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Chapter 6

Laboratory reactors

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1. Introduction

The study of catalysts and of catalytic reactions aims at collecting different kinds of information. The comparison of different catalysts for a given reaction, the evaluation of reaction kinetics, of the sensitivity of catalyst to possible poisons, of catalyst durability and regenerability are the most common goals [1,2]. Therefore, the choice of the proper experimental apparatus is of utmost importance, in order to obtain reliable data. In kinetic studies, for instance, unfortunately no methods are yet available, by which the parameters of a catalytic reaction rate equation can be obtained merely by calculation. The determination of such parameters must be based on the analysis of specific experimental data. However, every catalytic process is always accompanied by many physical and physicochemical transport and adsorption–desorption phenomena, which may affect markedly the kinetics of the overall process. Therefore, in such studies the catalyst must be tested in the absence of any temperature and concentration gradients. These conditions may be difficult to be fulfilled, especially in relatively large catalyst beds. Moreover, measures are usually carried out on the bulk fluid reactants and products, so leading only to average values, referring to the overall catalyst mass. To evaluate the intrinsic reaction kinetics, the data must be free from diffusive intrusions and this can be obtained only by accurately designing the experiences and by properly choosing the experimental setup. In addition, the accuracy and reliability of the data must be matched with the time and cost constraints.

In some cases if the shape of the industrial catalyst has been preoptimized (e.g., cylindrical pellets), and fluid-dynamic conditions are similar to the industrial ones, concentration and temperature gradients between the bulk fluid phase and the pellet can be accepted in some way, determining a macrokinetics that include the diffusive effects.

Of course, such kinetics cannot be extrapolated to a different catalyst shape.

The goal of the present contribution is not to present a comprehensive review of the whole set of experimental systems coming from the literature, but to describe the most significant apparatuses usually employed in intensive laboratory experimentation and to provide a few significant examples of how some technical problems have been faced and solved in special, but not infrequent situations. Indeed, every catalytic system may be considered atypical, at least in part. So, unfortunately, one reactor type will not produce the desired data for all situations and the "universal" reactor cannot be imagined, although many reactions present common aspects, which can be studied by means

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of more or less standardized apparatuses. Therefore, for each new reacting system, the "best" laboratory reactor has to be chosen by comparing the "pros" and "cons" of the ca. 20 different kinds of available reactors for that particular case.

1.1. Laboratory reactors

The very large number of papers and reviews on the subject makes it difficult not only to write a complete list, but even to classify the various laboratory devices for catalytic investigation [3–32]. The knowledge needed for a proper selection is not trivial and the choice is imposed by the specific reaction system and by the kind of information needed. The most frequently employed laboratory reactors may be summarized as follows.

1.1.1. Ideal reactors

Ideal reactors are those in which any temperature or concentration gradients may be considered absent. Isothermal, adiabatic, plug-flow, CSTR, either differential or integral batch, semibatch or continuous tubular reactors fall within this class. For gas–solid catalytic reactions the most commonly used are the fixed-bed, tubular, continuous reactors, while for liquid–solid catalytic reactions the slurry CSTR (continuous stirred tank reactors) are usually chosen. For gas–liquid–solid triphase systems the trickle-bed reactor is the choice of election. Both the differential and integral reactor technique may be employed. In the first case the overall conversion is kept as low as possible, by simply varying the catalyst weight or the reactants feeding rate, at least within given limits. This usually ensures ideal behaviour also with fixed-bed tubular reactors, unless very highly exothermic reactions have to be studied. In this case diluting the catalyst with inert solid may help in reducing the local hot spots. The best isothermal behaviour is obtained through different dilution in the various parts of the catalyst bed.

The main advantage of a differential reactor, with respect to the integral one, is the extremely simple form of the reaction rate (r) equation:

$$r = (y_f - y_o)/\tau \qquad (1)$$

y_f and y_o being the molar fractions of reactant at reactor outlet and inlet, respectively, and τ the time factor. On the other hand, the differential reactor technique may be employed easily only for the determination of initial reaction rates for kinetic purposes. When higher conversions have to be studied, many problems may arise with fixed bed reactors, the main of which is to prepare the feeding mixture, the composition of which should be as similar as possible to that present at such conversion levels in the integral reactor. One critical situation is given by hydrocarbons selective oxidation, in which a high number of intermediates form in very small amount during the reaction. Such species are often very labile and cannot be isolated, but generally they determine the overall trend of the reaction. One could employ an integral reactor to feed the differential one, but the best way to overcome the trouble is to employ a gradientless, recirculating reactor (vide infra). Kinetic data obtained with integral reactors are generally more accurate, due to the easier analytical problems.

Liquid–solid slurry CSTR generally are not affected by temperature gradients, due to the buffering effect of the liquid phase, while trickle-bed gas–liquid–solid reactors are frequently affected by mass transfer limitations associated with the diffusion of the gaseous reactant through the film of the liquid reactant percolating through the bed of solid catalyst particles.

For testing the sensitivity to poisons of a series of catalysts, the pulse reactor technique may be employed. A steady flow of inert gas is passed through a small bed of catalyst and immediately sent to the analytical system. If a gaschromatograph is employed, the catalyst may be placed within the same GC column, just before the partition phase. The pulses of reactant are injected in the carrier gas by means of a hypodermic syringe, through a rubber septum or a multiway gas-sampling valve.

1.1.2. Gradientless or constant gradient recirculation reactor

The main advantage of constant gradient or gradientless reactor is that diffusive effects may be rendered negligible or carefully measured. The recirculation of the reacting fluid phase can be external or internal. Under such conditions, the reaction rate may be calculated by means of simple mass-balance equations. Two main types of reactors are available: the fixed-bed, with external or internal gas recirculation, and the stirred or spinning basket reactor. For gas–liquid–solid triphasic reactions, neither external nor internal fluid recirculating systems proved as effective as stirred or spinning basket systems.

