

REACTORS AND APPARATUS FOR TESTING HETEROGENEOUS CATALYSTS

W. Hölderich, W. D. Mross, and E. Gallei

BASF AG Ludwigshafen, 6700 Ludwigshafen,
Federal Republic of Germany

الخلاصة :

في هذا العرض يتم تقديم الأنواع الرئيسية للمفاعلات المتاحة لإختبار العوامل المساعدة ويجري وصف أنواع مختلفة من المفاعلات : ثنائية (صلبة/غازية) — ثلاثية (صلبة/غازية/سائلة) إضافة إلى أنظمة التفاعل المرحلي ، هذا وتم مناقشة قائمة كاملة لوحدة اختبار العوامل الحفازة التي تضم أنواعاً مختلفة من المفاعلات . ويختتم المقال بوصف موجز للمنشآت الصغيرة .

ABSTRACT

Principal types of reactor available for catalyst testing are presented in this review. Various types of two-phase (solid/gas) and three-phase (solid/gas/liquid) reactor systems are described. In addition, complete catalyst screening test units incorporating such reactor types are discussed. The article concludes with a brief description of miniplant technology.

REACTORS AND APPARATUS FOR TESTING HETEROGENEOUS CATALYSTS

1. INTRODUCTION

Bench and technical scale experiments are used to test catalytic performance, to investigate reaction kinetics, and to study different reactor types. The experimental data serve as a basis for the design of large-scale industrial reactors. By means of a suitable test procedure in various types of laboratory and pilot plant reactors, it is entirely possible to design an industrial reactor. In practice however, time, funds, and resources usually restrict the extent of these investigations [1]. Furthermore, it is impossible to measure the global characteristics of catalytic reactions in a laboratory reactor and then to design an industrial reactor based on 'scale-up' methods. Extensive cooperation between chemists (especially catalyst chemists) and chemical engineers is therefore necessary to resolve this dilemma.

2. PROPERTIES OF CATALYSTS

The suitability of solids as heterogeneous catalysts for industrial processes is based on five essential characteristics: activity, selectivity, catalyst lifetime, ease of regeneration, and mechanical strength. In addition, disposal problems have to be considered.

The catalyst test is intended to provide information on these interrelated characteristics. In practice, it is necessary to make a compromise between the various requirements that an industrial catalyst has to meet.

Besides the chemical composition, catalyst properties depend on a large number of physical parameters such as temperature, concentrations of reactants, residence time, and, in many cases, reactor dimensions, catalyst form, and flowrate of the fluid phase. Comprehensive testing of catalyst efficiency requires a great variety of apparatus and consumes a great deal of time. Only specific aspects are therefore usually tested in industry.

For a complete description of catalyst efficiency, it is necessary to have a detailed knowledge of the reaction mechanism and heat and mass transfer. The parameters involved are kinetic—such as rate constants, activation energies, and orders of reaction.

In kinetic equations, the reactions taking place at the catalyst surface have to be taken into account.

Furthermore, transport phenomena can influence the reaction. Heat and mass transfer, either between the fluid phase and the solid or into the porous solid, have to be taken into account.

It can be seen that the elucidation of the kinetics is a complex and expensive matter. Instead of these absolute kinetic data, it is often experimentally much simpler to determine formal kinetic data.

Parameters that can generally be determined easily experimentally and provide information on reaction and catalyst properties are:

- (1) conversion and selectivity as a function of temperature,
- (2) concentrations of reactants; and
- (3) residence time at the catalyst.

2.1 Activity Parameters

In a formal kinetic approach, it is sufficient to measure the reaction rates in the temperature and concentration ranges of interest with regard to the operation of the reactor. These reaction rates are given by the quotient of the reactants converted and the amount of catalyst used, and are based on a particular unit of time (Figure 1) [2, 3].

Other activity parameters are the space-time yield, the conversion at a particular temperature, the yield at a particular temperature, and the temperature for a particular conversion.

