree of conversion (χ) and the reaction order (n):

$$2N = Pe = \frac{L}{d_p} Bo > f(n,\chi) \tag{1}$$

in which

$$Pe = \frac{L v_L}{D_{ax}} \tag{2}$$

and

$$Bo = \frac{d_p v_L}{D_{ax}} \tag{3}$$

D_{ax} being the axial diffusivity and v_L the superficial velocity of the reactant, i.c. the liquid.

A criterion for adequate performance of fixed-bed reactors has been proposed by Mears (1971, 1974) on the basis of the assumption that the actual reactor should not contain more than 5% extra catalyst to achieve the same conversion as an ideal reactor. This criterion can be written as

$$Pe > 20n \ln\left(\frac{1}{1-\chi}\right) \tag{4}$$

A somewhat more relaxed criterion has been proposed by Gierman (1988) based on the argument that the accuracy of temperature definition in a practical case is not better than 1 °C. For reactions having activation energies of the usual magnitude, the following criterion is proposed

$$Pe > 8n \ln\left(\frac{1}{1-\chi}\right) \tag{5}$$

Combination of equations (5) and (3) gives the minimum length for a good reactor:

$$L > 8\frac{d_p}{Bo} n \ln(\frac{1}{1-\chi}) \tag{6}$$

A correlation between Bodenstein number and Reynolds number for single-phase flow and trickle flow is shown in Figure 23. This correlation proposed by Gierman (1988) is based on a variety of published data on axial dispersion in fixed beds. It shows that the Bodenstein number decreases as the Reynolds number increases, until it reaches a more or less constant values in the range of interest for small laboratory reactors. This is true for single-phase flow as well as for trickle flow. The constant level of Bo for trickle flow is about one order of magnitude lower than for single-phase flow, which means that axial dispersion in trickle flow is greater at comparable velocity and particle size.

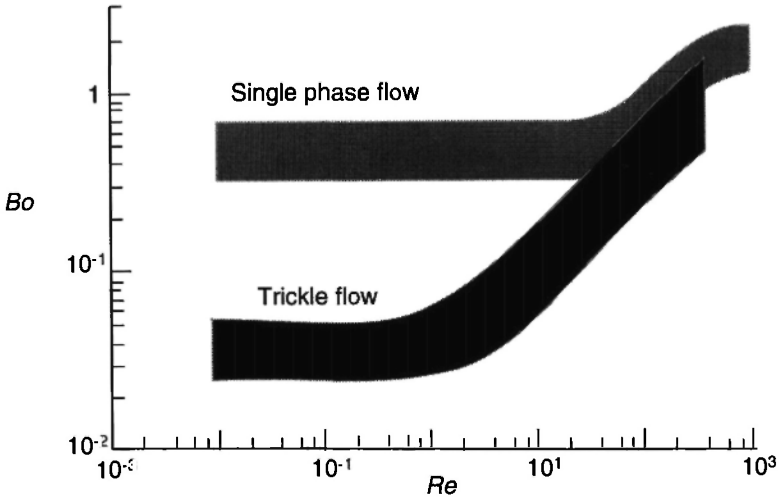


Figure 23. Correlation between Bodenstein and Reynolds numbers for single-phase flow and trickle flow (Gierman, 1988).

If Bo is set at 0.04 for the low Reynolds numbers of interest for laboratory trickle-bed reactors the minimum bed length is obtained by substituting this value in eq. (6), yielding the following simple formula:

$$L > 200\, d_p\, n \ln\left(\frac{1}{1-\chi}\right) \tag{7}$$

It can be seen from eq. (7) that the minimum reactor length is directly proportional to particle diameter and that it must be greater according as conversion is deeper and reaction order is higher.

For the previously considered pilot plant experiments with a catalyst of 3 mm diameter (Figure 22) the minimum bed length according to eq. (7) is 2.8 m (for second-order kinetics and 90% conversion). This is in line with the experimental finding that a 4.8 m long pilot plant reactor properly simulated the commercial reactor while the 1.6 m long one did not.

Maximum allowable catalyst particle diameter in reactors of different size

Equation (7) can be rewritten to determine the maximum size of catalyst particles that may be tested in reactors of different length:

$$d_p < 0.005 \frac{L}{n \ln\left(\frac{1}{1-\chi}\right)} \tag{8}$$

Figure 24 shows the maximum allowable particle diameter as a function of the

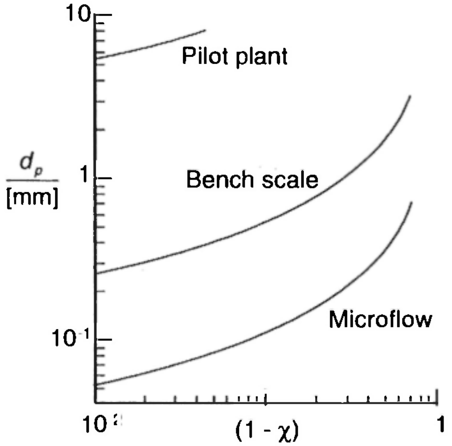


Figure 24. Maximum particle size in different laboratory reactors as function of conversion, with axial dispersion as determining factor (2nd order reaction).

conversion for laboratory reactors of different sizes and for a second-order reaction. The dimensions of these laboratory reactors are given in Table 8.

Table 8. Some typical data for laboratory trickle flow reactors of varying size.