The scheme of a recirculation reactor is shown in Fig. 1. A simple material balance

$$Fy_o + F_R y_f = (F + F_R) y_i \tag{2}$$

F_j being the flow rates and y_j the reactant molar fractions, shows that for a sufficiently high recirculation ratio, i.e. if $(F_R/F) > 25$, then $y_i \cong y_f$. Therefore, the reaction rate may be expressed by Eq. (1), no complex synthetic mixtures being requested to feed the reactor when high conversion rates have to be evaluated. However, a critical point of this arrangement is the recirculation pump, which must provide the necessary flow rate, without contaminating the fluid, nor presenting an excessive internal dead volume.

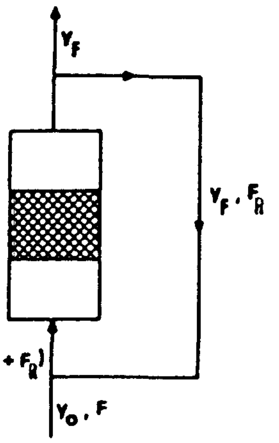

Fig. 1. Scheme of recirculation reactor.

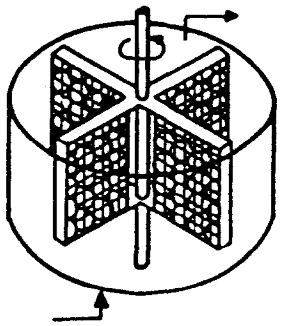

Fig. 2. Spinning basket (or Carberry or Notre Dame) reactor.

When employing a CSTR system, the latter can be designed in such a way that a given amount of reacting fluid is continuously recirculated. Such an arrangement allows to determine the degree of conversion as a function of the mixing degree or recirculation rate.

Stirred reactors and mainly spinning basket or Carberry reactors, (Fig. 2), may be operated at higher equivalent recirculating rate, corresponding to higher rotating speed of the catalyst basket. If the reactor is correctly designed, with proper form of both basket and baffles, gradientless conditions are easily attainable. However, the catalyst temperature cannot be measured directly. Such a disadvantage is overcome if the catalyst is put in a fixed basket of either cylindrical or annular form (Fig. 3). The reactor shown in Fig. 3b has been repeatedly improved up to the actually most used models commercialized as Berty or Mahoney reactors (Fig. 4).

As a practical elementary rule, the lower flow rate of recirculating gas or the lower spinning speed of the basket, still able to ensure negligible diffusive intrusions and perfect mixing of the fluid phase, should be determined under the actual reaction conditions. A rapid procedure for this check is to inject a steady flow of a tracer fluid (e.g. CO_2) in the carrier gas (e.g. He) flowing through the reactor and to plot

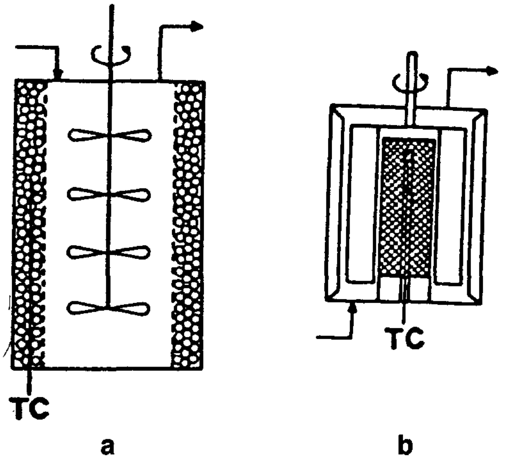

Fig. 3. Fixed basket recirculating reactor with: (a) annular, (b) cylindrical, basket.

$1/(C_0 - C)$ vs. tv/V, C_0 and C being the tracer concentration at reactor outlet and inlet, respectively, t the time, v the volumetric flow rate of the carrier and V the reactor volume. When a straight line is obtained, represented by the equation:

$$(C_0 - C)/C_0 = 1 - e^{-tv/V} \tag{3}$$

perfect mixing has been attained. In this experimental checking, care must be taken in order to prove also that a significant flow crosses the catalyst bed, since perfect mixing behaviour could be masked by good mixing in the impeller cavity only. The bed cross flow rate is easily checked by comparing the pressure drop generated by the impeller with that calculated through the usual pressure drop vs. flow relationships.

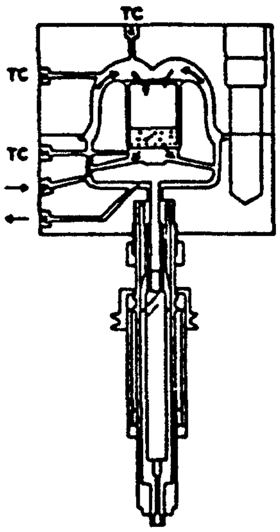

Fig. 4. Berty–Mahoney recirculating reactor.

A common design problem of both spinning basket and internal recirculation reactors is the overheating of shaft bearings, especially at high reaction temperature. Normal lubricants being excluded, to avoid contamination of reacting fluid, refrigerating jackets and long shafts, with bearings placed away from heated parts, are usually employed. Another problem is the gas tightness at the shaft exit points, normally solved by driving the shaft magnetically.

A further problem for the spinning basket reactor could be a different performance of catalyst pellets located near the shaft, with respect to those located at the end of basket wings. This is due to different heat and mass transfer characteristics, owing to different relative gas to solid rate.

1.1.3. Slurry, trickle-bed and fluidized bed reactors

Liquid–solid catalytic reactions are usually studied by means of slurry reactors, either batch or CSTR. In these reactors the powder of solid catalyst is suspended in the stirred reacting liquid mixture. Reactions between a gas and a liquid, catalyzed by a solid, are frequently studied by means of a reactor in which the liquid trickles down a bed of solid catalyst particles, while the gaseous reactant flows through the reactor, both countercurrently or cocurrently.

