

# The six-flow reactor technology

## A review on fast catalyst screening and kinetic studies

Javier Pérez-Ramírez\*, Rob J. Berger, Guido Mul, Freek Kapteijn, Jacob A. Moulijn

*Industrial Catalysis, Delft ChemTech, Faculty of Applied Sciences, Delft University of Technology,  
Julianalaan 136, 2628 BL Delft, Netherlands*

### Abstract

Catalyst testing in laboratory reactors requires careful experimentation and data interpretation. Current methods of catalyst development tend to be slow, laborious, and incapable of addressing most of the complex challenges, of multi-component chemical systems. In order to speed up this process in an efficient way, the six-flow parallel reactor technology is proposed. This enables parallel catalyst testing, which enhances the number of catalysts tested significantly and reduces the time for kinetic studies. Thus, operation costs are lowered and the success rate for important breakthroughs is increased. The six-flow set-up allows a proper catalyst testing, under more realistic and accurate conditions than in conventional combinatorial techniques, especially when the catalyst development stage is advanced and quantitative data are required. The application of this assessed technology is reviewed and combined with criteria for ideal behavior in reactor models and transport phenomena, crucial in order to achieve intrinsic catalyst performance data. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Six-flow technology; Laboratory reactor; Catalyst development; Catalyst testing; Kinetic studies; Combinatorial catalysis

### 1. State-of-the-art in catalyst development

The experimentation with a laboratory-scale reactor is, now more than ever, a prerequisite in the development of catalysts for a new process or the improvement of existing processes [1–3]. Discovering, developing, and optimizing new catalytic materials using current approaches is predominantly a process of trial and error, sequentially generating data from one experiment to another. This process yields low success rates, and requires long timescales and large expenditures, especially as desired materials increase in complexity.

The catalyst development work required before a new or modified process is introduced consists of

many stages. Fig. 1 schematically indicates the order of activities, initiated by the new idea for a process or catalyst: (i) catalyst preparation, (ii) catalyst screening, (iii) establishing reaction networks, (iv) kinetic studies, (v) stability tests, and (vi) scale-up on pilot plant level. During the development, there will be a continuous feedback from one activity to another to optimize the catalyst and/or the catalytic process.

The objectives of the different development stages vary:

- In the *combinatorial stage*, many catalyst formulations need to be prepared, investigated, and roughly compared on activity, selectivity, and stability. High-throughput synthesis and screening of the activity of these samples in a qualitative sense allow a rapid identification of potential “lead” catalysts.
- In the *quantification stage*, the testing of potentially interesting catalysts from the former stage on a more

\* Corresponding author. Tel.: +31-15-278-43-56;  
fax: +31-15-278-44-52.  
E-mail address: j.perezramirez@tnw.tudelft.nl (J. Pérez-Ramírez)

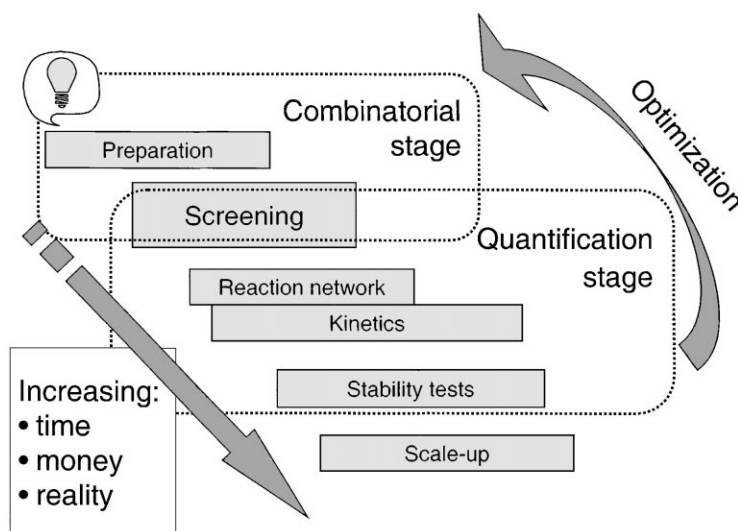


Fig. 1. Stages in a catalyst development program.

quantitative basis is performed, consisting of determining the reaction kinetics and obtaining a first insight into the catalytic stability.

Time consuming kinetic studies are indispensable for the development of the design, operation, and process control of a large-scale catalytic reactor. They require an exhaustive description of the catalytic rate as a function of the process variables, such as temperature, pressure, space–time, and composition of the reaction mixture. The basis for the kinetic modeling studies is obtained by investigating the catalytic reaction mechanism and establishing the reaction networks.

Stability studies in which the catalyst is tested during a longer time on stream, should be carried out to evaluate the practical application of the new catalyst before the scale-up is initiated. In current practice, however, these studies are usually performed during the bench or pilot scale testing with real feed and recycle streams and catalysts in its practical shape. These allow the investigation of the effect of trace impurities or accumulated components, not observed in laboratory-scale experiments.

Reducing the scale of experimentation (downscaling) for stability studies offers many advantages although it can never completely replace the larger-scale testing. Micro- and nano-flow units have been generally used in exploratory studies, and nowadays they

are also increasingly applied in development studies on more established processes. The incentives behind downscaling may include: (i) cheaper equipment to construct and install; (ii) fewer materials to consume, store, and dispose of; (iii) fewer demands on laboratory infrastructure; (iv) lower utility requirements; (v) intrinsically safer (reduced hazards of toxic emissions, explosions or fires); and (vi) high accuracy in experimentation and the use of representative samples [4]. The increase in research productivity resulting from catalyst testing on a smaller scale is illustrated by Fig. 2. It can be inferred that the more modern automated micro- or nano-reactor units operating without human attention require at least one order of magnitude less manpower than the traditional large pilot plants.

Obviously, the number of catalysts will decrease during the progress of catalyst development (Fig. 1), but the complexity, the time taken, and size increase and consequently, the costs involved. This demands an efficient and proper approach for laboratory-scale experimentation.

For drug screening in the pharmaceutical industry, high-speed screening (HSS) technology has been rapidly developed and applied since the end of 1980s. The application of HSS technology has been highly focused on the automated synthesis and fast screening

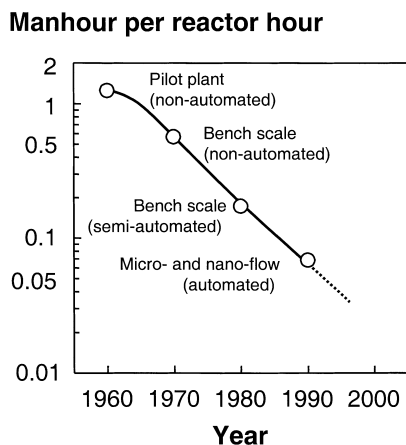


Fig. 2. Manpower needed for different reactor units as a function of the approximate introduction year for general use in oil process research.

of large libraries of target drug molecules with high degree of success [5–7]. However, the basic concepts of HSS technology are equally well and more broadly applicable to other areas of both product and process research and development, like in homogeneous and heterogeneous catalysis [8]. Application of HSS technology to the development of heterogeneous catalyst comprises of the generation of a *library* of candidate materials followed by performance testing of the resulting samples. For library generation, parallel testing is the preferred approach, rather than the *split-and-mix* techniques, which have been developed for combinatorial chemistry. Flow systems mimicking the multi-cup principle are hardly available in the market and operating under poorly defined conditions (temperature and pressure) are still limited to performing catalytic tests in moderately catalytic conditions. In this area in particular, testing conditions may exert a decisive role on the observed activity. Especially, mass and heat transfer phenomena, as well as reactor analysis should be carefully considered in order to interpret the measured data properly. In this sense, conventional combinatorial methods are of limited value and only serve as a qualitative indication.

In this manuscript, the past and present of the six-flow technology are reviewed. The six-flow set-up is proposed to be a proven technology used as an efficient tool as laboratory reactor allowing integration of the different stages involved in a general catalyst

development program. The paper focuses on the description of the features, advantages, and operation of this system, as an innovative and attractive approach compared to other catalyst screening techniques. General recommendations for proper catalyst testing and design criteria to avoid non-idealities in the catalyst bed are also emphasized to achieve accurate and intrinsic data on the catalyst performance.