	Pilot Plant	Bench Scale	Micro-flow
Catalyst Volume/ [m^3]	0.010	0.00015	0.000008
Diameter/ [mm]	40	20	10
Length/ [mm]	8000	500	100
Liquid velocity/ [mm/s]	4.5	0.3	0.06
Particle Reynolds Number	22	1.4	0.3

LHSV=2 m^3/ m^3/h; $\nu = 3 \times 10^{-7}$m^2/s; $d_p = 1.5$ mm

From Figure 24 one may deduce that quite large catalyst particles, i.e., having a diameter of up to 5 mm, may be tested in the pilot plant, as far as axial dispersion is concerned. This limit is on the conservative side since it is based on a Bodenstein number of 0.04, whereas at the prevailing Reynolds number a somewhat higher Bodenstein number may be expected (cf. Figure 23 and Table 8). Catalyst particles such as those typically used in hydrotreating, i.e. extrudates of 1.5 mm diameter, can therefore be tested without difficulty in this pilot-plant reactor. However, this is not true for the bench-scale and microflow reactors. At conversions above 80% only particles having a diameter substantially smaller than 1 mm can be tested as such in these reactors.

Effect of reactor dimensions on catalyst contacting by liquid

As stated before, the second condition for an ideal reactor is that all catalyst particles contribute to the overall conversion. In a trickle-bed, each catalyst particle should therefore be surrounded by a flowing film of liquid while gas passes through the remaining void space. The flux of liquid as well as that of gas should be the same in any part of a cross section of the bed. However, particularly at low velocities liquid may flow preferentially through a certain part of the bed, while gas flows predominantly through another part. This problem is aggravated by a poor initial distribution of liquid in a commercial reactor (as discussed before) but can also develop at low velocities even if initial distribution is correct, as is illustrated in Figure 25.

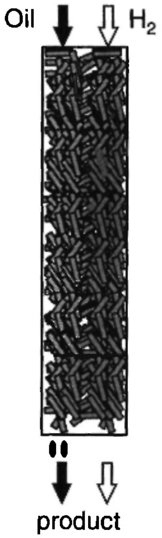


Figure 25. Schematic of a non-ideal trickle flow reactor suffering from liquid maldistribution.

The occurrence of liquid maldistribution can be visually observed in experiments with coloured liquid, but may also be studied by computer simulations. For example Funk et al. (1990) have investigated liquid flow patterns and non-uniform coverage of particles by liquid in computer-generated model packings. These simulations show, in accordance with experimental observations, that non-uniform coverage of particles by liquid occurs particularly when liquid loads are low.

This liquid maldistribution, which leads to incomplete utilization of the bed, is generally referred to as incomplete wetting. Whereas this term may be appropriate in a case such as depicted in Figure 25, where catalyst particles in parts of the bed indeed remain dry, the term uneven irrigation is preferred over incomplete wetting. This is because the notion of wetting is usually to be associated with interfacial tensions and contact angles and thus refers to a static phenomenon. But the problem discussed here is a dynamic one related to fluid flow. Interfacial forces, even in a favourable case where the catalyst surface tends to be "wetted" by the liquid, are not likely to rectify a macroscopic maldistribution as depicted in Figure 25 at a time scale of interest.

With normal catalyst particles and oily liquids incomplete wetting in the sense of interfacial tensions is rather unlikely on the scale of a particle because the oil generally tends to spread easily over the surface of the porous catalyst particle (the situation will be different, of course, when hydrophobic particles and water are used in model studies). But even such a case of complete "wetting" which may be further ensured by "prewetting" of a catalyst bed (i.e., temporarily filling the interstitial space with liquid prior to performing a catalytic test) is no guarantee for optimal utilization of the catalyst particle or bed. If part of the liquid film surrounding the catalyst particle is not refreshed at a sufficiently high rate, catalyst utilization may still not be optimal, as is illustrated by Figure 26 for a pore diffusion-limited reaction.

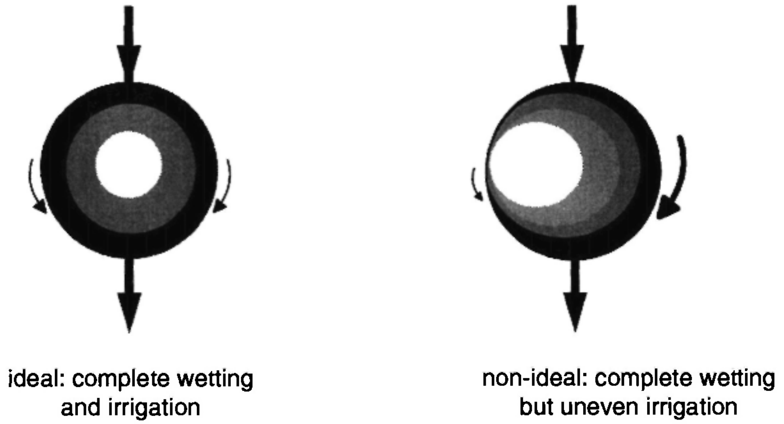


Figure 26. Effect of non-even irrigation on catalyst utilization in the case of a pore-diffusion limited reaction.

Hence, "complete wetting" is a necessary but insufficient condition for an ideal reactor, whereas "even irrigation" appears to be a more stringent and more appropriate requirement, which correctly associates the phenomenon of liquid maldistribution with dynamic (flow-related) forces, rather than a static force balance (interfacial tensions).

In the occurrence of liquid maldistribution the force of gravity plays an important role. A situation of maldistribution can be sustained if the flow of liquid is largely dictated by gravity and hardly influenced by frictional forces. If the latter forces become predominant, the liquid will tend to spread over every available channel and thus distributes itself over the entire bed cross section. Hence, the condition of even irrigation in trickle flow may be stated as predominance of impedance to flow over gravity, as expressed by the following equation:

$$\frac{(dP/dh)_{\mathrm{flow}}}{(dP/dh)_{\mathrm{gravity}}} = \frac{180\,\eta_L d_\mathrm{p}^{-2}(1-\varepsilon_L)^2 \varepsilon_L^{-3} v_\mathrm{L}}{\varepsilon_L \rho_\mathrm{L}\, g} > 1 \tag{9}$$

in which (dP/dh) is the pressure gradient in a vertical (axial) direction, η_L the dynamic viscosity , ρ_L the density of the liquid, g the gravitational acceleration and ε_L the fraction of the bed occupied by liquid in the interstitial space (liquid hold-up).