With slurry and trickle bed reactors, the main problems arise from some at present largely understudied interphase phenomena, such as those connected with gas–liquid and gas–liquid–solid heat and mass transfer. Other still badly answered questions are how and to what extent interphase surface areas depend on various operative parameters, such as reactants flow rates, stirring speed, reactor and baffles geometry, and so on.

Fluidized bed reactors have been originally developed by petroleum industry, to overcome the drawbacks due to rapid coke deposition over the catalyst. In such reactors the bed of finely powdered catalyst is crossed upwards by the flow of reacting gas at a flow rate sufficiently high to suspend (fluidize) the solid particles. A part of the latter may be continuously entrained out of the reactor by the gas, so to be regenerated in a different reactor. Ideal conditions are practically unattainable in laboratory fluidized-bed reactors, due to the unavoidable temperature, concentration and fluid flow disuniformities. As a consequence, it proves usually quite harmful to scale-up data from laboratory to larger scale fluidized-bed reactors.

1.2. Criteria for choosing and sizing a laboratory catalytic reactor

The choice of the reactor is usually made by considering the following points:

(i) Type of information required.

(ii) Performance factors upon which the selection is to be made.

(iii) Type of reactors to be considered.

(iv) Listing of each of the performance factors for each of the reactors.

(v) Ranking the choices available on the basis of the performance factors for each reactor.

In order to identify the performance factors, it is important to consider the objective of the experiments and the data needed. These, in turn, depend on the application, i.e. on the type of information required.

Let us consider, for example, a kinetic study to be carried out on a multiphase catalytic system. The main requirement is that meaningful and reliable kinetic data are obtained. The latter must be free from diffusive intrusions, catalyst deactivation effects and perfectly isothermal. Further troubles could arise from sampling and analysis of the product, from initial and/or operational cost, from the time to obtain the data and from problems in data handling. Ranking in importance the attributes for selecting the reactor for this particular case, one gets:

- isothermality
- mass-transfer intrusions
- data analysis and sampling
- catalyst deactivation
- construction difficulty and cost
- operational cost.

The first performance factor is the uniformity of temperature in time and position within the reactor. Indeed, temperature non-uniformity can greatly affect the rate of competing reactions. Isothermality can be affected by heat of reaction, intrinsic reaction rate and mixing pattern within the reactor. The latter, in turn, depend on reactor size and shape, on reactants flow rate and on catalyst particle size.

Mass-transfer limitations depend on the relative rate of mass transfer of reactants and products with respect to reaction rate. Factors affecting this performance factor are the intrinsic reaction rate, mass transfer coefficients, effective diffusivities and particle size.

Data analysis and sampling performance factors refer to the easiness of sampling and accuracy of analysis of reactants and products. Sampling is particularly difficult for multiphase systems. In–out material balance around the reactor is perhaps the most sensitive parameter for testing these performance factors, that are affected mainly by product composition (gas–liquid–solid), intrinsic reaction rate and degree of mixing within the reactor.

The catalyst deactivation performance factor depends on the extent to which this factor masks the measured reaction rate and on the ease of decoupling these effects. Deactivation frequently affects preferentially one reaction path with respect to the others. The reactors with longer residence time are more susceptible to this effect. Factors affecting this parameter are catalyst deactivation rate, reaction rate, mode of reactor operation and residence time.

Construction difficulty and cost performance factors weigh the easiness of construction and cheapness of the selected reactor. Factors affecting this parameter are reactor type and size, reaction rate, reaction heat, and type of catalyst.

Operational cost performance factor refers to the cost of reactants and of reactor operation and maintenance.

Similar considerations may be made for any different case. However, the most common situation encountered in catalysis studies is a gaseous reactant, which is transformed into products over a solid catalyst, through a more or less exothermic reaction. Hence, in the following only the most commonly employed reactors will be considered, aiming at collecting the information needed for designing a fixed-bed, adiabatic or multitubular commercial reactor, for a catalytic exothermic reaction.

1.2.1. Exploratory reactor

The goal of this reactor is to characterize and compare the activity of several catalyst samples (catalyst screening), in the absence of diffusive intrusions, both of heat and mass. It is usually made of a straight or U-shaped tube, heated by immersion in a fluidized sand bath or through a massive metal block, to minimize any temperature gradient. The sand bath or the metal block are heated by an electric furnace. The tube diameter is rather small (0.5 to 2 cm) and temperature is measured by thin thermocouples inserted in axial thermowells and/or in the external metal block. Straight tubular reactors are kept vertically, to avoid the risk of reactants bypassing, due to possible "sitting down" of catalyst particles. Downward flow of the reacting gas is preferred, to avoid entrainment of catalyst powder.

By charging small amounts (0.5 to 10 g) of catalyst, many different samples can be tested in short time, optimizing simultaneously also the gas composition and reaction temperature. The size of catalyst particles ranges preferentially between 400 μm and 2 mm, to keep reasonably low the pressure drop of the reacting gas through the catalyst bed, to reduce the risk of internal diffusion limitations and of reacting gas bypassing phenomena. Properly ground inert material can be added to very fine catalyst particles, to avoid sticking and to ensure a sufficiently high gas flow rate, without unreasonable pressure drop. Blank runs in the absence of catalyst, but in the presence of these additives are always to be carried out, to check the possible catalytic effect of such materials or of reactor tube wall, or the presence of uncatalyzed gas-phase reactions.

Low surface area materials, such as quartz, α-alumina, silicon carbide or glass are preferred as diluting solids, due to their real inertness. High surface area materials, such as silica gel, although intrinsically inert, may show undesired effects, since they can adsorb and release harmful impurities, acting as poisons or coke precursors.

