Applied Catalysis, 43 (1988) 277-286
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

Design of Laboratory Hydrotreating Reactors

Scaling Down of Trickle-flow Reactors

H. GIERMAN
Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research B.V.), Badhuisweg 3, 1031 CM Amsterdam (The Netherlands)

ABSTRACT

Once it has been decided that a trickle-flow reactor should be used for a particular laboratory hydrotreating experiment, the most suitable scale of operation has to be determined. In most instances the aim is for the smallest possible scale. In this paper the role and relative importance of a number of phenomena are discussed. It is shown that most hydrotreating experiments can be carried out in very small reactors provided that the catalyst bed dilution technique is used.

INTRODUCTION

The design of a laboratory reactor for hydrotreating processes (i.e. removal of sulphur, nitrogen and metals from oil and cracking of oil fractions) involves the selection of the most appropriate type of reactor, determination of the main dimensions and the mechanical design.

On a commercial scale a hydrotreating reaction is commonly carried out by feeding a liquid (oil fraction) and a gas (hydrogen) over a fixed bed of catalyst particles. The reaction rates are limited by the transport of the liquid phase. Conditions are usually such that the reactor operates in the trickle-flow regime. A laboratory reactor is not necessarily a small-scale replica of a commercial reactor. The choice of reactor type depends largely on the purpose of the experiments envisaged. Guidelines for such a choice have appeared frequently in the literature and will not be repeated here in detail. A recycle reactor and a trickle-flow reactor represent the two extremes.

A typical experiment in a recycle reactor would be to pass a feed consisting of one or more model compounds over a bed of finely crushed catalyst particles. With an internal or external recycle over the bed it may be possible to achieve a situation in which gradients are absent. This set-up could be ideal for studying the kinetics and mechanism of a particular reaction. To compare different catalysts it is preferable to adjust the space velocities to obtain the same conversion level (comparison at the same space velocity is only meaningful if the

0166-9834/88/$03.50

conversion is not too high). Such a set-up could also be used to obtain fundamental deactivation data [1].

For the evaluation of commercial catalysts for a particular refinery application, a totally different kind of experiment might be chosen. Suppose the aim was to produce a yield structure comparable to that which would be obtained in the refinery. A possible reason for this might be to be able to measure relevant product properties directly. Instead of model components the actual feed would be used, to ensure that the full network of reactions and interactions encountered in the real situation would be simulated. Also, catalyst particles would not be crushed, because in commercial operation the catalyst effectiveness factor may be < 1; moreover, crushing would disguise any skin effect that the commercial catalyst might display. If there is a sizeable heat of reaction, (simulation of) adiabatic operation on a small scale might even be considered.

No matter what type of experiment (reactor) is chosen, and whatever the purpose, be it to obtain true intrinsic kinetics or to obtain reactor design data, the effects and interrelationships of physical and chemical processes always have to be evaluated.

In the remainder of this paper we shall assume that the decision has been taken to use a trickle-flow reactor to investigate a particular hydrotreating problem.

SCALING-DOWN STRATEGY

Once the type of reactor has been selected, the main dimensions have to be established. Sometimes a fairly large reactor may be required, e.g. if a sizeable amount of product has to be prepared for marketing purposes. However, the aim is usually towards the smallest possible scale in the laboratory as it is safer, cheaper and faster. Moreover, there is sometimes only a limited amount of catalyst and/or feedstock available.

Generally, two different approaches can be followed to scale down a trickle-flow process [2]: maintenance of fluid dynamic similarity or the phenomenological approach.

To maintain fluid dynamic similarity, experiments should be carried out not only at the same space velocity as in the commercial situation but also at the same liquid and gas linear velocities. Most of the problems of scaling up are then avoided; however, pilot plants of, say, 10 m high are required. Obviously this approach is costly, and it is followed only if almost nothing is known of the process under investigation.