Other parameters readily obtained experimentally include (Figure 2):

- **reaction rate r**

$$r = \frac{\text{reactant converted}}{\text{mass or volume of catalyst} \times \text{time}} \quad \left[\frac{\text{mol}}{\text{kg or l} \times \text{h}} \right]$$
- **space time yield STY**

$$\text{STY} = \frac{\text{desired product}}{\text{catalyst volume} \times \text{time}} \quad \left[\frac{\text{mol}}{\text{l} \times \text{h}} \right]$$
- **conversion at a given temperature T_U**

$$U = \frac{\text{reactant converted}}{\text{reactant fed}} \times 100 \quad \left[\frac{\text{mol} \times \%}{\text{mol}} \right]$$
- **yield A at a given temperature T_A**

$$A = \frac{\text{product desired}}{\text{reactant fed}} \times 100 \quad \left[\frac{\text{mol} \times \%}{\text{mol}} \right]$$
- **temperature for a given conversion**

Figure 1. Catalyst Activity Parameters

- **selectivity S**

$$S = \frac{\text{desired product}}{\text{converted feed}} \times 100 \quad \left[\frac{\text{mol} \times \%}{\text{mol}} \right]$$
- **catalyst lifetime Z**

$$Z = \frac{\text{total thru' put prior to given deactivation}}{\text{catalyst mass} \times \text{time}} \quad \left[\frac{\text{kg}}{\text{kg} \times \text{h}} \right]$$
- **space velocity**

$$\text{GHSV} = \frac{\text{total amount of gas (NTP)}}{\text{catalyst volume} \times \text{time}} \quad \left[\frac{\text{l}}{\text{l} \times \text{h}} \right]$$

$$\text{residence time } \tau = \frac{1}{\text{GHSV}}$$

$$\text{LHSV} = \frac{\text{total amount of liquid}}{\text{catalyst volume} \times \text{time}} \quad \left[\frac{\text{l}}{\text{l} \times \text{h}} \right]$$

$$\text{WHSV} = \frac{\text{total amount of liquid}}{\text{catalyst weight} \times \text{time}} \quad \left[\frac{\text{kg}}{\text{kg} \times \text{h}} \right]$$

Figure 2. Selectivity and Loading Parameters

2.2 Selectivity Parameter

The selectivity provides information on a specific reaction path. It is determined from the molar ratio of the desired reaction product to the reactants converted, at constant temperature and/or constant conversion and/or constant space velocity.

2.3 Life and Space Velocity Parameters

A measure of the aging of a catalyst is the catalyst lifetime, and this is defined appropriately for each specific case. For example, the parameter used can be the amount of product that can be passed over a catalyst before the conversion or selectivity falls below a certain value.

In the case of fixed-bed catalysts, parameters for the reactor throughput are frequently used instead of the residence time, which is usually stated. The gas hourly space velocity (GHSV) is the total amount of gas per catalyst volume and per unit time, at 1 bar and 0°C, which has passed through the reactor. The reciprocal of the GHSV gives the residence time of the reactants in the catalyst bed. The liquid hourly space velocity (LHSV) and the weight hourly space velocity (WHSV) are the analogous parameters for liquids measured by volume or by weight. All these parameters can be determined in a simple screening test and permit ready comparison of catalysts.

3. TYPES OF REACTOR

It is necessary to differentiate between two fundamental types of reactor: the integral reactor and the differential reactor (Figure 3) [2–19].

- | | |
|---|-----------------------------------|
| ● integral reactors | ● differential reactors |
| - fixed bed integral reactor
adiabatic, isothermal | - single pass reactor |
| - fluidized bed reactor | - recycle reactor |
| - trickle bed reactor | - continuous stirred-gas reactor |
| - suspension reactor | - single pellet diffusion reactor |
| | - pulse reactor |

Figure 3. Reactor Types for Testing Heterogeneous Catalysts

3.1 The integral fixed-bed reactor can be operated isothermally or adiabatically, continuously or batchwise, and high conversions are achieved.

3.2 Reactors that have an agitated catalyst bed, such as the isothermal fluidized-bed reactor, are also used.

3.3 For three-phase systems (i.e. gas/solid/liquid), trickle-bed reactors and various suspension reactors are used.

3.4 Amongst differential reactors with differential conversion, reactors with a single passage of the reactants through the catalyst bed must be distinguished from reactors in which the reaction mixture passes several times through the catalyst by means of an external or internal recycle.