An order-of-magnitude estimate of the requirement for even irrigation may be obtained by assuming ε_L to be 0.15 (i.e., half of the interstitial space is occupied by liquid) and substituting this value in eq. (9). Thus, the condition for even irrigation can be written as

$$\frac{\eta_L d_\mathrm{p}^{-2} v_\mathrm{L}}{\rho_\mathrm{L}\, g} > 4\times 10^{-6} \tag{10}$$

In this equation the quotient to the left of the inequality sign represents a dimensionless number generally known as the "wetting number" (W). The above estimate of the minimum value of the wetting number agrees very well with the minimum value established on the basis of experimental data (Gierman,1988). The experimentally established criterion is given by

$$W \equiv \frac{\eta_L d_\mathrm{p}^{-2} v_\mathrm{L}}{\rho_\mathrm{L}\, g} > 5\times 10^{-6} \tag{11}$$

From the last two equations it follows that the liquid velocity (determined by reactor length at a given space velocity), the particle diameter, and the kinematic viscosity of the liquid are the main variables that determine the uniformity of catalyst irrigation. Particle size appears to be a particularly important variable.

Table 9 lists some wetting numbers calculated for a typical case of hydrotreating with catalyst particle diameters of 2 mm and 0.1 mm in beds of different lengths. It can be seen

Table 9. Wetting numbers in gasoil hydrotreating with catalyst beds of different length and with catalyst particles of different diameter.

L/[m]	10	1	0.1	1	0.1
v_L/ [mm/s]	8	0.8	0.08	0.8	0.08
d_p/ [mm]	2	2	2	0.1	0.1
$W \times 10^6$	60	6	0.6	2400	240

WHSV=2000 kg/ m³/h; $\eta_L = 2 \times 10^{-4}$ N s/m²; ρ_L= 670 kg/m³

that with the larger size catalyst the criterion for even irrigation ($W \times 10^6 > 5$) is fully met with a bed length of 10 m, a bed of 1 m length being a borderline case. With the fine catalyst this criterion is met for all bed lengths considered, even including a bed length as small as 0.1 m.

Using equation 11 maximum particle sizes can be calculated for the different reactors listed in Table 8. Figure 27 shows maximum allowable catalyst particle diameters as a function of liquid kinematic viscosity for the different reactors listed in Table 8.

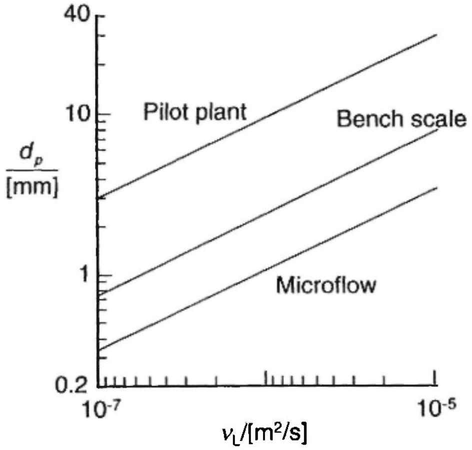


Figure 27. Maximum particle diameter in different reactors as a fuction of liquid kinematic viscosity, with uniform irrigation as determining factor.

From Figure 27 it can be inferred that for a typical liquid in trickle-flow hydrotreating ($v_L = 3 \times 10^{-7}$ m^2/s) a catalyst of 1.5 mm diameter can safely be tested in the pilot-plant reactor. The applicability of the bench-scale reactor in this case is marginal, while the microflow reactor is clearly unsuitable. The latter reactor can only be applied for catalyst testing in trickle flow if the particles have a diameter of less than 0.5 mm.

In the previously discussed comparison of pilot plant reactors of different lengths and a commercial reactor for hydrodesulphurization of gas oil inadequate irrigation of the 3 mm catalyst particles may also have contributed to the sub-optimal performance of the 1.6 m long reactor (see Fig. 22). From eq. (11) it can be calculated that the minimum reactor length should be about 3 m to satisfy the criterion for uniform irrigation at a space velocity of 2.

Dilution of catalyst beds with fine inert particles

From the foregoing discussion it emerges that particle size is the main factor to be considered in determining the applicability of small laboratory reactors for trickle flow process studies. The maximum particle diameters permitted in pilot-plant, bench-scale and microflow reactors as dictated by respectively wall effects, axial dispersion in the packing and catalyst irrigation are shown in Figure 28. This Figure represents a typical case of gasoil hydrotreating.