Frequently catalyst samples showing high initial activity become unacceptable after 50–100 h on-stream. Samples surviving to this first check generally become stable or decay very slowly, due to progressive poisoning or fouling.

Finally, the absence of thermal and concentration gradients must always be checked, by carrying out parallel runs with reactors of different diameter (by at least 50%) and with different catalyst particle size.

An example of exploratory laboratory reactor is shown in Fig. 5. It represents the current end point of the evolution of such a model in the author's laboratory. The main feature is the built-in fluidized sand bath, by means of which up to 50 cm^3 of catalyst bed volume may be heated with very good temperature uniformity (±1°C). More than fifty reactors of this model have been used by the author, with diameter and length of reaction tube specially adapted to the various reactions at hand. Most of them are made of Pyrex glass, for temperatures up to 550°C. Some have been made of quartz, for temperature up to 800°C. Crushed silicon carbide (60–70 mesh) proved to be the best fluidizable "sand", as for thermal resistance and crushing strength at any temperature. By employing such a reactor many catalyst screenings, kinetic and mechanistic studies have been car-

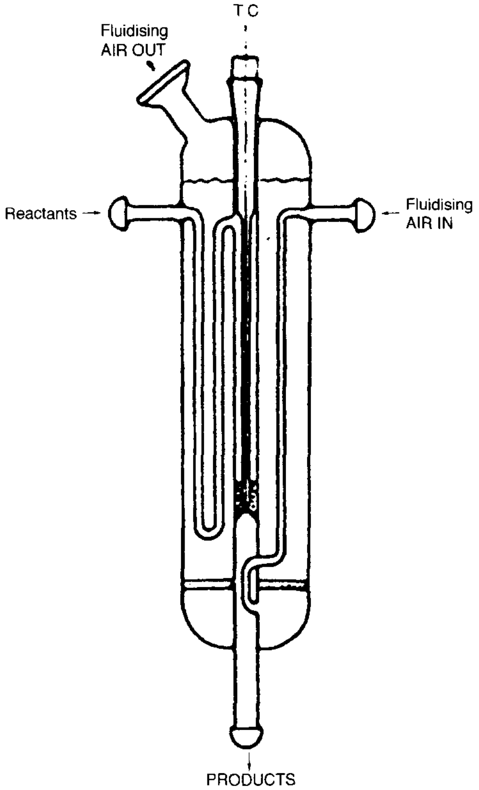

Fig. 5. Exploratory reactor, heated through built-in fluidized sand bath.

ried out under both oxidising and reducing conditions, at temperature ranging from 100 to 750°C.

Many reactions of industrial interest take place at high pressure: this of course makes necessary the use of steel reactors.

1.2.2. Catalyst optimisation reactor

The best catalysts selected through the previous screening undergo a further screening, after preparation and forming in a shape (pellets, extrudates, spheres, saddles, hollow cylinders, etc.) suitable for the commercial reactor. This of course entrains a considerable number of comparison runs, to test different preparation procedures, or different supports and/or binders.

The reactor for these tests must have a larger diameter, preferably of the order of the commercial reactor, if the latter will be multitubular. A typical value is in the range 10–40 mm with length ranging from 50 to 100 cm. Usually a 3 mm o.d. axial thermowell is fitted in the tube, to monitor the axial temperature profile. Thermal and concentration gradients can now be present very frequently. The former can be reduced by heating the reactor through a series of furnaces heated at different temperatures and by diluting the catalyst with different amounts of inert material along the bed. When such gradients are unavoidable, a relatively complex mathematical model can be employed, to simulate the temperature profile and to optimize the diameter and length of the reactor and the flow rate of reactants. Sometimes an excessively low value of catalyst effectiveness, leading to low selectivity, pushes the researcher to reformulate the catalyst structure, e.g. through a bimodal distribution of pore diameter, or the deposition of a thin layer of active phase over a large-pored, low surface area support, such as α-alumina. Furthermore, even if the process will be carried out at atmospheric pressure, the catalyst has to be tested also at a slightly higher pressure, corresponding to the pressure drop through the catalyst bed and the product-recovery system, following the reactor. Typical values are 2 to 4 bar. Such a pressure increasing can affect significantly the kinetics of the reaction and entangle the dissipation of heat generated by the reaction. Indeed, e.g. for a first-order reaction, to increase the pressure from 1 to 4 bars means a fourfold increasing of the reaction rate, accompanied by a fourfold increasing of heat evolved per unit volume of catalyst bed. This entrains a radical modification of temperature profile, which can be easily monitored by the axial thermocouple.

If the fluidized bed reactor has been chosen, the usual diameter of the tube for both the exploratory and optimising steps is 1 to 2″ (ca. 2.5 to 5 cm). Wall effects are practically unavoidable in this case, especially for lower diameter tubes. This usually leads to better catalyst performance, with respect to the very large commercial reactors, since the gas–solid contact is worse, the larger the diameter of the reactor and the higher the superficial flow rate of the reacting gas.

1.2.3. Prototype reactor

When a multitubular reactor has been identified as the best solution for the commercial unit, some further tests are needed, by employing a single tube of the same diameter and length of the final reactor, in order to check as tightly as possible the behaviour of the latter. Usual dimensions for the tubes of fixed-bed reactors are 2.5 to 5 cm in diameter and 3 to 6 m in length. Of course, runs on this prototype reactor are rather expensive, due to the dimensions of the reactor, to the amount of reactant consumed and to the much more complex nature of the overall reaction unit, requiring additional control instruments, additional heating furnaces, etc. However, the information collected through these experiences may be very important for the following reasons.

(i) The higher flow rate of reacting gas and the different diameter of the reactor may change significantly the temperature profile, entailing a significant change in catalytic behaviour. Though this behaviour can be simulated through more or less sophisticated mathematical models, the correlation for the evaluation of thermal conductivity of the beds of solid particles are rather inaccurate. This is particularly true when the size of catalyst particles is relatively large, so that the ratio of tube diameter (d_t) over particle diameter (d_p) is relatively low, i.e. of the order of 3 to 6, a typical situation in practice.