In the phenomenological aproach an attempt is made to isolate the various phenomena that affect the apparent reaction and to establish appropriate correlations for each of them (assuming separable mechanisms). An example is reactor models in which it is assumed that the reaction is pseudo-homogeneous and the phases are in plug flow. For a first-order one may therefore write

$$\ln(1-X)^{-1}=k_{\mathrm{app}}/s$$

with $k_{\mathrm{app}}=\beta k$. All scale-dependent factors are included in β. A vast amount of literature has been published on what the most appropriate correlation is for β. There is disagreement over the validity of these relationships and especially about the prediction of the point from which $\beta=1$. This piece of information is, however, essential as it is the reference point for commercial-scale operation. The applicability of these types of reactor models for hydrotreating processes is further limited by the fact that, in many situations, the intrinsic kinetics of the various reactions are not well enough known to be included in the model.

What the "smallest" scale of operation is will depend on the type of process to be investigated and on the kind of information required. In view of the unknown factors with regard to the reaction mechanism and intrinsic kinetics of oil conversion processes, the preferred strategy for process research is often to choose such experimental conditions that the composition of the reactor product is independent of the scale of operation.

For trickle-flow processes it is essential that complete irrigation of each catalyst particle is ensured (as is the case in a properly designed commercial reactor; non-irrigated areas cause reduced, scattered conversion and may give rise to local hot spots). Deviation from plug flow should be minimal and in some instances mass and heat transfer resistances on a small scale have to be known.

Variables

In the design of the hydrotreating experiment there are therefore three variables left if the process conditions (space velocity, temperature, pressure, feed, catalyst) are fixed: length and diameter of the catalyst bed and size of the catalyst particle.

For practical reasons one prefers to work with standard-sized reactors in a laboratory. Table 1 shows the names and sizes of commonly used reactors (the nomenclature will be used throughout this paper):

We have assumed that, in the envisaged hydrotreating experiments, the catalyst particles will not be crushed. By adding a certain amount of inert material of a different size, the average hydraulic diameter can, however, be controlled. The effectiveness of this method is well proved [3] and widely applicable. Care should be taken to avoid excessive dilution of the bed as this may cause significant by-passing of catalyst particles [4].

LIMITATIONS TO SCALING DOWN

Deviation from plug flow

Axial mixing of the flowing phases in fixed beds has been studied intensively and various models have been proposed. A realistic model appears to be the

TABLE 1

Standard reactor sizes

Name of reactor	Catalyst volume (ml)
Nanoflow	0.5
Microflow	5
Bench-scale	50
Small pilot-plant	500
Large pilot-plant	5000

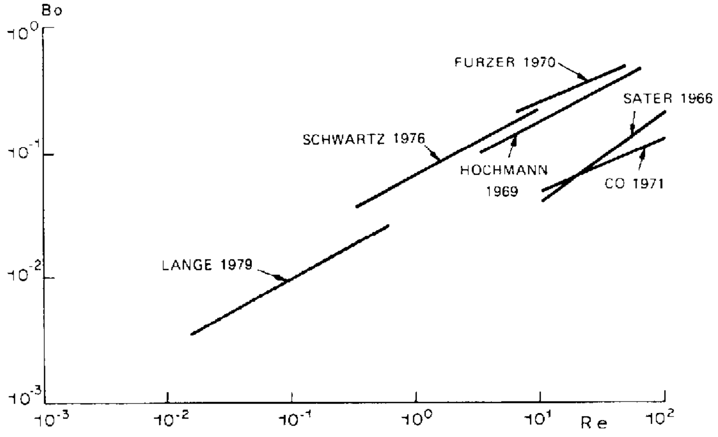

Fig. 1. Experimental estimates of the axial Bodenstein number in trickle flow.

cross-flow model [5], which is based on the assumption that part of the liquid is in plug flow and in contact with a stagnant portion of the liquid (parameters are the fraction of liquid that is flowing and the transfer coefficient between the flowing and the stagnant portion). It is unfortunate that only few attempts have been published to find general correlations for the two parameters [6].