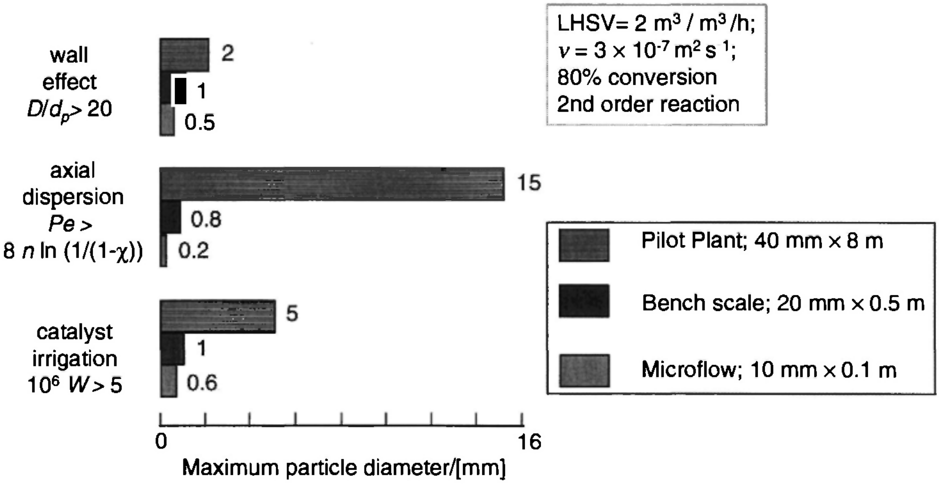


Figure 28. Maximum particle diameters for different reactors as dictated by different criteria.

It can be deduced that a catalyst in a commonly used form of extrudates of 1.5 mm diameter needs to be tested in the pilot-plant reactor. The bench-scale as well as the microflow reactor are only suited for testing substantially smaller catalyst particles, viz., maximal 0.8 and 0.2 mm, respectively. Such catalyst particles are impractical for use in industrial fixed beds because of excessively high pressure drop.

Although a practical catalyst may be crushed to obtain smaller particles suitable for testing in laboratory reactors, the results obtained may not be meaningful for the commercial process and can even be misleading. This is because in catalyst particles of industrial size diffusion effects may affect not only activity, but selectivity and deactivation behaviour as well. Whereas testing of crushed catalyst may be quite acceptable for fundamental catalysis studies, it is seldom suitable for obtaining predictive information for industrial operation. The data in Table 10 shows that particle size of the catalyst does affect the apparent rate constant for trickle-flow hydrodesulfurization of gasoil, demonstrating the occurrence of diffusion limitation with catalyst of practical size. Therefore, also particle shape is a factor of importance for the performance of industrial catalysts, as is demonstrated by the data in Table 11.

Table 10. Apparent 1st order reaction rate constants for gasoil hydrodesulfurization as a function of catalyst particle size (Hanika and Sporka, 1992).

Particle diameter/[mm]	Rate constant/ [L/min/kg/kPa]	Effectiveness factor
0.07	41.1	1*
0.24	33.7	0.82
1.2	24.2	0.59
2.6	20.6	0.5
5.6	16.5	0.4

*) Presumed
Co/Mo/Alumina catalyst, $T = 300$ °C; $P = 3$ MPa;
Experiments in a Berty-type autoclave

Table 11. Effect of particle shape on the activity of Co/Mo/Alumina catalysts for hydrodesulfurization of gasoil (Hanika and Sporka, 1992).

Particle Shape	Diameter/ [mm]	Composition/[%w]		Relative activity
		MoO_3	CoO	
Pellets	5	16.2	3.5	60
Raschig rings	4.5×1.5	16.2	3.5	70
Cyl. Extrud.	1.6	13.8	5.1	100
Cyl. Extrud.	1.2	12.5	2.8	112
3-Lobe Extrud.	1.3	13.2	3.2	112
4-Lobe Extrud.	1.5	11.2	3.1	124
Assym. Cross. Extrud.	1.1	14.7	3.2	128

Co/Mo/Alumina catalyst, $T = 300\ °C$; $P = 3$ MPa;
Experiments in a Berty-type autoclave

One way to satisfy the requirement of small particle diameters in the packing and still determine the catalytic performance of the full-size catalyst is to dilute the large catalyst particles with fine particles of catalytically inert material such as silicon carbide or corundum. Thus, the hydrodynamics are largely dictated by the packing of small particles, whereas the catalytic performance is that of the full-size catalyst. Figure 29 presents a schematic drawing of this catalyst dilution principle.

Residence time distribution measurements with diluted and undiluted beds in laboratory trickle-bed reactors, e.g., by van Klinken and van Dongen (1980) confirm that the axial dispersion in diluted beds is considerably less than in undiluted beds. If the hydrodynamics in a diluted bed are indeed mainly determined by the small particles of the inert diluent, one should expect the axial dispersion to be decreased by a factor equal to the size ratio of catalyst over diluent, since in the range of Reynolds numbers of interest the

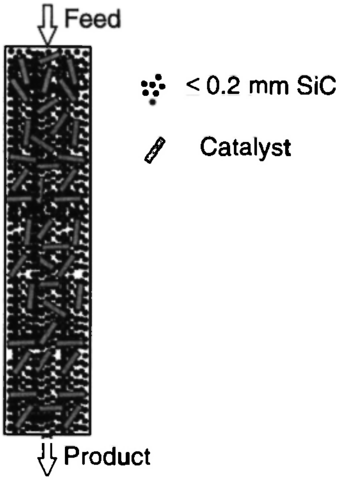


Figure 29. Schematic of catalyst dilution principle.

Bodenstein number is approximately constant. The data listed in Table 12 tend to confirm this hypothesis.

Table 12. Effect of bed dilution on axial dispersion (Van Klinken, see Sie, 1991).

Reactor filling	Undiluted	Diluted
Bed diameter/ [mm]	20	20
Bed length/ [mm]	910	910
Mean residence time/[s]	546	1008
Variance	0.28	0.025
Number of mixing stages	3.1	40

Filling: 1.5 mm glass beads with or without 0.2 mm SiC

Feed: Kuwait flashed distillate labelled with 14-C

T = 366 ^{o}C; P= 125 bar; LHSV = 1 m^3/ m^3/h

Hydrogen/Oil = 1Nm^3/kg

The catalyst bed dilution technique has an additional advantage, viz., it improves the isothermicity of the bed due to the lower amount of heat generated per unit volume of the bed, and the high heat conductivity of a diluent such as silicon carbide. This technique allows meaningful testing of catalyst of practical size in small trickle-bed reactors. It has been discussed in a number of papers, e.g., by De Bruijn (1976), van Klinken and van Dongen (1980), Koros (1976), Carruthers and Dicamillo (1988), and Sie (1991).