(ii) Pressure drop along a long tube may be relatively high, so to affect considerably the pumping cost for the reactant and the kinetics of the reaction, especially just after the reactor inlet, where the reactant is highly concentrated.

(iii) The resistance to heat transfer is usually localized within the reactor, sitting by ca. 50% at the inner tube wall and by ca. 50% across the bed of particles. As a consequence, it is important to determine very carefully the temperature profile, which is a function also of gas flow rate and of thermal properties of the fluid phase.

(iv) Frequently a different pressure drop through the catalyst bed is noticed for different packing of the reactor, especially for low values of the d_t/d_p ratio. This must be checked, to avoid different flow rates in the various tubes of the multitubular commercial reactor. Furthermore, the heat transfer coefficient at the inner wall of the reactor depends significantly on shape and size of catalyst particles, because the mode of packing of the latter depends on such parameters.

(v) The design of the commercial reactor entails also the solution of several problems concerning the mode of cooling the external wall of reactor tubes, e.g. through a recirculating fluid, or the uniform distribution of the reactant to the whole set of reactor tubes. The latter problem is usually solved during packing of catalyst, by adjusting the amount of catalyst in the various tubes, so to have the same pressure drop in each of them.

(vi) It is usually important to produce a relatively large amount of reactor effluent, in order to check the constancy of its quality over longer time-on-stream periods, to test the separation procedure for recovering the product at the desired purity and to provide samples for marketing evaluation.

If the reaction will be performed adiabatically in an industrial fixed bed reactor, experimentation can be programmed (including isothermal tests at different temperatures), to obtain a model to design the industrial reactor.

Moreover, a pilot adiabatic reactor can be operated as a slice of a larger-bed reactor.

1.3. Fundamental accessories of laboratory catalytic reactors

The reactor constitutes the heart of any apparatus for testing catalyst activity, for collecting kinetic data, etc. However, no reactor can be employed in the absence of at least some fundamental accessories. The list of the latter includes means for heating and maintaining the reactor at the desired temperature and pressure, for feeding the reactants at the desired flow rate, for recirculating the reacting fluid at the desired rate, for collecting and analyzing the products, so to determine conversion and selectivity to the various species and check the material balance around the reactor. This minimal list is usually implemented by a series of more or less sophisticated devices, allowing to carry out the reaction runs, to collect, weigh and analyze the samples of reactor effluent more or less automatically, or even in a computer-driven, completely unattended, automated way. A considerable number of "all-included", multipurpose, almost "turn-key" apparatuses are also on the current market.

1.3.1. Isothermal heating media

In principle, any method ensuring the reaction zone to be kept under isothermal conditions can be used to heat laboratory reactors. Thermostatic baths or jackets, with water (up to 100°C), oil (up to 250–300°C), fused salts (from 250 to 520°C), molten metals (from 350 to 700°C), have been proposed and employed. Fused salts and metals may be harmful, in spite of their excellent heat transfer properties. Induction heating and electrically heated large metal blocks are also used in many cases. However, among the most versatile and safe methods, the fluidized sand bath is largely employed. As mentioned, temperatures up to 800°C can be easily attained, with temperature uniformity hardly obtainable by other means.

1.3.2. Temperature and pressure meters and regulators

Thermocouples and Pt-wire thermal sensors are the most common devices for detecting temperature of laboratory apparatuses. Simple on–off temperature controllers or more sophisticated devices, providing a proportional (P), or a proportional-derivative (PD), or a proportional-integral-derivative (PID), or a proportional-integral-double-derivative (PIDD) action, based on the difference between actual and set-point temperature, are largely employed. Of course, the best results, usually within ±0.5°C of set-point, are provided by the most complex PIDD apparatuses.

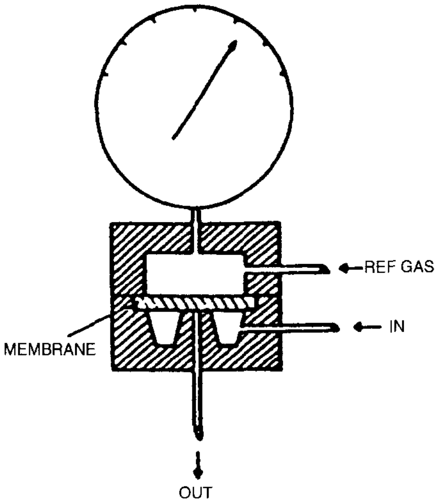

Fig. 6. Pneumatic relief valve.

Pressure can be controlled by means of relief valves, preferably equipped with a filter and/or a small well, to prevent malfunctions due to solid particles entrained by the fluid. Counteraction on relief device by metallic springs ensures accuracy hardly better than ±5% of set-point. Much better results, usually within ±0.5% of set-point, are ensured by a reference gas, pressurized to set-point value, acting on a metal, rubber or PTFE membrane, as in Fig. 6.

Although U-tube differential manometers are frequently employed at low pressure, the latter is usually monitored by Bourdon manometers or membrane-type sensors, able to provide an electrical signal for computer interfacing.