The model most extensively used (but probably less realistic) is the one-parameter piston diffusion (PD) model (e.g. ref. 7): plug flow with a "Fick's diffusion" type of process superimposed. The parameter by which the residence distribution of the liquid is described is the Peclet number (*Pe*). Based on the particle diameter, this parameter is called the Bodenstein number (*Bo*). Many investigators (examples in Fig. 1) have shown that *Bo* can be correlated by the Reynolds number (*Re*), in a form such as $Bo = aRe^b$. In most instances the investigations have taken place in the range $Re = 1$–100. Small-scale trickle-flow experiments, however, typically operate at $Re = 0.001$–0.1. One report on investigations at lower values of *Re* [8] suggests that the value of *Bo* continues to decrease with decreasing *Re*. In contrast, our experience (based on radioactive tracer experiments in bench-scale equipment) indicates that *Bo* levels off to a constant value at low *Re* (Fig. 2). Although we have no sound theory as to why this should be, it is remarkable that the same phenomenon has been observed in single-phase flow (albeit at a higher value of *Bo*).

Now that the deviation from plug flow as a function of *Re* has been quantified, a standard has to be set for the minimum value of *Pe*. Mears [9] has shown that for an *n*th-order of reaction (using the PD model) the deviation from plug flow (expressed in terms of required bed length for a given conversion) is less than 5% if $Pe > 20n \ln(1-X)^{-1}$. In practice we found this criterion to be rather conservative. One of the reasons is that in laboratory practice it is seldom possible to derive rate constants to an accuracy greater than, say, 10%. By studying laboratory data, we found that a sufficient condition is $Pe > 8n \ln(1-X)^{-1}$.

We are now able to determine the smallest scale of operation for our experiment. Fig. 3 shows the effect of the most important variables (particle diameter and conversion) for a typical hydrotreating experiment. As commercial catalysts usually have an effective diameter of 1–3 mm, bed dilution with fine material is nearly always necessary to avoid significant deviation from plug flow in small units.

In case of a deviation from plug flow, one can calculate (via the PD model and the calculated value of *Pe*) what the conversion would have been in the case of plug flow [10,11]. This method is not recommended if the deviation from plug flow is large ($Pe < 10$).

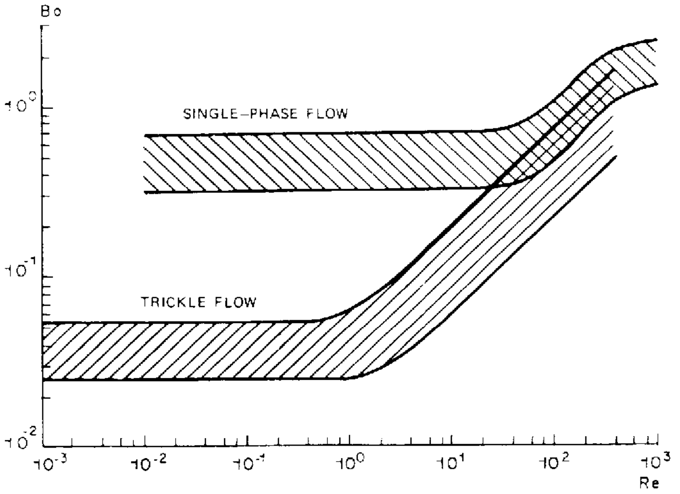

Fig. 2. Recommended values of *Bo* for trickle flow and single-phase flow.

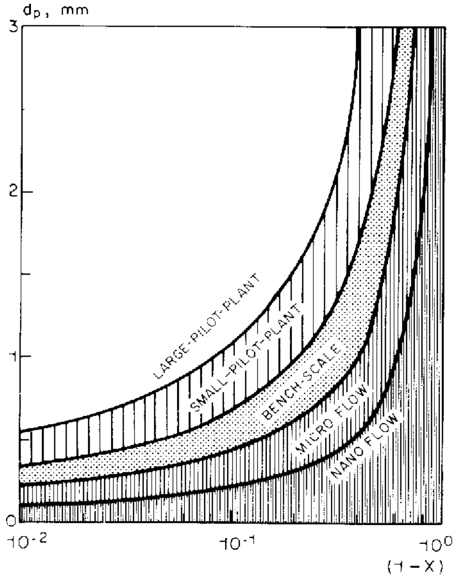

Fig. 3. Axial dispersion.