Accuracy and meaningfulness of results obtained in small trickle-beds with diluted catalyst

Comparison of Pilot-Plant and smaller-scale reactors

As demonstrated before, large pilot plants with catalyst volumes of at least 0.01 m^3 and bed lengths of at least 4 m can provide process data which are sufficiently representative for commercial trickle-flow hydrotreating processes. In such reactors, catalyst particles as normally used in practice can be tested as such. However, with the technique of bed dilution with fine inert particles, catalyst testing and generation of chemical process data can also be done with smaller process development units, viz., bench-scale and even microreactors.

This is demonstrated by the data listed in Table 13, comparing results on hydrodenitrogenation of a vacuum gas oil in a pilot plant reactor without catalyst bed dilution and in a bench-scale reactor with a bed of diluted catalyst. It can be inferred that the degree of nitrogen removal in the bench-scale reactor is as high as that obtained with the pilot plant. Since the degree of nitrogen removal is very high in both cases, these experiments imply a severe test on the closeness to ideal plug flow.

Table 13. Comparison of pilot-plant and bench-scale reactors for hydrodenitrogenation of vacuum gasoil (630 ppmw N) over a sulphided Ni/Mo/F/Alumina catalyst shaped as cylindrical extrudates of 1.6 mm diameter (Van Klinken, see Sie, 1991).

	Pilot plant undiluted bed	Bench-scale diluted bed (0.2 mm SiC)
ppmw N in product	1.9	1.3
HDN conversion/[%]	99.7	99.8

Figure 30 compares results of tests carried out on two catalysts both shaped as cylindrical extrudates of 1.5 mm diameter, for hydrodesulfurization of a heavy gas oil. The tests were carried out in bench-scale and microflow reactors both containing catalyst beds diluted with 0.2 mm SiC particles. The figure clearly demonstrates that the results obtained with the two types of reactors are identical, notwithstanding the difference in scale.

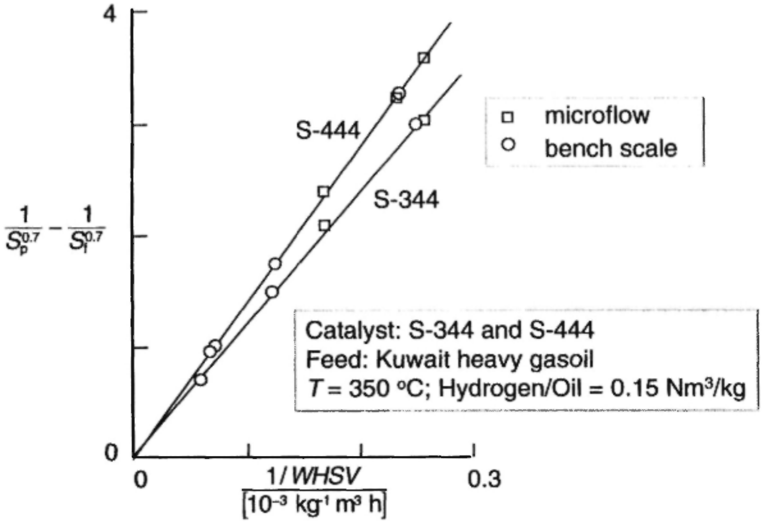


Figure 30. Comparison of bench scale and micro-flow reactors for hydrodesulfurization of a heavy gasoil over hydrotreating catalyst shaped as cylindrical extrudates, diluted with 0.2 mm particles of SiC (De Vries, see Sie, 1991).

Meaningfulness of laboratory tests for commercial practice

With the technique of catalyst bed dilution, bench-scale and microflow reactors can now be applied for process development studies that in the past were reserved for large pilot plants. For most trickle-flow processes of interest, data on catalyst performance in terms of activities, selectivities, and deactivation behaviour generated in such small reactors are not only accurate, but can be used to predict performance under industrial conditions and be used as a basis for design.

This is demonstrated by the data in Table 14, showing a comparison of a bench-scale test result on the hydrodenitrogenation of a gasoil blend over a sulfided Ni/Mo/Alumina cata-

Table 14. Comparison of bench scale test result and commercial performance in hydrodenitrogenation of a gasoil blend (Ryan, see Sie, 1991).

	Temperature required for HDN to 5 ppmw N(99.8% conversion)*
Bench Scale Unit	365 °C
3200 t/d plant	363 °C

*) Weighted average bed temperature (WABT)

Feed: Blend of heavy straight-run gasoil,
light cat-cracked cycle oil, and light coker gasoil

Catalyst: Ni/Mo/Alumina, 1.5 mm extrudates

lyst with the outcome of a later test run in a commercial unit.

It can be seen that the predicted temperature requirement from the bench-scale test agrees quite well with commercial experience. It is of interest to note that the degree of nitrogen removal is very high (99.8%), which places severe demands on the degree to which plug flow has to be approached.

As shown before, microflow reactors can provide equally good results as larger units when applying the catalyst bed dilution technique. The incentive to use microflow reactors instead of larger units in process R & D is that the productivity in experimental testing may be enhanced, particularly when the units are automated so that constant operator attention is no longer needed (see Sie and Krishna (1998a)). A picture of microflow reactors suitable for studies on trickle-flow hydroprocessing of oil is shown in Figure 31.