1.3.3. Flow meters and regulators

The cheapest, but accurate flow meters for low-pressure service are the capillary Poiseuille devices, coupled with a simple U-tube differential manometer. Rotameters are also frequently employed. By proper armouring, the latter can be used up to 100 bar pressure. However, usually they cannot have a max/min flow range

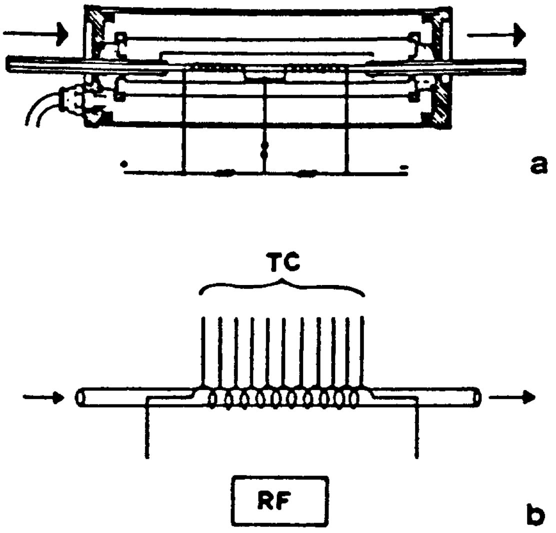

Fig. 7. Thermal-conductivity-based mass flow meters: (a) Setaram, (b) Hastings–Raydist.

larger than 10/1 and they are relatively less accurate. Better accuracy is provided by thermal-conductivity-based mass flow meters, which essentially read the temperature change, due to fluid flow, of electrically heated filaments, wound around the walls of the metering tube (Fig. 7).

Flow rate control may be obtained by manually operated needle valves, or by electrically operated membrane valves, driven through the signal generated by the flow meter. The valves must be always protected against dust particles, by a thin-pore (5 μm or less) filter. Liquids flow is frequently regulated by metering pumps. The latter can be those normally employed in HPLC. For very low flow rates, positive displacement syringe pumps are preferred, due to the absence of any pulsation.

Many different types of pumps have been suggested for the external recirculation of the reacting fluid: diaphragm, rotary, electromagnetic, peristaltic, centrifugal and bellow pumps, driven either electrically, electromagnetically or by means of pressurized gas. Their common critical point is the risk of contaminating the fluid by traces of lubricant or the possible catalytic action of the internal walls of the device.

1.3.4. Techniques for the analysis of reactants and products

Different analytical methods are employed, according to the nature of the fluid, to the reactor adopted and to the goal of the research. With continuous reactors, in-line methods are usually preferred when "instant" conversion data have to be collected, or when continuous monitoring of reactor effluent composition is needed, or when using completely computer-driven, automatic-sampling reaction apparatuses. Off-line analysis is preferred for collecting "integral" conversion data, because of the possibility of repeating the analysis of collected samples.

An elementary safety policy is the systematic, periodical checking of the reliability and effectiveness of the adopted method, especially when complex mixtures have to be analysed. The check should be done by different-nature methods, not only as a control of the analytical correction factors, but also to verify that neither quantitative, nor, even worse, qualitative errors were made.

The most common analytical techniques are GC, HPLC, UV-vis, IR and chemiluminescence spectrometries, MS, EPR, NMR, radioactive tracer monitoring, conductimetry, refractometry, and viscometry.

Gas chromatography (GC) is by far the most employed routine technique, due to versatility, reliability, easy use and relatively low cost. Fully computer-driven instruments are normally available, for in-line analysis, avoiding any intervention of the operator. In many cases this technique is practically irreplaceable, especially for complex hydrocarbons mixtures. HPLC (high pressure liquid chromatography) is conceptually similar to GC. A liquid solvent being the carrier fluid, high pressure is often needed to keep it in liquid phase. This technique is particularly useful for some classes of high molecular mass, complex structure species.

Some spectrometric techniques, such as UV-vis, IR and chemiluminescence, enjoy a long tradition and extensive diffusion, owing to their simple use, good reliability and relatively low cost. Mass spectrometry (MS) is also frequently employed, mainly with simpler quadrupolar, lower cost instruments. In spite of high cost, the GC-MS combination proves unique, during the optimisation of the analytical procedure, to recognize the various species, separated by the GC, and to check if the various GC peaks correspond to single or multiple species. Although less frequently, GC and spectroscopic techniques are combined for analysing less common, complex mixtures.

Radioactive tracers detection proves sometimes unique, for investigations concerning the intimate mechanism of the reaction, permitting to monitor the complex path of a given species.

The main advantages of conductimetry, refractometry and viscometry for analyzing liquid mixtures are low cost and easy application. On the other hand, their accuracy is not very high. Refractometry and viscometry are particularly valuable for the analysis of polymeric substances.

1.4. Diffusional, wall and segregation effects

Diffusional effects in heterogeneously catalyzed reactions have been studied quite extensively [33–55]. As repeatedly mentioned, it is of utmost importance to check for their presence or absence, before the study of any catalytic reaction, and mainly before the collection of any kinetic data.

1.4.1. Analysis of concentration and temperature gradients

For a catalyst particle immersed in a flow of fluid reactant, different reaction regimes may establish when varying temperature. When temperature is sufficiently low, the chemical reaction may be so slow that most of the available potential is consumed for the chemical reaction itself, any diffusion phenomena being faster. This case is referred to as a chemical regime. In it the whole catalyst surface, external and internal, is exposed to the same concentration of reactant, present in the bulk fluid phase.

With increasing temperature, the diffusion coefficient grows less than reaction rate constant, which grows exponentially. A growing fraction of the available potential is then consumed to favour diffusion and an appreciable concentration gradient can be detected along the radius of the catalyst particle and, by further increasing temperature, also across the fluid film surrounding the particle. A significant effect of pore diffusion is now present and the process is under internal diffusion regime. For gas–solid catalytic reactions, the effect of temperature on diffusion rate usually shows an apparent activation energy of 4 to 12 kJ/mol, at least one order of magnitude lower than for the chemical reaction. This means that for the internal diffusion regime the apparent activation energy is about halved, with respect to the chemical regime. Furthermore, the apparent reaction order tends to shift towards first order (e.g. a reaction of second order will appear of an order of about 1.5, etc.).

The internal diffusion effect is usually expressed through the effectiveness factor η of the catalyst, defined as the ratio of the observed reaction rate to the rate one could observe if the whole internal catalyst surface would be exposed to the same concentration of reactant, present on the external surface of the particle.