## 2. Laboratory reactors

Many different types of reactors can be applied for catalyst testing, and it is of primary importance to select the proper reactor configuration to obtain the required information. Several overviews of test reactors and recommendations for a proper reactor selection in the laboratory as well as in an industrial application have been published [9–22].

In order to obtain intrinsic catalyst properties (activity, selectivity, deactivation, and reaction kinetics) from experimental data, the following criteria should be fulfilled:

- sufficient contact between the reactants and the catalyst;
- absence of mass and heat transport limitations inside and outside the catalyst particles;
- availability of a good description of the reactor characteristics, with well-defined residence time distributions under isothermal conditions.

The criteria generally imply the use of ideal reactor types such as the plug-flow reactor (PFR) and the continuously-stirred tank reactor (CSTR).

The choice of the reactor is usually made via the following scheme [3]:

1. Determine which type of information is required from the experiments.
2. Define the performance factors that determine the selection to be made, e.g. experimental conditions, catalyst shape, reaction features, and complexity of reaction networks.
3. Choose the type of reactors that should be considered.
4. Rank the choices available on the basis of the performance factors for each reactor.

A classical and complete reactor classification based on the operation can be found in [1]. Reactors operating at steady state, and in particular packed-bed

Table 1  
Summary of relative reactor ratings (L: low; M: medium; H: high)

Aspect	Reactor type						
	PFR			CSTR			Batch
	Differential fixed bed	Integral fixed bed	Solids transport (riser)	External recirculation	Internal fluid recirculation	Spinning catalyst basket	Internal fluid recirculation
Ease of use	H	H	H	M–H	M	L–M	M
Ease of construction	H	H	L	M	M	L–M	M
Cost	L	L	H	L–M	M–H	M–H	M
Sampling and analysis ease	M	H	L	H	H	H	M
Approach ideal type	H	H	M	H	M–H	L–M	H
Fluid–catalyst contact	H	H	M	H	M–H	L–M	H
Isothermicity	H	M–H	H	M–H	H	M	H
Temperature measurement	H	H	H	H	M–H	L	H
Kinetics	H	H	M	M	M–H	L–M	M
Deactivation noticed	H	H	L	M	M	M	L
Gas–liquid–solid use	L–M	M–H	L	M–H	M–H	M	H

reactors, are most widely applied in catalyst testing due to the ease of operation and the low costs. Transiently operated reactors, however, are used much less for the mere goal of catalyst testing. Batch operation has the disadvantage that possible deactivation during the progress of the experiment cannot be observed directly and should be verified afterwards, e.g. by repeating the experiment. Pulse reactors, such as the TAP and the Multi-track [23,24], operate at catalyst conditions that are usually quite different from those at steady-state operation. However, this disadvantage does not apply for transient operation in the case of switching between isotopically labeled species at steady-state conditions [25]. Transient operation is mainly applied for obtaining mechanistic information and to establish reaction networks [26].

Kapteijn and Moulijn [2] have reviewed advantages and drawbacks of frequently used laboratory reactor types, the results of which are reproduced in Table 1. Based on these guidelines and on the general requirements for catalyst testing, the fixed-bed reactor is applied in the six-flow technology. The fixed-bed reactor is simple, cheap, easy to handle, and applicable for both gas- and liquid-phase systems and, with some caution, also for three phase systems. Moreover, the reactor requires relatively small amounts of catalyst and deactivation is noted directly if the reactor is operating at steady-state conditions. Drawbacks are that: (i) the PFR experiments yield conversions rather than rates; (ii) low flow rates can lead to concentra-

tion and temperature gradients over the stagnant layer surrounding the catalyst pellets; and (iii) care must be taken to ensure plug-flow behavior. Integral operation (high conversion) is adopted for most activity and stability tests, while for kinetic studies, where a low conversion is preferably required, differential operation is applied.

### 3. Six-flow technology

#### 3.1. General description

The basic principle of the six-flow reactor can be seen in Fig. 3. The operation principle of the system is similar to that of a single-flow reactor system. Three different sections can be distinguished: gas mixing section, reactor section, and analysis section. The set-up contains six small easily accessible fixed-bed reactors that run in parallel. The flow rate, the composition of the catalyst bed, and the reactor pressure can be selected independently, whereas the feed composition and the temperature are the same in all reactors. Nowadays, mass-flow controllers for both liquid and gas streams are capable of providing stable molar flow rates, ideally for kinetic studies. Pressure controllers maintain a constant feed pressure for the mass-flow controllers to synthesize a desired flow mixture to be used in the six reactors. A back-pressure regulator serves to maintain the feed

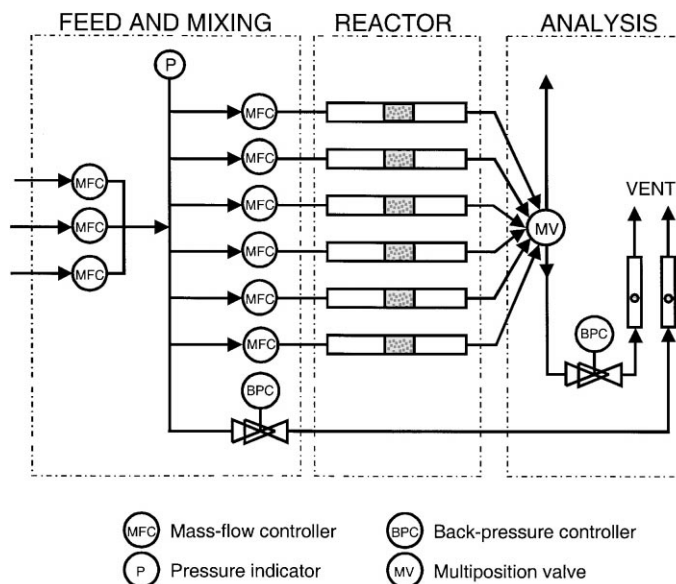


Fig. 3. Schematic flow-sheet of the six-flow reactor system for fast catalyst screening and kinetic studies.

pressure for the six distributing mass-flow controllers to the individual reactors. The excess of the mixture needed to maintain the pressure is vented. Downstream back-pressure regulators maintain the pressure in each reactor. A selection valve sequentially selects the product mixture of each reactor. Various methods of product analysis are available and depend highly on the system under investigation. Usually these analysis techniques are sufficiently fast compared to the time needed to reach a stable catalyst activity. The set-up is PC-controlled and runs unattended. All these features facilitate and accelerate catalyst testing and kinetic investigations. Further reduction of the experimental effort can be obtained by sequential experimental design, carefully planning new experimental conditions, based on previous results [20,27–29].

Of course, the number of six parallel reactors is not a hard, fixed value. More or less, reactors can be put in parallel, depending on the demands. The oven containing the various reactors then needs to be adapted and space restrictions will have to be considered. More reactors also put more demand on the speed of the analysis method. Mass spectrometry is very fast, but cannot always be used. Gas chromatography, which is preferentially used in many cases such as in Fischer–Tropsch synthesis product analysis is inherently much slower.

Nevertheless, even in this case, six reactors were chosen, since the catalysts need a long time to stabilize, which outweighs the longer analysis time.