A comparison between test results obtained in such a microflow reactor and a commercial reactor is presented in Table 15 for the hydrodesulfurization of a heavy gasoil. It can be seen that the results are in close agreement. Hence with the catalyst dilution technique representative data for commercial trickle-flow processes can be obtained on a scale as small as that of microreactors.

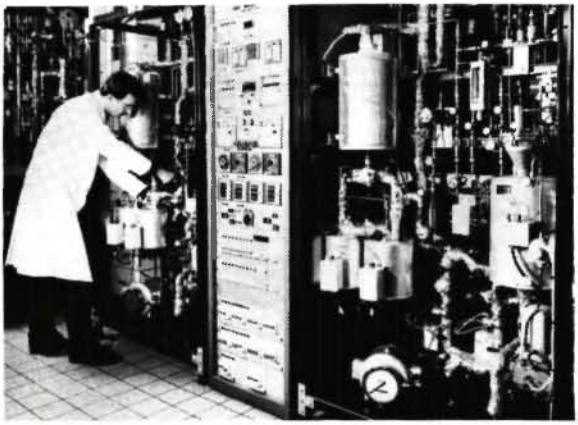


Figure 31. Picture of a dual microflow unit suitable for study of trickle flow hydroprocessing of oils, constructed in the early eighties.

Table 15. Comparison of microflow test results with commercial data on hydrodesulfurization of a heavy gasoii

	Commercial	Microflow
Catalyst Inventory	122 m^3	9.35 mL
WHSV/[kg/m^3/h]	1800	1760
T/[°C]	380 (WABT)	382
(H_2 /Oil)/ [Nm^3/kg]	0.19	0.19
P_{H2} (inlet)/[bar]	30	30
P_{H2S}(outlet)/[bar]	1.5	1.5
S in product, %w	0.082	0.075
HDS conversion, %	95.0	95.4

Feed: Light Arabian Heavy Gasoii (1.64 % w S);

Catalyst: Co/Mo/Alumina; 1.2 mm trilobe extrudates

Alternative methods for studying trickle-flow processes on a laboratory scale

The catalyst bed dilution technique is not the only way in which small-scale kinetically representative tests for trickle-flow processes can be carried out in the laboratory. In principle, any method which achieves the basic requirements specified before, viz., narrow residence time distribution of the liquid and complete contacting of the catalyst, is suitable. An alternative technique to catalyst bed dilution which has been proposed is to operate with liquid and gas in upflow, instead of downflow. This technique, which has for instance been advocated by De Wind et al. (1988), will provide a better guarantee for contacting every catalyst particle than in the case of downflow without bed dilution (De Wind et al., 1988). However, contact of every particle with liquid does not automatically mean that catalyst utilization will be optimal. If liquid flow around the catalyst particles is very uneven, parts of the liquid may not be refreshed at a sufficient rate, resulting in suboptimal catalyst utilization (cf. previous discussion on catalyst irrigation versus catalyst wetting).

A more important limitation of the upflow technique, however, is that it does not solve the problem of axial dispersion in small reactors. The effects of the wall in case of narrow reactors with full-size catalyst particles and the axial dispersion in the coarse packing at low linear velocities are likely to remain important. Hence, particularly at high conversions and for reactions of a high order it is doubtful whether substantial downscaling of reactors will be possible without loss of accuracy and meaningfulness of results.

In studies on the hydrodynamics in packed beds with liquid upflow, Lamine et al. (1992) observed significant velocity profiles: due to the higher porosity close to the wall the local velocity in this region is increased (wall channeling). The problem of uneven flow in upflow is exacerbated when, as is often the case in laboratory equipment, the temperature of the reactor content is maintained by heating of the reactor walls. In that case upward convection currents add to inhomogeneity of flow. Figure 32 shows axial dispersion coefficients measured with tracer techniques for a column of 2.7 m height and 100 mm diameter. It can be inferred that at liquid loadings below 1 kg/(m^2 s), i.e., the liquid loadings of interest for bench-scale and smaller reactors (see Figure 9) the measured Péclet numbers decrease dramatically to values of 10 or lower.

The axial dispersion data of Figure 32 pertain to single-phase upflow (liquid only).

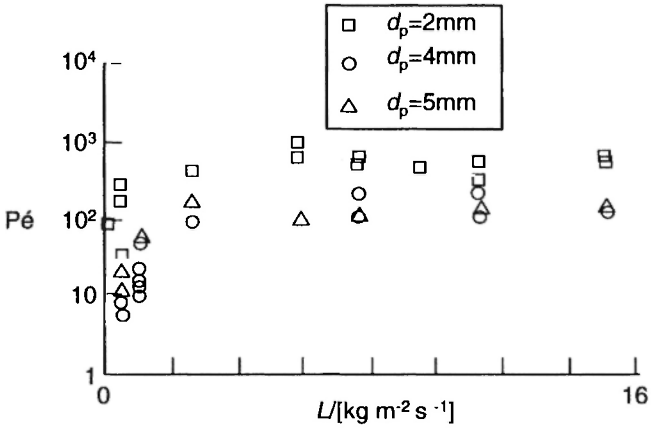


Figure 32. Axial dispersion versus liquid flow rate in liquid upflow through a 2.7 m long and 100 mm wide column. (Lamine et al., 1992).

The presence of a second phase (gas) is likely to increase dispersion (Cf. Bodenstein numbers for single-phase and trickle flow, Figure 23). Figure 33 demonstrates that the presence of gas increases the axial dispersion of the liquid.