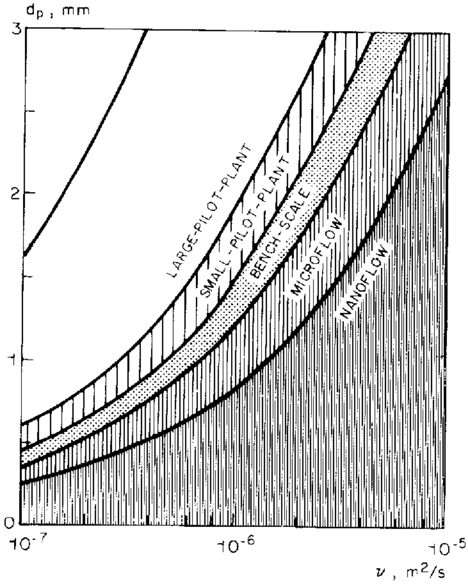

Fig. 4. Catalyst irrigation.

Irrigation of catalyst particles

A problem unique to the scaling-down of trickle-flow reactors is to ensure that all catalyst particles remain irrigated during the process. Modelling this irrigation process is one of the more intriguing problems in trickle-flow reactor design. [Note: this phenomenon is usually referred to as "catalyst wetting efficiency". Porous catalyst particles are in principle always wet under hydrotreating conditions, even if they are only touched once by a stream of liquid (complete internal wetting). As it is essential to ensure that the liquid inside the catalyst particles is continuously renewed, we prefer to use the term "irrigation".]

On the basis of a physical model of catalyst irrigation we have developed a criterion that enables us to calculate the conditions under which all particles are irrigated. The criterion has been validated by analysing numerous laboratory cases of trickle-flow experiments and has been used for a number of years now in our laboratories.

An indicator of an important variable in this respect is the viscosity of the liquid (under reaction conditions). The effect of liquid viscosity and particle diameter on the operating range that is feasible (with respect to complete irrigation) for a typical hydrotreating experiment is given in Fig. 4. Very small reactors can be used provided that the liquid is very viscous (short-residue type of feed). For less viscous streams small units may be used, provided that the catalyst bed is sufficiently diluted with fine material.

Sample inhomogeneity

It is not always realized that a limitation to scaling down might arise if the catalyst batch to be sampled is known to be inhomogeneous. This could be the result of, for example, a small fraction of the catalyst carrier being doubly impregnated or, alternatively, not impregnated at all. Assume that the fraction f_a can be characterized by a rate constant k_a and the remaining fraction by a rate constant k_b. Further assume a non-biased sampling procedure and a maximum tolerated standard deviation (between repeated experiments) in average rate constant of 5%. For a particular composition (f_a) and reactor volume (number of particles) we can calculate the maximum value of k_a/k_b that can be tolerated (see Fig. 5).

As would be expected, a large catalyst sample (large reactor) has to be used if the catalyst batch is known to contain a small fraction that is considerably

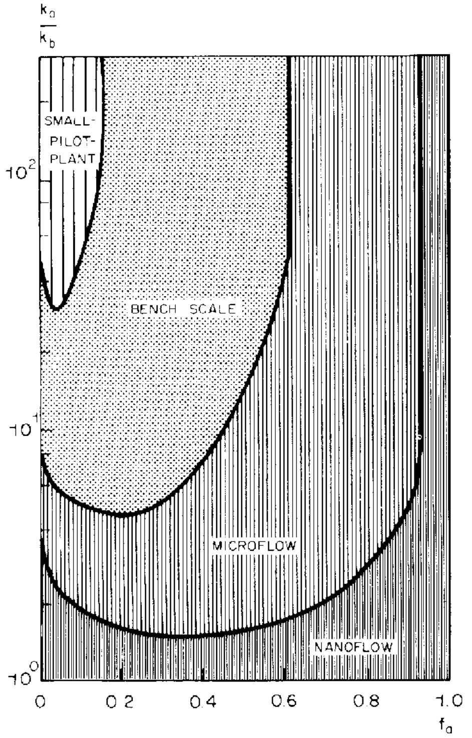

Fig. 5. Sample inhomogeneity.