An interesting idea that was recently put forward in relation to PC-controlled equipment is the temperature scanning reactor (TSR) for kinetic studies [30–32]. The conversion levels at various experimental settings of temperature and space-time are investigated by temperature programmed experiments. Generally, one is only interested in a limited temperature range of about 100 K. In this technique, the data collection grid is so dense that interpolations allowed in an even isothermicity along the reactor axis are in principle, not a strict requirement anymore. Generation of data sets of conversion and exit temperatures as a function of the space-time ( $W/F_A^0$ ) at the same inlet temperature is possible. By polynomial interpolation one can numerically differentiate the  $x$  versus  $W/F_A^0$  curve to obtain the reaction rate at different values of the corresponding space-time. The corresponding reaction temperature is derived from the temperature–space-time correlation. This can be repeated for several pressures and compositions. Finally one obtains a large data set of ( $W/F_A^0$ ,  $x$ ,  $r$ ,  $T$ ) points, that can be used for a thorough kinetic analysis. In principle this seems a promising approach, especially

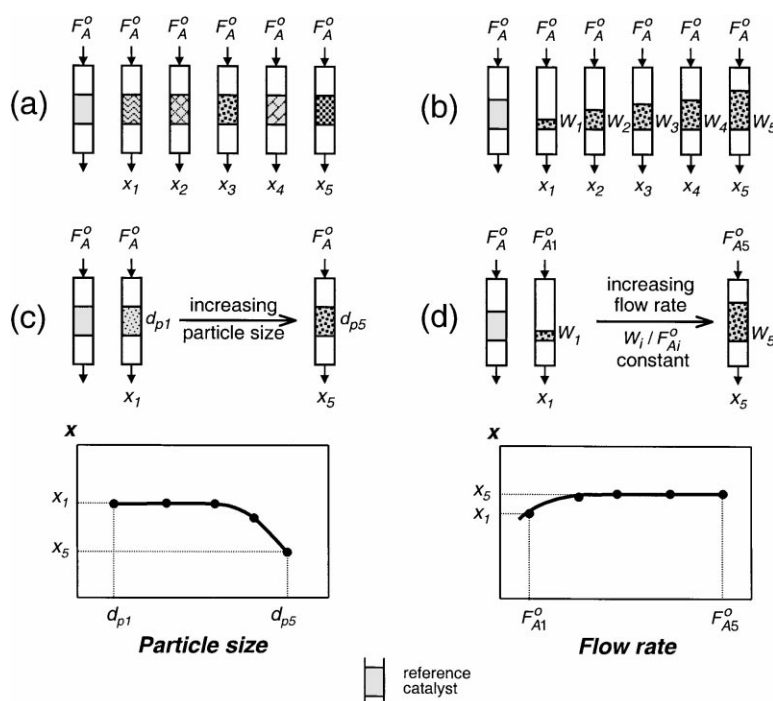


Fig. 4. Operation modes in the six-flow reactor set-up: (a) activity tests and life-time experiments; (b) kinetic studies; (c) and (d) diagnostic experimental tests for the presence of intraparticle limitations and extraparticle limitations, respectively.

when combined with the six-flow set-up, provided that the catalyst does not suffer from deactivation during the whole experimentation.

### 3.2. Operation modes

Fig. 4 shows different possibilities for experiments carried out in a six-flow set-up. Generally, for screening purposes, the reactors can be filled with the same amount of five different catalysts (it is recommended to use always one reactor as reference) (Fig. 4a), and for kinetic studies with different amounts of the same catalyst (Fig. 4b). Activity and stability tests with the same set of catalysts can be carried out in a single experimental run. Variation of  $W/F_A^0$  by changing the amount of catalyst  $W$  or  $F_A^0$  allows a broad range of conversions to be covered in a single run. The six-flow set-up also offers the possibility to investigate the stability of six different catalysts at identical conditions or six samples of the same catalyst at different conditions simultaneously. If both the temperature and the feed composition have to be varied, it was experienced

that it is faster to vary the temperature at a given feed composition and repeat that for different compositions than the other way around. Linear or step-wise temperature programmed experiments and many kinetic experiments are usually carried out during screening.

Finally, it is worthwhile to note the flexibility and convenience of the six-flow reactor in comparison with a single-flow set-up for performing diagnostic experimental tests to verify the presence or absence of transport limitations, which are described in Section 4. Fig. 4c and d show typical results when checking the influence of the particle size (effect of intraparticle limitation) or the effect of the gas flow rate at constant space-time (effect of extraparticle limitation) in the observed reaction rate.

### 3.3. Evolution and evaluation of the six-flow set-up

The six-flow system has been successfully applied in catalyst testing and kinetic studies in our group. PFR have been used in all cases. Table 2 summarizes the past and the current catalytic systems studied and

Table 2

Utilization of the six-flow technology in catalyst development: screening and kinetic studies<sup>a</sup>

Process	Catalytic system	Product analysis	Refs.
CO oxidation	Cu/Cr/activated carbon	GC NO <sub>x</sub> -analyzer	[33–36]
NO <sub>x</sub> reduction with CO	Cu/Cr/activated carbon		
	Cu/Cr/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>		
Water–gas shift reaction	Cu/Cr/activated carbon		
NO <sub>x</sub> reduction with ammonia	Cu/activated carbon	MS	[37–40]
	Mn oxides/activated carbon		
	Mn oxides/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>		
	Modified activated carbons		
	Mn <sub>2</sub> O <sub>3</sub> –WO <sub>3</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>		
Soot oxidation	Ag/Mn/ZrO <sub>2</sub>	NDRI HC -analyzer	[41–44]
	Cu–V/Al <sub>2</sub> O <sub>3</sub>		
	Cu/K/Mo/(Cl)/ZrO <sub>2</sub>		
	Cu/K/Mo/(Cl)/TiO <sub>2</sub>		
	Cu/ZrO <sub>2</sub>		
	Mo/ZrO <sub>2</sub>		
	V/ZrO <sub>2</sub>		
	Cs <sub>2</sub> MoO <sub>4</sub> –V <sub>2</sub> O <sub>5</sub>		
	CsVO <sub>3</sub> –MoO <sub>3</sub>		
	Cs <sub>2</sub> SO <sub>4</sub> –V <sub>2</sub> O <sub>5</sub>		
Chlorofluorocarbons (CFC) hydrogenolysis	[Rh, Ru, Re, Pt, Pd, Ir]/activated carbon	GC NO <sub>x</sub> -analyzer	[45–47]
	Pd/activated carbon		
	Pd–zeolite Y		
	Pd–Mordenite		
N <sub>2</sub> O decomposition	Calcined hydrotalcites (Co, Pd, La, Rh)	GC NO <sub>x</sub> -analyzer	— <sup>b</sup>
	[Fe, Co, Rh, Pd]–ZSM-5		
NO <sub>x</sub> reduction with hydrocarbons	Pt/Al <sub>2</sub> O <sub>3</sub>		
	Pt–ZSM-5		
Fischer–Tropsch synthesis	Co–zeolite Y	GC	— <sup>b</sup>
	Co/SiO <sub>2</sub>		

<sup>a</sup> GC: gas chromatography; NO<sub>x</sub>: nitrogen oxides; MS: mass spectrometer; HC: hydrocarbons; NDIR: non-dispersive infra-red.<sup>b</sup> Current applications.

developed by us. A remarkable example of a successful implementation of some of these ideas was the kinetic study of the selective catalytic reduction of NO over alumina-supported manganese oxide [38]. Product analysis was performed by a mass spectrometer. This yielded data at five different space–times (the sixth reactor served as a blank reference). In one month all kinetic data had been collected. The tremendously increased speed of data generation (5–6 times faster than with a single flow set-up) with this parallel testing system completely outweighs the relatively small additional investment compared to a single-flow

set-up. In fact, this investment only accounts for the addition to the system of the flow distribution and product selection in the reaction section.

*Case study: removal of nitrogen oxides from exhaust gases:* The decomposition of nitrous oxide and the reduction of nitric oxide by hydrocarbons (applicable for nitric acid plants, fluidized-bed combustors and car exhaust clean-up) are currently investigated. A general photograph of the set-up is depicted in Fig. 5. Fig. 6 shows the detailed flow-sheet of the set-up. The above-mentioned sections can be distinguished: feed and mixing, reaction, and analysis. The amount of



Fig. 5. Photograph of the six-flow reactor set-up for nitrogen oxides ( $\text{NO}_x$ – $\text{N}_2\text{O}$ ) removal.

equipment and instrumentation gives an idea of the magnitude of the experimental system. The dimensions of the reactors and the operating conditions for one of these applications are summarized in Table 3.