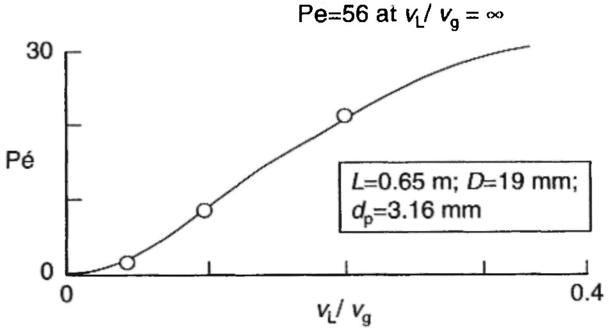


Figure 33. Axial dispersion of liquid in a bench-scale reactor with G/L upflow as a function of the ratio of liquid and gas superficial velocities (Papayannakos et al., 1992).

From Figure 33 it can be inferred that Pė numbers for this bench-scale reactor are very low at the liquid to gas velocity ratios of interest in trickle-flow hydroprocessing of oils, viz., v_L/v_G ratio below 0.1. Therefore, it is doubtful whether the upflow technique with undiluted beds of practical catalysts allows reactors of such size to be used except for low conversions and reactions of low order. The problem of axial dispersion will be even more serious upon further downscaling to the size of microreactors.

A rather unconventional approach to small-scale kinetic simulation of a trickle-flow reactor has been described by Yang and Cussler (1987). In their system, liquid and gas flow through separate spaces: the liquid flows through the interstitial space in the packing, whereas the gas flows through hollow fibers positioned in the bed. The walls of the fibers are permeable to gas but not to liquid. Since there is only one single fluid which flows through the bed the problem of catalyst contacting is eliminated or at least reduced while axial dispersion will be less than under trickle-flow conditions (cf. Figure 23). However, the availability of suitable hollow-fibre materials may be a problem in the case of hydroprocessing of oils at high temperatures and pressures. Whilst the method may be used for studying interactions between mass transfer and kinetics, it does not seem very practical for routine testing of catalyst and for process development studies on trickle-flow processes in general.

Concluding remarks

The catalyst bed dilution technique has made it possible to obtain meaningful information for trickle-flow processes such as hydrotreating of oils in bench-scale and microflow reactors. It provides a very efficient tool for process R & D on trickle-flow processes and the information obtained with this tool allows in many cases to design commercial trickle flow processes involving novel catalysts and/or new feedstocks. The replacement of older large pilot plants by small scale reactor units which can operate in unattended fashion has resulted in a considerable increase of cost effectiveness of R & D on trickle-flow processes.

The small-scale reactors with diluted catalyst beds are only representative of an actual trickle-flow reactor in reaction kinetic sense and such a reactor is no small-scale replica of a commercial reactor in all respects. A study of the hydrodynamic aspects of commercial-scale trickle beds including liquid and gas holdups, pulsing, phase distributions, and measurement of pressure drop, heat and mass transport require separate experiments, e.g., in suitable cold flow models.

Notwithstanding the wide applicability of bench-scale and microflow reactors in process R & D, large pilot plants are still required for reasons as set out in Sie and Krishna

(1998a). These reasons include the need for sufficiently large quantities of a novel product for field tests or for market development, complex line-ups of the process including separating equipment and recycles, and problems of a physical/mechanical nature which cannot be studied in considerably scaled-down equipment. An example in the latter category is the fouling of catalyst beds by particulates in the feed or the behaviour of catalyst particles in a moving trickle bed.

Situations in which a large pilot plant is indispensable generally pertain to the development of a first-of-a-kind technology. In these cases process development is in principle a scaling-up exercise in which the pilot plant should be representative of the future commercial plant in as many as possible, but at least in all important respects. Hence it is generally an integral pilot plant and not just a large reactor for catalyst testing. On the other hand, substitution of new catalysts and/or feedstocks in existing trickle-flow technology can be studied with considerably scaled-down reactors as discussed in the present paper.

Notation

Bo	Bodenstein number
c	concentration
D_{ax}	axial dispersion coefficient
d_p	particle diameter
g	gravitational acceleration
h	vertical position in reactor
k	reaction rate constant
L	reactor length
LHSV	Liquid Hourly Space Velocity
N	number of mixing stages
n	reaction order
P	pressure
Pe	Peclet number
R	reaction rate
Re	Reynolds number
v_L	superficial liquid velocity

W	wetting number
WHSV	Weight Hourly Space Velocity

Greek letters

ε	interstitial porosity
η	dynamic viscosity, also effectiveness factor
ν	kinematic viscosity
ρ	density
χ	conversion

References

Benenati, R.F. and Brosilow, C.B.,1982, Void Fraction Distribution in Beds of Spheres, AIChE J., **8**, 359 - 361.

De Bruijn, A.,1976, Testing of HDS Catalysts in Small Trickle Phase Reactors, in Proc. 6th Int. Symposium on Catalysis, Eds. G.C. Bond, P.B. Wells and F.C. Tomkins, The Chem. Society Publishers, 951 - 961.

Burghardt, A., Bartelmus, G., Jaroszynski, , and Kolodziej, A., 1995, Hydrodynamics and mass transfer in three-phase fixed bed reactor with co-current gas-liquid downflow, *Chem.Engng Jl*, **58**, 83-99

Carruthers, J.D. and Camillo, D.J., 1988, Pilot Plant Testing of Hydrotreating Catalysts. Influence of Catalyst Conditions, Bed Loading and Dilution, *Appl. Catal.*, **43**, 253 - 276.

Charpentier, J.C. and Favier, M, 1975, Some liquid holdup experimental data in trickle bed reactors for foaming and non-foaming hydrocarbons, *A.I.Ch.E.J.*, **21**, 1213.

Chu, C.F. and Ng, K.M., 1989, Flow in Packed Tubes with a Small Tube to Diameter Ratio, *A.I.Ch.E.J.*, **35**, 148 - 158.