3.5 The smallest unit of a laboratory reactor is the single-particle diffusion reactor, in which a single catalyst pellet is investigated.

3.6 Microreactors such as the pulse reactor, which employ 20–2000 mg of catalyst, have also been developed for testing catalysts.

The choice of a suitable reactor type and its characteristic dimensions depends on:

- (1) the type of process;
- (2) the fundamental process parameters such as residence time, temperature, pressure, and mass transfer between various phases in multiphase processes; and
- (3) on the available desired detailed information on the catalyst.

4. INTEGRAL REACTORS

The most important types of industrial test reactor are the integral reactors, particularly for two-phase systems (i.e. for the heterogeneous catalysis of gas-phase reactions [4, 6, 7, 10, 17, 18] and for three-phase systems—gas/solid/liquid—[2, 3, 16]).

In integral reactors, high conversions are usually achieved by means of long contact times. These result from the use of relatively large amounts of catalyst in relation to feed rate. The conversion can be controlled by altering this ratio.

Integral reactors can be operated continuously or batchwise. The batchwise test gives only qualitative and preliminary information, since in many cases the initial activity of the catalyst is not representative. Instead, most catalysts achieve a plateau of constant activity and selectivity only after a conditioning period. As a result, it is advisable to carry out continuous measurements.

4.1 Fixed-Bed Integral Reactor

Figure 4 shows a typical fixed-bed integral reactor [7]. High conversion means that the composition of the reaction mixture and the temperature vary along the reactor. The reactions therefore take place at different rates at different points in the reactor. It is useful to equip the reactor with instruments for measuring the concentration and temperature profiles.

When a test is carried out in the fixed-bed integral reactor, the resulting kinetics often cannot be evaluated independently of physical phenomena. Mass transfer and/or heat transfer effects are usually present within a single catalyst particle, between individual catalyst particles, and within the reactor.

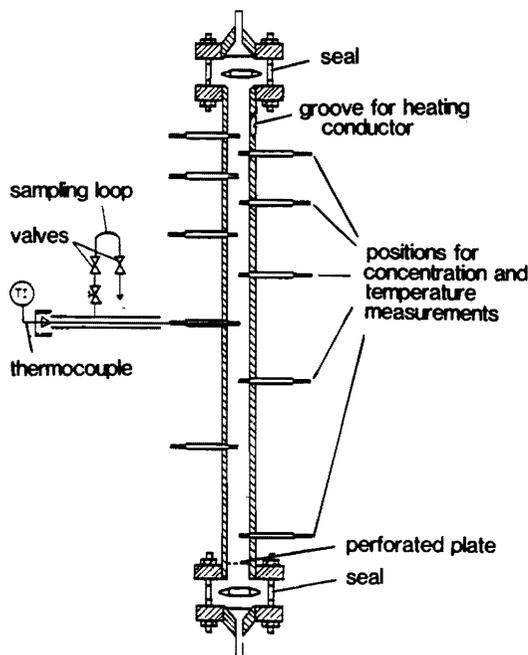


Figure 4. Catalytic Fixed-Bed Integral Reactor [7]

In estimating the intrinsic rates, pore diffusion limitations have to be avoided [4, 20]. The presence of such intraphase resistances can easily be determined by investigating the reaction on decreasing the size of the catalyst particles. When the reaction rate no longer changes, the catalyst size is sufficiently small to permit reaction without pore diffusion limitations.

The advantages of this simple procedure have led to a wide application. However, these methods can also lead to errors in the interpretation of the test results if the catalyst particle is not homogeneous in respect of its chemical composition, structure, and porosity (as is frequently the case for impregnated and pelleted catalysts).

Another disadvantage is that small catalyst particles may build up high pressures as a result of increased packing density and modified flow characteristics, so that the Reynolds number falls below the minimum desirable value of 30 [4, 21]. The Reynolds number must be kept above 30 (i.e. high turbulence) in order to be able to realize plug flow (i.e. a uniform velocity profile). Plug flow is desirable in order to simplify the interpretation of the conversion data as far as possible. In reality, slip effects (wall bypass) occur in packed reactors, in particular in production reactors, as a result of varying packing density [4, 21].