Several improvements have been made in the six-flow set-up compared to the original one (see references in Table 2):

- The mixing of the feed gases is done in a manifold, which consists of different modules (one for each feed gas). Each module contains a system of two open–close valves, which allow either the entrance of the gas to the system or the purge to the vent. This system produces an optimal mixture of the gases involved, decisive for homogeneity, and minimizes the dead volume.
- Liquid reactant (water in this case) is stored in a stainless steel reservoir, and is fed to the system by means of a liquid mass-flow controller. After mixing with the carrier gas, the stream enters the evaporation chamber unit. Subsequently, the vapor is mixed with the stream coming from the above-mentioned manifold.
- The entire reactor section furnace is placed in an oven maintained at 60–70°C to avoid the need for a separate heating of the lines (Fig. 7a). The maximum allowed temperature of the reactor section is 70°C due to the presence of electronic parts in the digital mass-flow controllers and back-pressure regulators.
- The reactor furnace (Fig. 7b) is made of brass (alloy of copper and zinc with a high thermal diffusivity) although silver or aluminum may also be considered, and tightly fixed to the reactors for an efficient heat exchange. In the metal block, different electrical heating sections are provided, each having its own controller. This arrangement allows the tuning of the electrical input of the various sections during operation, and also to compensate temperature gradients in the catalytic bed due to the reaction.
- Each reactor outlet is equipped with a back-pressure regulator, enabling an independent control of the reactor pressure.
- One of the reactors is used to check for any homogeneous reactions by filling this reactor with an inert sample (usually the diluent).
- The stream to be analyzed is selected with a manifold of two-way valves and not by means of a multi-position valve as suggested in Fig. 3. The main advantage of the manifold is the possible extension when more reactor outlets need to be analyzed, by simply addition of new modules. In addition, versatility should be pointed out too, by independent operation of each module. The dead volume of this device is minimized and no stagnant regions are developed.
- The excess flow stream, vented by the back-pressure regulator before the reactor feeding mass-flow controllers is also analyzed in order to check the exact composition of the feed.
- The set-up is fully PC-controlled and predesigned kinetic runs (pressure and temperature variation) could be carried out automatically within a short period of time. Automation comprises the use of ADAM<sup>®</sup> modules and a Lab-View<sup>®</sup> software package. Compared to automation packages previously used in our laboratory, Lab-View<sup>®</sup> is easier to use and does not require specific programming



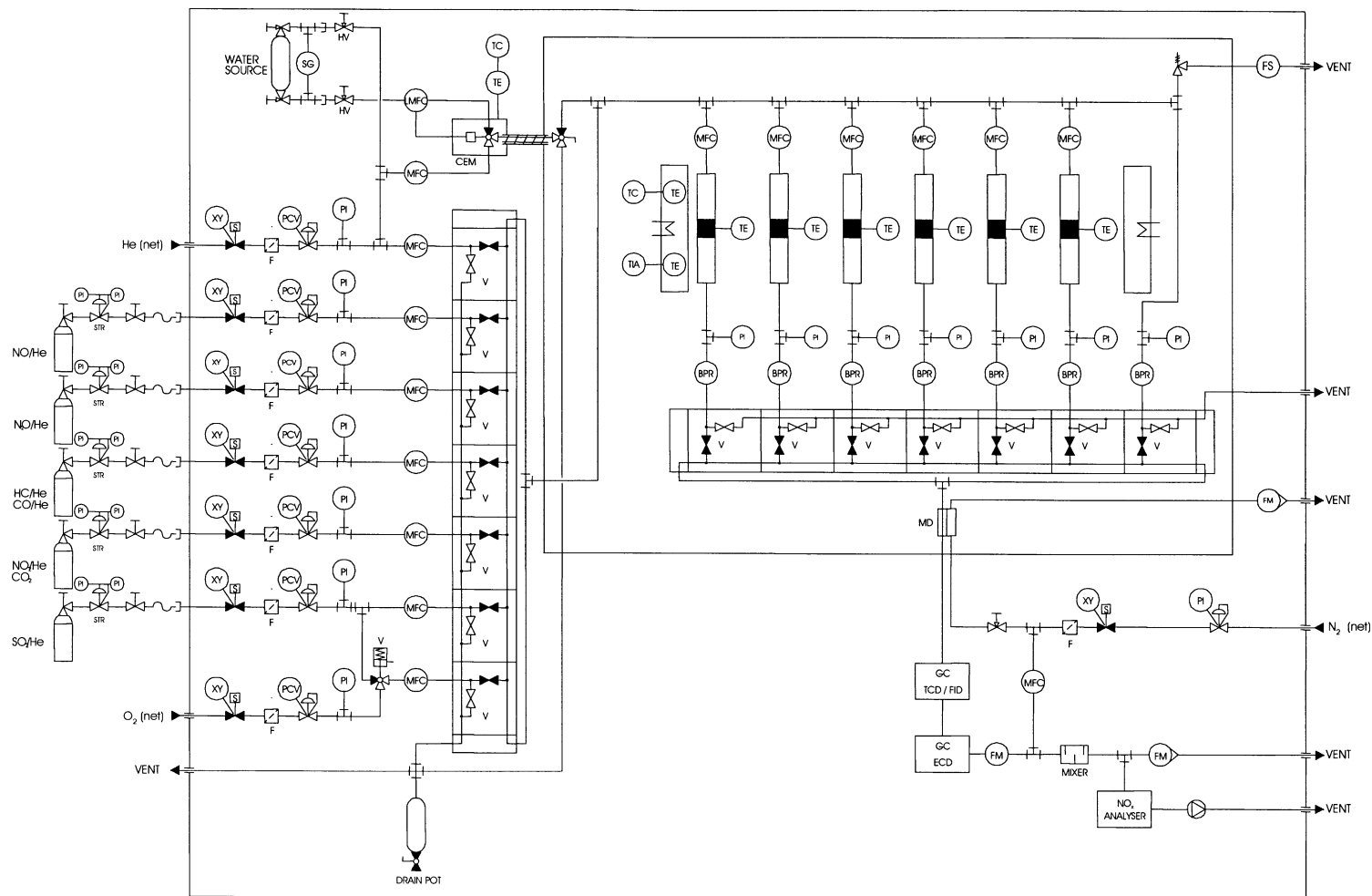


Fig. 6. Detailed flow-sheet of the six-flow reactor set-up for nitrogen oxides (NO<sub>x</sub>-N<sub>2</sub>O) removal.

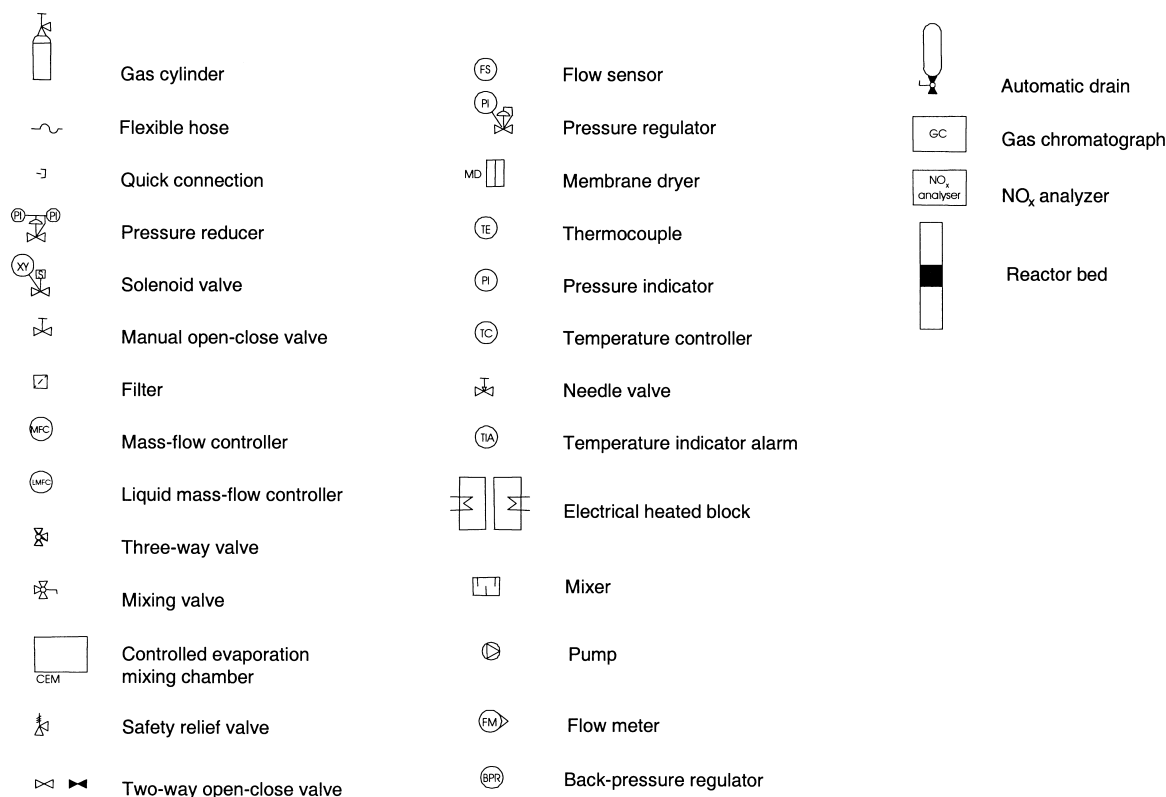


Fig. 6. (Continued).

knowledge, while many sub-routines (VIs) present in the software package can be used for interfacing hardware. The automation of the set-up was completed in four weeks. The data generated during the whole experiment are automatically saved, being directly readable with a standard spreadsheet.