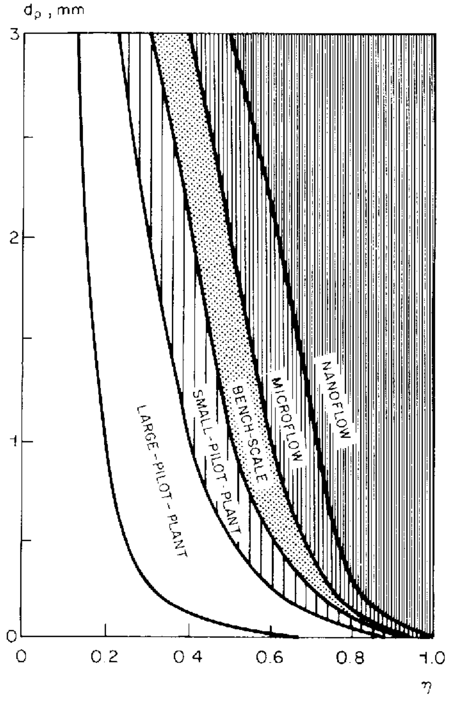

Fig. 6. Mass transfer.

more active than the remainder of the batch. In contrast, small samples can still be used if the batch contains a small fraction of less active (or even inert) material.

Inter-phase mass transfer

In commercial-size reactors the mass transfer (from the bulk of the fluid to the surface) is generally not limiting provided that the catalyst effectiveness factor (as defined in the Thiele concept) is larger than 0.1 [12]. In laboratory reactors, however, mass transfer may affect the overall rate of reaction.

A 10% criterion is formulated if we stipulate that the difference between the reactant concentration in the bulk of the fluid and that on the (external) catalyst surface has to be smaller than 10% of the surface concentration. From a mass balance across the liquid film and the catalyst particle, in which a first-order reaction takes place, it then follows that $Sh \geqslant 5/3\Phi$. The Sherwood number (Sh) is usually correlated with the Reynolds and Schmidt numbers but published correlations are of dubious accuracy [13] and not validated at low Re numbers. Rather arbitrarily, we therefore use [14].

$$Sh = 4.4\,Re^{0.5}Sc^{0.33}(1-\epsilon)^{0.5}$$

The result is demonstrated in Fig. 6. (Note: in contrast to the other figures, the particle diameter in this plot represents the diameter of the equivalent spherical catalyst particle and not the average of catalyst and dilution material.) It is clear that, even for small reactors (low Re), the catalyst effectiveness factor should be rather low before mass transfer may become limiting. Still, it may be relevant for hydrotreating (and especially demetallization) of high-molecular-weight molecules.

Radial gradients

To ensure proper radial mass distribution is a problem that exists in large units only (proper design of multi-point distributor). In a laboratory unit one commonly uses a single-point distributor and one can calculate [2] the length required to achieve an equilibrated condition: a few centimetres (of inert material) are usually sufficient.

The hydrotreating conditions may be such that the heat of reaction is significant. Heat transfer effects (both inter-phase and inter-reactor) are therefore often more significant than the mass transfer effects. This may pose a problem if one desires to operate in an isothermal mode. Axial gradients can only be avoided if the heat is transferred sufficiently rapidly from the catalyst particles to the reactor tube. This necessarily creates a radial gradient and will impose an upper limit on the diameter of the catalyst bed. [Note: a lower limit of the reactor diameter also exists because at a certain moment the liquid flow along the wall (due to the higher bed porosity) becomes significant with respect to the flow through the bed. It has been stated (and more or less accepted) that the tube diameter should be at least 16 particle diameters wide [15].]

Criteria for estimation of the significance of the thermal gradient have been developed [16], but no reliable correlations exist for calculating the heat transfer coefficient at the wall of the laboratory reactor. The effective conductivity of the bed can be increased by using a well conducting inert substance as dilution material (for example, silicon carbide). Although the effects of a radial gradient should therefore be minimal, it is recommended that temperatures both at the wall and at the centre of the bed should always be measured if the diameter of the bed is more than 3 cm.