In order to achieve approximate plug flow, a sufficiently high linear gas velocity and particular reactor dimensions are necessary:

- (a) The ratio of the reactor diameter to the catalyst particle diameter should be between five and eight. In view of the increasing slip effect, the ratio should not fall below this value. On the other hand, the tube diameter must not be too large—in order to avoid radial temperature and concentration gradients.
- (b) The ratio of the reactor length to the catalyst particle diameter should be between 30 and 100 in order to be able to simulate the process reliably.

To check whether mass and heat transfer effects are important in a reactor, various criteria have been drawn up and material data and estimation formulae for mass and heat transfer parameters have been compiled in the literature [22–27]. However, these will not be discussed here.

Fixed-bed integral reactors can be operated adiabatically or isothermally (see Subsections 4.1.1 and 4.1.2).

4.1.1 Adiabatic Fixed-Bed Integral Reactor

In the adiabatic fixed-bed integral reactor, exothermic and endothermic gas-phase processes can be carried out over solid catalysts.

The flow diagram in Figure 5 shows an adiabatic reactor integrated into a test apparatus. The reactants are pumped from storage vessels, vaporized, and passed through the reactor, which is heated electrically. Temperature sensors are mounted at several points in the reactor, and the catalyst bed is equipped with a movable thermocouple for monitoring the temperature or the migration of the temperature profile.

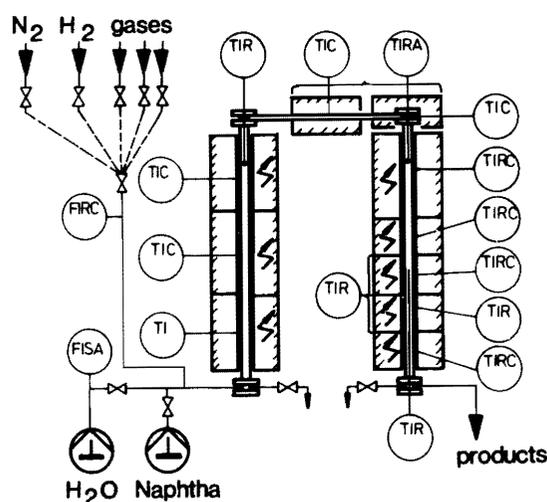


Figure 5. Adiabatic Fixed-Bed Tubular Reactor

Reactions in such reactors can be tested very easily. A large number of test results relating to the activity and selectivity of the catalyst can be obtained by means of a small number of experiments. Such a reactor type is also very useful for measuring the time-on-stream of the catalyst, because the migration of the temperature profile through the catalyst bed can be monitored.

4.1.2 Isothermal Fixed-Bed Integral Reactor

Exothermic reactions in which reactants, products, and selectivity are sensitive to temperature require isothermal rather than adiabatic reaction conditions.

The efficiency of localized heat removal can be influenced by the following factors:

- (1) distributing the catalyst over a narrow tube reactor. (Decreasing the tube diameter means that the heat exchange surface per unit of

- catalyst volume becomes larger. However, as already mentioned, a ratio of tube diameter to catalyst particle diameter of less than between five and eight is regarded as disadvantageous);
- (2) taking up the excess heat of reaction by a gaseous or liquid medium surrounding the tube;
- (3) diluting the catalyst with an inert material;
- (4) diluting the reaction mixture with an inert gas;
- (5) increasing the linear gas velocity, which can result in a flattening of the temperature profile or an increase in the hot spot temperature until temperature 'runaway' occurs.

Substantially isothermal behavior along the reactor axis is achieved by a combination of several of such factors.

Figure 6 shows a flow diagram of a laboratory test unit for catalyst screening under isothermal conditions. The catalyst efficiency of zeolite catalysts in the conversion of methanol to olefins can be studied in this apparatus.