### 3.4. Summary of features of the six-flow set-up

The six-flow nano-reactor system integrates both combinatorial and quantification functions necessary for a catalyst development program, and is therefore considered as a powerful tool for efficient and high throughput catalyst screening and kinetic studies. Typical features of the set-up are:

1. enhancement of the throughput of catalysts to be tested;
2. decrease of time required for kinetic studies and diagnostic experimental tests;

Table 3

Experimental conditions applied in the six-flow reactor for the catalytic decomposition of N<sub>2</sub>O from nitric acid plant exhaust gases

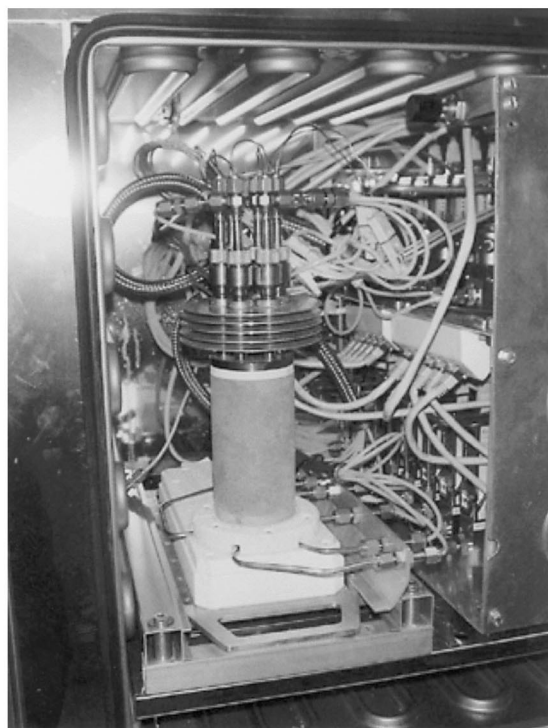
<i>Reactor</i>	
Reactor diameter (mm)	4
Bed length (mm)	10–50
Particle size (mm)	0.1–0.2
Fraction of dilutant (SiC)	0–0.8
<i>Operating conditions</i>	
Temperature (°C)	200–500
Total pressure (bar)	2.5
Total flow (ml/min (STP))	100
GHSV <sup>a</sup> (h <sup>-1</sup> )	30000
Pressure drop (mbar)	<20
<i>Gas mixture<sup>b</sup></i>	
N <sub>2</sub> O (ppm)	1000
O <sub>2</sub> (vol.%)	2
NO (ppm)	250
NO <sub>2</sub> (ppm)	100
H <sub>2</sub> O (vol.%)	1

<sup>a</sup> Gas-hourly space velocity.

<sup>b</sup> Typical for nitric acid plant tail-gases.



**(a)**



**(b)**

Fig. 7. Photograph of the reaction section: (a) reaction furnace containing the reactor oven, mass-flow controllers and back-pressure regulators; (b) detailed photograph of the reactor oven.

3. individual flow and pressure control in each reactor;
4. moderately increased cost compared to a single reactor set-up.

#### 4. Analysis of fixed-bed reactors: a summary of testing criteria

The parallel-flow technology as an efficient tool in procuring data on catalyst activity, stability, and kinetics is not effective if no caution is taken to avoid various phenomena of non-ideal reactor behavior, mass and heat transport limitations on the reactor scale and on the catalyst particle scale, that disguise intrinsic catalytic activities and selectivities. Therefore, the related criteria are briefly reviewed in this paper. The discipline “Catalytic Reaction Engineering” [27,48–53] covers the description of these phenomena since it integrates catalysis, reactor analysis and transport phenomena to aid in procuring and interpreting, and reaction mechanisms.

For a fixed-bed reactor operated under steady conditions, the most important scaling factors are the dimensions of the catalyst bed and the catalyst particles [4]. Usually, hydrodynamics plays a less relevant role than chemical kinetics and intraparticle diffusion in determining the conversions and the selectivities in most fixed-bed processes of practical interest. However, hydrodynamics is important in relation to the pressure drop, several heat transport phenomena hold-up in multi-phase flow systems, and the distribution of fluids over the reactor cross-section.

A series of recommendations and criteria to assure accurate measurements of intrinsic reaction rates are given by Eqs. (1)–(10) shown below. The background of some of these equations is briefly considered hereafter.

1. Minimum bed length (to neglect effect of axial dispersion):

$$\frac{L_b}{d_p} > \frac{20n}{Bo} \ln \left( \frac{1}{1-x} \right) \quad (1)$$

2. Minimum reactor diameter (to neglect wall effects in gas–solid operation):

$$\frac{d_t}{d_p} > 10 \quad (2)$$

3. Maximum reactor diameter (to neglect wall effects in liquid–solid operation):

$$\begin{aligned} d_t^2 &< \frac{L_b D_{rad}}{2u(\kappa/\varepsilon)n \ln(1/(1-x))} \\ &= \frac{2D_{rad}}{SVn \ln(1/(1-x))} \end{aligned} \quad (3)$$

4. Pressure drop in the catalyst bed (Ergun):

$$\begin{aligned} \frac{\Delta P_b}{L_b} &= \frac{150\mu_g}{d_p^2} \frac{(1-\varepsilon)^2}{\varepsilon^3} u + \frac{1.75\rho_g}{d_p} \frac{(1-\varepsilon)}{\varepsilon^3} u^2 \\ &< 0.2 \frac{P_{tot}}{L_b} \end{aligned} \quad (4)$$

5. Extraparticle mass transfer (to neglect extraparticle mass transfer limitation):

$$Ca = \frac{r_{v,obs}}{a'k_f c_b} < \frac{0.05}{|n|} \quad (5)$$

6. Extraparticle heat transfer (to neglect extraparticle heat transfer limitation):

$$\begin{aligned} \gamma\beta_e Ca &= \left( \frac{E_a}{RT_b} \right) \left| \frac{(-\Delta H_r)k_f c_b}{hT_b} \right| \\ &\times \left( \frac{r_{v,obs}}{a'k_f c_b} \right) < 0.05 \end{aligned} \quad (6)$$

7. Intraparticle mass transport (to neglect intraparticle diffusion limitation):

$$\Phi = \eta\phi^2 = \left( \frac{r_{v,obs}L^2}{D_{eff} c_s} \right) \left( \frac{n+1}{2} \right) < 0.15 \quad (7)$$

8. Intraparticle heat transport (to neglect intraparticle heat transport limitation, assuming spherical particles):

$$\begin{aligned} \gamma\beta_i(\eta\phi^2) &= \left( \frac{E_a}{RT_b} \right) \left| \frac{(-\Delta H_r)D_{eff} c_s}{\lambda_{eff,p} T_b} \right| \\ &\times \left( \frac{r_{v,obs}L^2}{D_{eff} c_s} \right) < 0.1 \end{aligned} \quad (8)$$

9. Radial temperature gradient (to neglect effect of radial temperature gradient on reactor scale):

$$\begin{aligned} \frac{E_a}{RT_w} \left| \frac{(-\Delta H_r)r_{v,obs}(1-\varepsilon)(1-b)r_t^2}{\lambda_{eff,b} T_w} \right| \\ \times \left( \frac{1}{8} + \frac{1}{Bi_w} \frac{d_p}{d_t} \right) < 0.05 \end{aligned} \quad (9)$$

10. Bed dilution (to neglect effect of bed dilution on the conversion):

$$\frac{2.5bd_p}{(1-b)L_b} < 0.05 \quad (10)$$

#### 4.1. Assumption of ideal plug-flow behavior

In an ideal PFR, the fluidum can be assumed to flow as a straight front through the reactor. Diffusion and local flows around the catalyst particles and along the wall, however, may cause a disturbing axial dispersion [54]. If the maximum allowed deviation from PFR is set at 5%, a criterion can be set for the minimum ratio of bed length and particle, see Eq. (1) [55,56].