CONCLUSIONS

It is readily possible to carry out trickle-flow hydrotreating experiments on a small scale such that the product is representative of commercial-scale operation. In most instances the catalyst bed dilution technique is a prerequisite for meaningful results. Today, a priori calculations make it possible to calculate the smallest possible scale of operation for a particular experiment. It is a pity that cases are still encountered (as judged from publications in the literature) in which investigators have neglected to do these calculations, thus rendering their results less meaningful.

ACKNOWLEDGEMENTS

Thanks are due to G.J. Harmsen and S.T. Sie for their contributions to the development of criteria for catalyst irrigation and sample inhomogeneity, respectively.

NOTATION

Bo	Bodenstein number $(=\frac{vd_p}{D})$
d_p	Particle diameter
D	Diffusion coefficient
f	Weight fraction
k	Reaction rate constant
k_m	Mass-transfer coefficient
L	Catalyst bed length
n	Order of reaction

Pe	Peclet number $\left(=\frac{vL}{D}\right)$
Re	Reynolds number $\left(=\frac{vd_p}{\nu}\right)$
s	Space velocity
Sc	Schmidt number $\left(=\frac{\nu}{D}\right)$
Sh	Sherwood number $\left(=\frac{k_m d_p}{D}\right)$
v	Linear fluid velocity
X	Fractional conversion
β	Scale factor
ϵ	Bed porosity
η	Catalyst effectiveness factor
ϕ	Dahmkohler number (modified Thiele modulus $=\eta \cdot \frac{d_p^2}{4} \cdot \frac{k}{D_e}$ for first order reaction)
ν	Kinematic viscosity

REFERENCES

1 E.E. Petersen and M.A. Pacheco, ACS Symposium Series, 237 (1984) 365.
2 R.M. Koros, in: A.E. Rodrigues, J.M. Calo and N.H. Sweed (Eds.), Scale-up Considerations for Mixed Phase Catalytic Reactors, Multiphase Chemical Reactors. Vol. 2 Design Methods, Sijthoff and Noordhoff, Alphen a/d Rijn, 1981, p. 429.
3 J. van Klinken and R.H. van Dongen, Chem. Eng. Sci., 35 (1980) 59.
4 C.V. van den Bleek, K. van der Wiele and P.J. van den Berg, Chem. Eng. Sci., 16 (1969) 681.
5 C.J. Hoogendoorn and J. Lips, Can. J. Chem. Eng., 43 (1965) 125.
6 J.M. Hochmann and E. Effron, Ind. Eng. Chem. Fund., 8 (1969) 63.
7 O. Levenspiel, Chemical Reaction Engineering, 2nd ed., Wiley, New York, 1972, Ch. 9.
8 R. Lange and A. Busch, Chem. Techn., 31 (1979) 232.
9 D.E. Mears, Chem. Eng. Sci., 26 (1971) 1361.
10 J.F. Wehner and R.H. Wilhelm, Chem. Eng. Sci., 26 (1956) 89.
11 O. Levenspiel and K.B. Bischoff, Ind. Eng. Chem., 53 (1961) 313.
12 C.N. Satterfield, A.A. Pelossof and T.K. Sherwood, AIChE J., 15 (1969) 226.
13 M.P. Dudukovic and P.L. Mills, Catalyst Effectiveness in Three-phase Systems, Paper presented at the session "Interaction of Diffusion and Chemical Reaction" of the 77th AIChE Annual Meeting, Chicago, IL, November 1985.
14 D.W. van Krevelen and J.T.C. Krekels, Recueil Trav. Chim/ Pays-Bas, 67 (1948) 512.
15 M. Herskowitz, Performance of Trickle-bed Reactors, Ph.D. Thesis, Univ. of Calif., Davis, 1978.
16 D.E. Mears, J. Catal., 20 (1971) 127.
17 P. Co and R. Bibaud, Can. J. Chem. Eng., 49 (1971) 727.
18 I.A. Furzer and R.W. Michell, AIChE J., 16 (1970) 380.
19 V.E. Sater and O. Levenspiel, I&EC Fund., 5 (1966) 86.
20 J.G. Schwartz, E. Weger and M.P. Dudukovic, AIChE J., 22 (1976) 953.