Fahien, R.W. and Stankovic, I.M., 1979, An Equation for the Velocity Profile in Packed Columns, *Chem. Eng. Sci.*, **34**, 1350 - 1354.

Funk, G.A. Harold, M.P. and Ng, K.M., 1990, A Novel Model for Reaction in Trickle-Beds with Flow Maldistribution, *Ind. Eng. Chem. Res.*, **29**, 738 - 748.

Gianetto A. and Specchia, V., 1992, Trickle-bed Reactors: State of Art and Perspectives, *Chem. Eng. Sci.*, **47**, 3197 - 3213.

Gierman, H., 1988, Design of Laboratory Hydrotreating Reactors. Scaling Down of Trickle-flow Reactors, *Appl. Catal.*, **43**, 277 - 286.

Govindarao, V.M.H. and Froment, G.F., 1986, Voidage Profiles in Packed Beds of Spheres, *Chem. Eng. Sci.*, **41**, 533 - 539.

Hanika, J. and Sporka, K., 1992, Catalyst Particle Shape and Dimension Effects on Gas Oil Hydrodesulphurization, *Chem. Eng. Sci.*, **47**, 2739-2744.

Van Klinken, J. and van Dongen R.H., 1980, Catalyst Dilution for Improved Performance of Laboratory Trickle Flow Reactors, *Chem. Eng. Sci.*, **35**, 59 - 66.

Koros, R.M., 1976, Proc. 4th Symposium Chem. Reaction Eng., Heidelberg, 1976, p. 372.

Lamine, A.S., Colli Serrano, M.T. and Wild, G., 1992, Hydrodynamics and Heat Transfer in Packed Beds with Liquid Upflow, *Chem. Eng. and Processing*, **31**, 385 - 394.

Le Nobel, J.W. and Choufour, J.H., 1959, Development in Treating Processes for the Petroleum Industry, Proc. 5th World Petroleum Congress Sect. III, 5th WPC Inc., New York,

p. 233 - 243.

Mears, D.E., 1971, The Role of Axial Dispersion in Trickle-flow Laboratory Reactors, *Chem. Eng. Sci.*, **26**, 1361 - 1366.

Mears, D.E., 1974, The Role of Liquid Holdup and Effective Wetting in the Performance of Trickle-Bed Reactors, Proc. 3rd Int. Symposium Chem. Reaction Eng., Advances in Chemistry Series 133, Am. Chem. Soc., p. 218 - 227.

Morales, M., Spinn, C.W. and Smith, J.M., 1951, *Ind. Eng. Chem.*, **43**, 225.

Papayannakos, N.G., Galtier. P.A., Bigeard, P.H. and Kasztelan, S, 1992, Hydrodynamic Effects in Bench Scale Hydrotreaters Operating in the Cocurrent Gas-Liquid Upflow Mode, *Chem. Eng. Sci.*, **47**, 2275-2280.

Ramachandran, P.A. and Chaudhari, R.V., 1983, Three Phase Catalytic Reactors, Gordon and Breach Science Publishers.

Ross, L.D., 1965, Performance of Trickle Bed Reactors, *Chem. Eng. Progress*, **61**, No. 10, 77 - 82.

Satterfield, C.N., 1975, Trickle Bed Reactors, *A.I.Ch.E.J.*, **21**, 209-228.

Shah, Y.T., 1979, Gas-Liquid-Solid Reactor Design, McGraw Hill, New York.

Sie, S.T., 1991, Scale Effects in Laboratory and Pilot Plant reactors for Trickle-flow Processes, *Rev. Inst. Franc. du Petrole*, **46**, 501 - 515.

Sie, S.T. and Krishna, R., 1998a, Process development and scale up: I. Process development strategy and methodology *Reviews in Chemical Engineering*, 14, No. 1, 47-88

Sie, S.T. and Krishna, R., 1998b, Process development and scale up: II. Catalyst Design Strategy, *Reviews in Chemical Engineering,* 14, No. 3, 159-202

Schwartz, C.E. and Smith, J.M., 1953, *Ind. Eng. Chem.*, **45**, 1209.

Tarhan, M.O., 1983, Catalytic Reactor Design, McGraw Hill, New York.

Vortmeyer, D. and Schuster, J., 1983, Evaluation of Steady Flow Profiles in Rectangular and Circular Packed Beds by a Variational Method, *Chem. Eng. Sci.*, **38**, 1691 - 1699.

Wammes, W.J.A., 1990, *Hydrodynamics in a cocurrent gas-liquid trickle-bed reactor at elevated pressures.* Ph.D. thesis in Chemical Engineering, University of Twente, Enschede, The Netherlands.

Westerterp, K.R. and Wammes, W.J.A., 1992, Three-Phase Trickle-Bed Reactors, Chapter in Ullmann's Encyclopedia of Industrial Chemistry, Volume B4, Principles of Chemical Reaction Engineering and Plant Design, Editors: B. Elvers, S. Hawkins and G. Schulz, 5th Edition, VCH Verlagsgesellschaft mbH, Weinheim.

De Wind, M., Plantenga, F.L., Heinerman, J.J.L. and Homan Free, H.W., 1988, Upflow versus Downflow Testing of Hydrotreating Catalysts, *Appl. Catal.*, **43**, 239 - 252.

Yang, M.-C. and Cussler, E.L., 1987, A Hollow-Fiber Trickle-Bed Reactor, *A.I.Ch.E. J.*, **33**, 1754 - 1756.

Zimmerman, S.P. and Ng, K.M., 1986, Liquid Distribution in Trickling Flow Trickle-Bed Reactors, *Chem. Eng. Sci.*, **41**, 861 - 866.