The difference between the packing density in the interior and that near the wall and the flat surface of the wall may also cause a deviation from ideal plug flow. This wall effect causes a higher local velocity near the wall, resulting in a non-flat radial velocity profile, and possibly also bypass of gas along the wall. For gases, the wall effect can be neglected if the ratio between bed diameter and particle diameter is larger than 10 (Eq. (2)) [57].

For liquids, however, the criterion for the bed diameter cannot be used due to a much lower diffusivity and larger ratios are required. Alternatively, the criterion of Eq. (3) should be used for liquids [4]. Note that this implies that there is a *maximum* limit on the bed diameter for liquids, whereas for gases there is a *minimum* diameter to allow neglecting the wall effect. A typical value of the flow profile parameter  $\kappa$  in packed-chromatographic columns with  $d_t/d_p < 5$  is 0.04 [58].

#### 4.2. Pressure drop

The pressure drop over the catalyst bed can be estimated using the Ergun equation, Eq. (4) [59]. The first term in this equation represents the Blake–Kozeny equation for laminar flow and forms the major contribution in laboratory reactors. A rule of thumb is that the pressure drop should be lower than approximately 20% of the total operation pressure in the reactor. Alpay et al. [60] give a method to correct rate coefficients for the effect of the pressure drop.

#### 4.3. Analysis of the mass and heat transport limitations

Effects of transport limitations in heterogeneously catalyzed reactions have been studied extensively [61–68]. It is of utmost importance to check for their presence or absence in particular before performing an extensive kinetic investigation.

For laboratory scale gas–solid operation, the following order in relative importance of the various gradients is usually valid [1]:

$$(T\text{-grad})_{\text{bed}} > (T\text{-grad})_{\text{extra}} > (c\text{-grad})_{\text{intra}}, \quad (T\text{-grad})_{\text{intra}} > (c\text{-grad})_{\text{extra}}$$

The temperature gradients on reactor scale and those due to extraparticle heat transfer are usually the most critical transport phenomena because of the poor heat conductivity of gas–solid fixed-beds. In the case of liquids, however, concentration gradients are usually the most important because liquids have a much higher density and heat conductivity and lower diffusivities.

Although several of the above-mentioned concentration and temperature gradients may occur simultaneously, the proposed criteria are derived neglecting the effects of a combination of gradients.

A highly exothermic or endothermic reaction in combination with a low thermal conductivity of the catalyst bed may cause significant temperature gradients within the particle (*intraparticle*) at its interface with the external fluid phase (*extraparticle*), and in the *radial* and *axial* direction of the reactor.

For *extraparticle* mass transfer, Eq. (5) applies as criterion, where the Carberry number relates the concentration difference over the film to procurable quantities [49]. For extraparticle heat transfer, Eq. (6) applies as criterion [69]. For the heat and mass transfer coefficients in fixed-beds, there are correlations available in terms of dimensionless numbers [50,52, 68,70].

The criterion for *intraparticle* mass transport for an *n*th order reaction under isothermal operation is given by the so-called Wheeler–Weisz modulus, Eq. (7), which also gives a procurable and observable quantity. Mears [69] analyzed the problem of the intraparticle heat transport limitation and obtained an approximate

solution for the maximum temperature rise in the catalyst bed. Based on this result, a criterion for less than 5% deviation from the isothermal rate can be given by Taylor series expansion of the rate, considering the whole cross-section of the reactor for an average reaction rate, see Eq. (8) [56,71].

A criterion for the *radial temperature gradient* in a PFR has also been derived [69], see Eq. (9). The first term represents the dimensionless activation energy, based on the reactor wall temperature; the second term represents the ratio of the heat production rate and the heat conduction rate in radial direction; the last term accounts for the relative contributions of the radial conductivity and the heat transfer at the reactor wall. The latter contains the particle to bed radius ratio and the Biot number for heat transport at the wall. Different correlations can be used for the calculation and estimation of the different parameters involved in the former expression [27,72–74]. From Eq. (9) it follows that dilution of the catalyst bed with inert solids and the use of small tube diameters favor the radial isothermicity. More discussion concerning the use of bed dilution follows in Section 4.5.

#### 4.4. Experimental checks for the presence of transport limitations

Any of the preceding criteria should be considered at best only as a preliminary check, to be confirmed through proper experimental test runs. Additionally, experimental checks may indicate the presence of other effects for which no criterion exists, such as the formation of preferential routes through the catalyst bed (channeling).

Different diagnostic experimental tests have been described elsewhere [1,75]. For the *extraparticle* concentration gradients, it consists of varying the flow rate and the amount of catalyst simultaneously, while keeping the space–time  $W/F_A^0$  constant. If no limitations exist, the resulting conversions should be the same. If temperature effects also interfere, however, these might (over)compensate the concentration effects. This method should therefore be used with caution.

For the *intraparticle* concentration gradients, variation of the particle size, e.g. by crushing and sieving the catalyst, and tests under identical conditions should indicate whether internal diffusion inter-

feres. At small particle sizes the reaction is chemically controlled and independent of the particle size. Only for larger particles a decrease in the observed rate occurs. In particular, at the low-Reynolds number flow rates typically occurring in laboratory exploratory reactors, the method can fail if the check is performed over a too narrow range of flow rates [3]. Hence the range explored should be sufficiently large (i.e. 1–2 orders of magnitude).

The best experimental way to investigate the presence of *temperature gradients* on reactor scale is to dilute the catalyst bed with an inert and good heat conducting material. If gradients are present, lower conversions should result for exothermic reactions and higher for endothermic reactions. The presentation of crude rate data in *Arrhenius plots* to inspect the temperature behavior can give indications of the presence of limiting transport processes by a changing slope ( $\propto$  activation energy) [75]. However, one should be aware of the fact that other phenomena can also induce this: change of the rate determining step, catalyst deactivation or fouling, approach of thermodynamic equilibrium, and ignition phenomena.

#### 4.5. Catalyst bed dilution

The application of catalyst-bed dilution considerably improves the catalyst testing process since it acts upon different aspects such as the dispersion and heat transfer limitation [48]. This dilution technique has been successfully applied in hydrotreating research using trickle flow reactors [4,76]. Low surface area materials such as quartz,  $\alpha$ -alumina, glass, and especially silicon carbide (SiC) are preferred as diluting solids because of their relative inertness.

Dilution of the catalyst bed results in the following decisive positive effects (Fig. 8):

- improved heat conduction in the bed;
- spreading of heat production (or consumption) over a larger volume;
- decreased effect of axial dispersion due to increase of the catalyst bed height;
- investigation of complete catalyst bodies possible, when using fine inert particles, decoupling hydrodynamics and kinetics.