For complex reactions, the yield to the various products or intermediates can be different from that obtainable in the absence of internal diffusion limitation. For consecutive reactions, e.g. $A \rightarrow B \rightarrow C$, the yield to B will be lower, down to about 50% for $\eta \cong 0.3$. For parallel reactions, such as $A < {}^{B}_{C}$, the selectivity to B and C will remain unchanged if the reactions are both of the same order n. If, on the other hand, the reaction leading to B is of higher order than that leading to C, the B/C ratio will decrease with decreasing η. Indeed, the decrease of reactant concentration within the catalyst particle affects to a larger extent the reaction of higher order.

By further increasing temperature, the chemical reaction can become so fast that practically the whole concentration gradient is localized across the fluid film outside the catalyst particle, the reactant being rapidly consumed as it reaches the catalyst external surface or immediately below it. This is referred to as external diffusion regime. In this regime the apparent activation energy corresponds to that of bulk diffusion, i.e. 4 to 12 kJ/mol for gases, 10 to 20 for liquid hydrocarbons and 8 to 10 for aqueous solutions. Furthermore, all reactions appear of first order, being the diffusive mass transfer a first order process, and all catalysts seem to show the same activity and selectivity.

When the reaction, as frequently occurs, is also highly exothermic, significant temperature gradients may establish within the particle and mainly at its interface with the external fluid phase. This, besides affecting yield rather deeply, may also entrain some harmful instability phenomena.

At last, for very high temperature, the gas-phase, homogeneous uncatalytic reaction becomes so fast to compete with the catalytic one or even to overcome it, because the activation energy of the former is usually higher than for the latter. In this case we refer to homogeneous reaction regime.

For simple reactions and when the temperature difference between gas and solid can be neglected, all these regimes may be represented by means of an Arrhenius plot (Fig. 8), on which the relative position of the four straight lines depends on various factors. For instance, in internal diffusion regime, the reaction rate may be increased, by decreasing the catalyst particle size, or by modifying the pore structure. This of course does not change the activation energy, so that the straight line, corresponding to this regime onto the plot, simply shifts up, maintaining the same slope. Furthermore, for a non porous catalyst, no internal diffusion regime can occur and a direct transition from chemical to external diffusion regime can be observed by increasing temperature. On the other hand, the external mass transfer rate can be increased by increasing the linear velocity of reactants through the catalyst bed, in some cases up to complete disappearing of external diffusion regime. At last, the relative importance of homogeneous and catalytic process may be modified by varying the ratio of gas volume to catalyst surface.

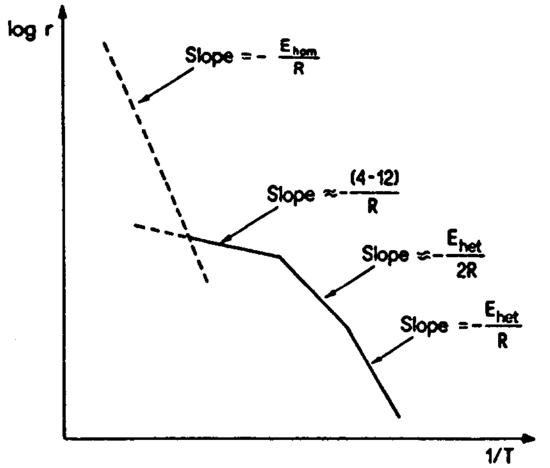

Fig. 8. Arrhenius plot for the various regimes of a catalytic reaction.

Other factors may cause concentration or temperature gradients within a bed of catalyst particles. Axial dispersion of the reactant fluid flow, excessive contribution of the reactor tube wall to heat transfer and formation of preferential ways within the catalytic bed are among the most probable. In addition, if the bed behaves as a bad thermal conductor, as frequently happens, both radial and axial thermal gradients may be generated. All these factors are referred to as wall and segregation effects and the gradients so generated as reactor gradients.

A way frequently followed for classifying gradients in catalytic reactions is to divide them in to intraparticle, interparticle and interphase, to distinguish the phenomena taking place within the particle, or between adjacent particles or between the external surface of the particle and the fluid phase, respectively. The relative probability of limitations due to some gradients is as follows:

- general: interparticle > interphase > intraparticle
- thermal: interparticle > intraparticle
- highly exothermal reactions: interphase > intraparticle > interparticle
- intraparticle: concentration > temperature
- radial, interparticle: temperature > concentration.

The principal causes of interparticle reactor gradients are:

- axial flow dispersion
- wall effect
- bypassing, especially due to excessive solid dilution
- low thermal conductivity of bed.

1.4.2. Experimental check methods for diffusive limitations

Intraparticle diffusion effects are usually detected by measuring the dependence of reaction rate on particle size. If the catalyst has to be diluted with inert solid, the latter and the catalyst should be of the same particle size, to minimize possible distortion of the fluid-dynamic behaviour of the reacting fluid through the catalyst bed. Both conversion and selectivity should be measured in each test run for the most reliable and meaningful checking. However, when working with zeolites or with similarly structured, very thin-pored catalysts, even the thinnest particles (e.g. 180–200 mesh), permitting a reasonable pressure drop for the reacting fluid through the catalyst bed, may still be several orders of magnitude larger than zeolitic crystals. As a consequence, this checking procedure can be meaningless. Indeed, the diffusion coefficient for the so-called conformational, or superficial diffusion through pores of molecular-size diameter, may be up to ten orders of magnitude lower than for bulk or Knudsen diffusion. In such cases the only way out is to prepare zeolite samples of different crystal size.