One should be aware that a very high degree of dilution may result in a disturbing sample inhomogeneity, causing an uneven distribution and also bypassing

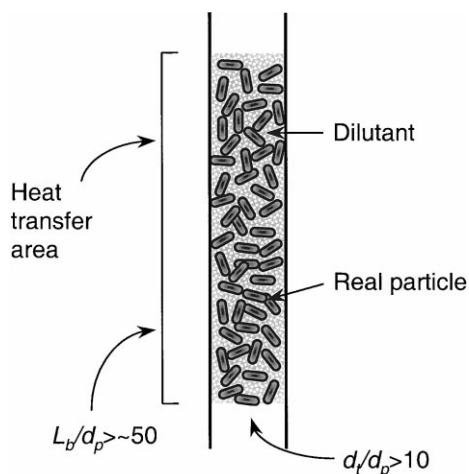


Fig. 8. Testing of complete catalyst bodies by dilution with small inerts.

of the catalyst. van den Bleek et al. [77] evaluated this problem. Eq. (10) applies for an inert bed fraction  $b$  and a 5% maximum acceptable deviation from the ideal situation. This criterion imposes constraints on the maximum particle size as a function of the bed dilution, and it is graphically represented in Fig. 9 for various bed lengths. Generally, catalyst samples should not be diluted more than 5–10 times.

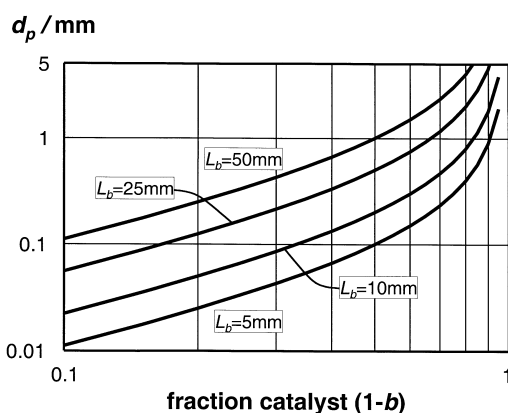


Fig. 9. Maximum allowed particle diameter ( $d_p$ ) as a function of the fraction of catalyst ( $1-b$ ) in a diluted bed at different bed lengths ( $L_b$ ).

## 5. Concluding remark

The six-flow set-up is considered as a powerful tool for efficient and high throughput catalyst screening and kinetic studies. However, several recommendations and design criteria should be fulfilled in order to allow easy and accurate interpretation of the extensive data measured.

## 6. Nomenclature

$a'$	specific external surface area of the catalyst particle ( $a'=6/d_p$ for spherical particles) ( $\text{m}^2 \text{m}^{-3}$ )
$b$	inert fraction of the bed (–)
$1-b$	catalyst fraction of the bed (–)
$c$	concentration ( $\text{mol m}^{-3}$ )
$d_p$	particle diameter (m)
$d_i$	reactor diameter (m)
$D_{\text{eff}}$	effective diffusivity in particle ( $\text{m}^2 \text{s}^{-1}$ )
$D_{\text{rad}}$	diffusivity in the radial direction ( $\text{m}^2 \text{s}^{-1}$ )
$D_{\text{ax}}$	dispersion in the axial direction ( $\text{m}^2 \text{s}^{-1}$ )
$E_a$	activation energy ( $\text{J mol}^{-1}$ )
$F_A^0$	molar flow of component A ( $\text{mol s}^{-1}$ )
$h$	gas–solid heat transfer coefficient ( $\text{J m}^{-2} \text{s}^{-1} \text{K}^{-1}$ )
$k_f$	mass transfer coefficient ( $\text{m s}^{-1}$ )
$L$	characteristic catalyst dimension ( $L=d_p/6$ for spherical particles) (m)
$L_b$	bed length (m)
$n$	reaction order (–)
$P_{\text{tot}}$	total pressure (Pa)
$r_{v,\text{obs}}$	observed reaction rate per unit particle volume ( $\text{mol s}^{-1} \text{m}_p^{-3}$ )
$R$	universal gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$SV$	space velocity ( $\text{s}^{-1}$ )
$T$	temperature (K)
$u$	superficial velocity ( $\text{m s}^{-1}$ )
$W$	catalyst mass (kg)
$x$	conversion (–)

### Dimensionless numbers

$Bo$	Bodenstein (or Péclet particle) number ( $Bo = ud_p/D_{\text{ax}}$ )
$Ca$	Carberry number ( $Ca = r_{v,\text{obs}}/k_f a' c_b = (c_b - c_s)/c_b$ )

$Bi_w$	Biot number at the reactor wall ( $Bi_w = h_w d_p / \lambda_{\text{eff}}$ )
$Re_p$	Reynolds number (particle) ( $Re_p = \rho_g u d_p / \mu_g$ )

### Greeks

$\Delta H_r$	heat of reaction ( $\text{J mol}^{-1}$ )
$\Delta P_b$	pressure drop in the catalyst bed (Pa)
$\varepsilon$	void bed fraction (–)
$1-\varepsilon$	bed fraction of the reactor volume (–)
$\eta$	effectiveness factor (–)
$\phi$	Thiele modulus ( $\phi = L \sqrt{k_v / D_{\text{eff}}}$ ) ( $k_v$ =rate constant per unit volume expressed in $\text{s}^{-1}$ ) (–)
$\kappa$	dimensionless number related to the flow profile (–)
$\lambda_{\text{eff}}$	effective thermal conductivity ( $\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$ )
$\lambda_g$	gas thermal conductivity ( $\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$ )
$\mu_g$	(dynamic) gas viscosity ( $\text{kg m}^{-1} \text{s}^{-1}$ )
$\rho_g$	gas density ( $\text{kg m}^{-3}$ )
$\Phi$	Wheeler–Weisz modulus ( $\Phi = \eta \phi^2$ )

### Subscripts

b	in bulk phase; also bed
eff	effective
g	gas
obs	observed
p	particle
s	at external particle surface
t	tube
tot	total
w	at the reactor wall

### References

- [1] F. Kapteijn, J.A. Moulijn, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), *Handbook of Heterogeneous Catalysis*, Vol. 3, VCH, Weinheim, 1996, p. 1359.
- [2] F. Kapteijn, J.A. Moulijn, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), *Handbook of Heterogeneous Catalysis*, Vol. 3, VCH, Weinheim, 1996, p. 1189.
- [3] L. Forni, *Catal. Today* 34 (1997) 353.
- [4] S.T. Sie, *AIChE J.* 42 (1996) 3498.
- [5] A.W. Czarnk, *Anal. Chem.* (June, 1998) 379A Vol. 70.
- [6] J.N. Kyranos, J.C. Hogan, *Anal. Chem.* (June, 1998) 389A Vol. 70.
- [7] P. Fairley, *Chem. Week* (August, 1998) 18 Vol. 160.
- [8] B. Jandeleit, H.W. Turner, T. Uno, J.A.M. van Beek, W.H. Henry, *Cattech.* 2 (1998) 101.
- [9] E.G. Christoffel, *Laboratory Studies of Heterogeneous Catalytic Processes*, Elsevier, Amsterdam, 1989.
- [10] L.K. Doraiswamy, D.G. Tajbl, *Catal. Rev. Sci. Eng.* 10 (1974) 177.
- [11] K.C. Pratt, in: J.R. Anderson, M. Boudart (Eds.), *Catalysis: Science and Technology*, Vol. 8, Springer, Berlin, 1987, p. 174.
- [12] J.R. Anderson, K.C. Pratt, *Introduction to Characterization and Testing of Catalysts*, Academic Press, Sydney, 1985.
- [13] J.M. Berty, *Plant Oper. Prog.* 3 (1984) 163.
- [14] J.J. Carberry, *Ind. Eng. Chem.* 56 (1964) 39.
- [15] C.O. Bennett, M.B. Cutlip, C.C. Yang, *Chem. Eng. Sci.* 27 (1972) 2255.
- [16] V.W. Weekman, *AIChE J.* 20 (1974) 833.
- [17] J.T. Richardson, H. Friedrich, *J. Catal.* 37 (1975) 8.
- [18] H. Kobayashi, M. Kobayashi, *Catal. Rev. Sci. Eng.* 10 (1975) 139.
- [19] J.A. Richardson, H.F. Rase, *Ind. Eng. Chem. Prod. Res. Dev.* 17 (1978) 287.
- [20] J.M. Berty, *Catal. Rev. Sci. Eng.* 20 (1979) 75.
- [21] C.D. Prater, W.E. Kaufman, *Chem. Eng. Prog.* (September, 1982) 46 Vol. 78.
- [22] J.M. Berty, in: B.E. Leach (Ed.), *Applied Industrial Catalysis*, Vol. 1, Academic Press, New York, 1983, p. 43.
- [23] J.T. Gleaves, J.R. Ebner, *Methods and apparatus for carrying out catalyzed chemical reactions and for studying catalysts*, US Patent No. 4,626,412 (1986).
- [24] J.T. Gleaves, J.R. Ebner, T.C. Kuechler, *Catal. Rev. Sci. Eng.* 30 (1988) 49.
- [25] K. Tamaru, S. Naito, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), *Handbook of Heterogeneous Catalysis*, Vol. 3, VCH, Weinheim, 1996, p. 1005.
- [26] F.H.M. Dekker, A. Bliet, F. Kapteijn, J.A. Moulijn, *Chem. Eng. Sci.* 50 (1995) 3573.
- [27] G.F. Froment, K.B. Bischoff, *Chemical Reactor Analysis and Design*, 2nd Edition, Wiley, New York, 1990.
- [28] G.F. Froment, L. Hosten, in: J.R. Anderson, M. Boudart (Eds.), *Catalysis: Science and Technology*, Vol. 2, Springer, Berlin, 1981, p. 97.
- [29] J.R. Kittrell, in: T.B. Drew, G.R. Cokelet, J.W. Hoopes, T. Vermeulen (Eds.), *Advances in Chemical Engineering*, Vol. 8, Academic Press, New York, 1970, p. 97.
- [30] B.W. Wojciechowski, *Chem. Eng. Sci.* 48 (1993) 2881.
- [31] B.W. Wojciechowski, M.J. Wojciechowski, *ChemTech.* 26 (1996) 32.
- [32] S.P. Aspey, N.M. Rice, B.W. Wojciechowski, *Catal. Today* 36 (1997) 209.
- [33] F. Kapteijn, S. Stegenga, N.J.J. Dekker, J.W. Bijsterbosch, J.A. Moulijn, *Catal. Today* 16 (1993) 273.
- [34] N.J.J. Dekker, J.A.A. Hoorn, S. Stegenga, F. Kapteijn, J.A. Moulijn, *AIChE J.* 38 (1992) 385.
- [35] S. Stegenga, R. van Soest, F. Kapteijn, J.A. Moulijn, *Appl. Catal. B* 2 (1993) 257.
- [36] S. Stegenga, Ph.D. Thesis, University of Amsterdam, 1991.
- [37] L. Singoredjo, R. Korver, F. Kapteijn, J.A. Moulijn, *Appl. Catal. B* 1 (1992) 297.
- [38] F. Kapteijn, L. Singoredjo, N.J.J. Dekker, J.A. Moulijn, *Ind. Eng. Chem. Res.* 32 (1993) 445.
- [39] L. Singoredjo, F. Kapteijn, J.A. Moulijn, J.M. Martín-Martínez, H.P. Boehm, *Carbon* 31 (1993) 213.



- [40] F. Kapteijn, L. Singoredjo, A. Andreini, J.A. Moulijn, *Appl. Catal. B* 3 (1994) 173.
- [41] J.P.A. Neeft, M. Makkee, J.A. Moulijn, *Appl. Catal. B* 8 (1996) 57.
- [42] J.P.A. Neeft, O.P. van Pruissen, M. Makkee, J.A. Moulijn, *Stud. Surf. Sci. Catal.* 71 (1995) 549.
- [43] G. Mul, J.P.A. Neeft, F. Kapteijn, M. Makkee, J.A. Moulijn, *Appl. Catal. B* 6 (1995) 339.
- [44] S.J. Jelles, B.A.A.L. van Setten, M. Makkee, J.A. Moulijn, *Appl. Catal. B* 21 (1999) 35.
- [45] E.J.A.X. van de Sandt, A. Wiersma, M. Makkee, H. van Bekkum, J.A. Moulijn, *Catal. Today* 35 (1997) 163.
- [46] A. Wiersma, E.J.A.X. van de Sandt, M.A. den Hollander, H. van Bekkum, M. Makkee, J.A. Moulijn, *J. Catal.* 177 (1998) 29.
- [47] A. Wiersma, E.J.A.X. van de Sandt, M. Makkee, H. van Bekkum, J.A. Moulijn, *Stud. Surf. Sci. Catal.* 101 (1996) 369.
- [48] F. Kapteijn, G.B. Marin, J.A. Moulijn, in: J.A. Moulijn, P.W.N.M. van Leeuwen, R.A. van Santen (Eds.), *Catalysis: an Integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysis*, Elsevier, Amsterdam, 1993, pp. 251–306.
- [49] J.J. Carberry, in: J.R. Anderson, M. Boudart (Eds.), *Catalysis: Science and Technology*, Vol. 8, Springer, Berlin, 1987, p. 131.
- [50] L.K. Doraiswamy, M.M. Sharma, *Heterogeneous Reactions: Analysis, Examples and Reactor Design*, Vol. 1, Wiley, New York, 1984.
- [51] C.N. Satterfield, *Mass Transfer in Heterogeneous Catalysis*, MIT Press, Cambridge, MA, 1970.
- [52] P. Trambouze, H. van Landeghem, J.-P. Wauquier, *Chemical Reactors. Design/Engineering/Operation*, Editions Technip, Paris, 1986 (Chapter 11).
- [53] J.C.R. Turner, in: J.R. Anderson, M. Boudart (Eds.), *Catalysis: Science and Technology*, Vol. 1, Springer, Berlin, 1981, p. 43.
- [54] H.F. Rase, *Fixed Bed Reactor Design and Diagnostic*, Butterworths, Boston, MA, 1990.
- [55] H. Gierman, *Appl. Catal.* 43 (1988) 277.
- [56] D.E. Mears, *Chem. Eng. Sci.* 26 (1971) 1361.
- [57] C.F. Chu, K.M. Ng, *AIChE J.* 35 (1989) 148.
- [58] S.T. Sie, G.W. Rijnders, *Anal. Chim. Acta* 38 (1967) 3.
- [59] A. Ergun, *Chem. Eng. Prog.* 48 (1952) 89.
- [60] E. Alpay, L.S. Kershenbaum, N.F. Kirkby, *Chem. Eng. Sci.* 50 (1995) 1063.
- [61] P.B. Weisz, C.D. Prater, *Adv. Catal.* 6 (1954) 143.
- [62] E.E. Petersen, *Chem. Eng. Sci.* 18 (1963) 147.
- [63] K.B. Bischoff, *Chem. Eng. Sci.* 22 (1967) 525.
- [64] W.E. Stewart, J.E. Villadsen, *AIChE J.* 15 (1969) 28.
- [65] W. Goldstein, J.J. Carberry, *J. Catal.* 28 (1973) 33.
- [66] F.J. Dumez, G.F. Froment, *Ind. Eng. Chem. Process. Des. Dev.* 15 (1976) 291.
- [67] G. Dogu, T. Dogu, *AIChE J.* 28 (1982) 1036.
- [68] A. Cybulski, M.J. van Dalen, J.W. Verkerk, P.J. van den Berg, *Chem. Eng. Sci.* 30 (1975) 1015.
- [69] D.E. Mears, *J. Catal.* 20 (1971) 127.
- [70] C.N. Satterfield, *Heterogeneous Catalysis in Industrial Practice*, 2nd Edition, McGraw-Hill, New York, 1992 (Chapter 11).
- [71] J.A. Moulijn, A. Tarfaoui, F. Kapteijn, *Catal. Today* 11 (1991) 1.
- [72] D. Kunii, O. Levenspiel, *Ind. Eng. Chem. Res.* 30 (1991) 136.
- [73] M.G. Freiwald, W.R. Paterson, *Chem. Eng. Sci.* 47 (1992) 1545.
- [74] R.J. Wijngaarden, K.R. Westerterp, *Chem. Eng. Sci.* 48 (1993) 1273.
- [75] C. Perego, S. Peratello, *Catal. Today* 52 (1999) 133.
- [76] J. van Klinken, R.H. van Dogen, *Chem. Eng. Sci.* 35 (1980) 59.
- [77] C.M. van den Bleek, K. van der Wiele, P.J. van den Berg, *Chem. Eng. Sci.* 24 (1969) 681.