Interparticle and/or interphase gradients are usually detected by measuring the dependence of reaction rate on reacting fluid linear velocities, at constant time factor. In such a test, one should remember that when working with the low-Reynolds-number flow rates, typical of laboratory exploratory microreactors, the method can fail if the check is performed over a too narrow range of flow rate values. Hence, the range explored should be sufficiently large (e.g. 1 to 2 orders of magnitude), so to permit the individuation of the minimum flow rate, ensuring a negligible effect of interparticle or interphase diffusion.

Axial flow dispersion and axial thermal gradients are usually negligible when the bed length to particle size (L/d_p) ratio is sufficiently high (≥ 10), so to ensure a good approximation to plug-flow behaviour. Diluting the catalyst with inert particles of the same size is the most followed way to reach this goal.

The effect of radial gradients, both of concentration and temperature, can be minimized only by properly diluting the catalyst, so reducing also the risk of hot spots formation within the catalyst bed. However, excessive dilution may entrain the risk of bypassing. Also a low ratio of tube to particle diameter (d_t/d_p) can help in reducing the risk of radial thermal gradients, but such a ratio should never be less than 4, to avoid the risk of wall effect.

Finally, it must be remembered that in continuous stirred tank or recirculation tank reactor (CSTR), the residence time distribution of reacting fluid is worse than in plug-flow tubular reactor (PFR), so that in CSTR any reaction is slower than in PFR, the faster the reaction, the more evident the difference.

1.4.3. Mathematical criteria for the absence of diffusion effects

Many papers in literature propose criteria to determine the presence or absence of diffusional or thermal effects in catalytic reactions through calculation, by means of some equations or disequations to be checked. The latter include proper parameters, such as diffusion and liminar coefficients, heat evolved or consumed by the

DILUTION EFFECTS

$$\frac{b\cdot d_p}{l\cdot\delta}<4\cdot 10^{-3}$$

INTERPHASE

mass

$$1-\frac{k_r d_p^{1.5}}{11\left(uD_B\right)^{0.5}}>0.9$$

$$\frac{r_v\left(V_p/S_p\right)}{k_g\cdot C}<0.15/n$$

heat

$$\left|\frac{\Delta H\cdot r_v\left(V_p/S_p\right)}{h\cdot T_b}\right|<0.15/\alpha$$

INTRAPARTICLE

mass

$$\frac{r_v\left(V_p/S_p\right)^2}{D_e\cdot C_s}<1$$

heat

$$\frac{\Delta H\cdot R_p}{k\cdot T_s}<0.75\cdot\alpha_s$$

OVERALL (INTERPHASE AND INTRAPARTICLE) MASS TRANSFER

isothermal

$$\frac{2\left(V_p/S_p\right)^2\rho_b\cdot S_t\cdot k_s\cdot C^{n-1}}{D_e(n+1)}\leq 0.03$$

nonisothermal

$$\frac{r_v\cdot R_p^2}{C\cdot D_e}<\frac{1+0.33\alpha\left(\frac{\Delta H\cdot r_v\cdot R_p}{h\cdot T_b}\right)}{\left|1-\alpha\beta\right|\left[1+0.33n\left(\frac{r_v\cdot R_p}{C\cdot k_g}\right)\right]}$$

INTERPARTICLE

radial heat transfer

$$\frac{\left|\Delta H\right|R_t^2(1-\varepsilon)r_v}{k\cdot T_v}<\frac{0.4}{\left[1+8\left(\frac{R_p}{R_t}\right)Bi_w\cdot\alpha_w\right]}$$

axial mass transfer

$$\frac{L}{d_p}>\frac{20n}{Pe}\ln\left(\frac{C_0}{C_f}\right)$$

Fig. 9. Examples of proposed mathematical criteria for checking diffusive intrusions.

reaction, physical and thermal properties of catalyst and of reacting fluid, observed reaction rate, etc.

In Fig. 9 there are some examples of the proposed mathematical criteria: if the disequations are verified, a negligible effect of the diffusive intrusion considered is expected. The most important papers proposing these and other mathematical criteria are listed among references.

In a given reacting system, any of the previously discussed gradients may be present separately, but usually most of them occur altogether. However, the proposed test equations, based on heat or mass balance procedures, usually refer to only one gradient and assume it as occurring separately, so to be treated in the absence of any other thermal or concentration gradient. Furthermore, the previously mentioned parameters, needed for calculation, are usually unknown, or badly known, or referred to different conditions. As a consequence, any of the proposed criteria should be considered at best only as a preliminary check, to be confirmed through the proper experimental test runs for a reliable and correct evaluation of any diffusional intrusion.

2. List of symbols

$Bi_w(=h_w d_p/k)$	Biot number (thermal) at tube wall
b	dilution = fraction inert
C, C_f, C_o, C_s	concentration, final, initial, at the surface (steady state)
D_a, D_B, D_e	diffusion coefficient: axial (eddy), molecular, effective (within the pores)
d_p	particle diameter
E_a	activation energy
h, h_w	liminar coefficient: fluid to particle, fluid to tube wall
ΔH	enthalpy of reaction
k	thermal conductivity of the solid
k_g	mass transfer coefficient
k_r, k_s	rate constant, based on unit of catalyst: mass, surface
l	length of undiluted catalyst bed
L	reactor tube length
n	reaction order
$Pe(=ud_p/D_a)$	diffusional Peclet number
R	gas constant
R_p, R_t	radius of: particle, reactor tube
r_v	observed reaction rate, based on catalyst volume unit

S_p, S_t	external surface area: of particle, overall
T_b, T_o, T_s, T_w	temperature: of bulk fluid, initial, of particle external surface (steady state), of tube wall
u	average fluid rate
V_p	particle volume
α, α_s, α_w,$(=E_a/RT)$	Arrhenius number: at bulk fluid temperature, at particle external surface, at tube wall temperature
$\beta(=[T_{max}-T_s]/T_s)$	Prater number (dimensionless maximum temperature rise)
ϵ	bed porosity
ρ_b	catalyst bed density

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