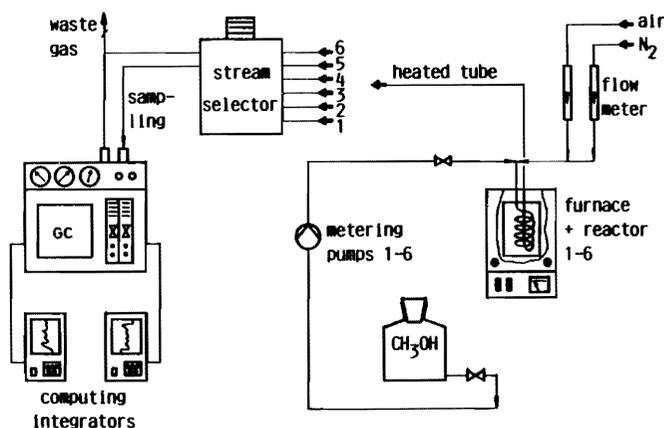


Figure 6. Diagram for Conversion of Methanol to Olefins

The reaction is carried out in a thin fixed-bed integral reactor that has an internal diameter of 0.4–0.6 cm and is in the form of a coil. In order to maintain almost isothermal conditions, the reaction temperature is kept constant in a hot-air oven by means of a vigorously-mixed air stream.

Six of these test ovens are arranged in parallel. One of the six reactors contains a standard catalyst for comparison. The methanol is fed from storage tanks into the reactors by means of metering pumps, and is reacted over the catalyst. The reaction products are fed for analysis (GC) in gaseous form through heated lines.



Figure 7. Screening Test Unit with Isothermic Integral Reactors

The plant runs completely automatically around the clock and requires no operators. A stored programme in the GC integrators permits the reactors to be sampled either at will or in a predefined cycle.

Figure 7 shows a similar screening test unit. The integral coil reactors are thermostated with salt baths in block furnaces. Removal of heat by means of salt baths ensures that isothermal conditions are better-maintained than in the case of hot-air ovens.

The extrapolation of the test results to the industrial scale is especially easy if the industrial reactor is designed as a multitube reactor and if one of these tubes is chosen as a test reactor—the so-called single-tube reactor. For example, in the industrial reactor designed for the production of phthalic anhydride, 10 000 individual tubes having an internal diameter of 2.5 cm are arranged parallel to one another [28]. The test reactor consists of a single reactor tube with the original dimensions, and is operated with the same feed either as a pilot plant or directly next to the large-scale plant.

4.2 Reactor Types for a Three-Phase System

The reactor types for reactions in a three-phase system involving gas/solid/liquid are described in Subsections 4.2.1 and 4.2.2 [16].

A liquid-phase process has the particular advantage that it can often be carried out at lower temperatures than in the gas phase. This makes it possible to prepare heat-sensitive compounds by a catalytic route, or to employ active or selectively-supported liquid-phase catalysts that are not very thermally stable, e.g. ion-exchange or heavy-metal complex catalysts.

4.2.1 Trickle-Bed Reactor

At present the trickle-bed reactor appears to be the most widely-used reactor for three-phase reaction systems (Figure 8). It is used widely for refining petroleum products and for the hydrogenation of organic intermediates.

In this reactor, the fixed catalyst bed is more or less in the form of a packed column, and is sprayed from above with a non-cohesive fluid phase having a relatively low liquid content. The gas diffuses through the liquid film on to the surface of the catalyst where it undergoes reaction. In this type of reactor, the gas is commonly recycled.

Compared with suspension reactors, fixed-bed reactors have the advantage that the catalyst does not have to be separated off from the reaction products. However, the catalyst has to be present in a coarse form (>0.1 cm), i.e. in a form which is less advantageous in terms of pore utilization, and therefore activity and selectivity.

In trickle-bed reactors, the lower limit for particle size is determined by hydrodynamics (pressure loss and flooding). In trickle-bed reactors the residence time distribution is generally better (narrower) than in suspension reactors, and generally deviates only slightly from plug flow characteristics.

On the other hand, in trickle-bed reactors local concentration and temperature gradients appear to form more readily, and presumably have an adverse effect on the desired selectivity. The comparatively small ratio of liquid to catalyst in trickle-bed reactors must be taken into account in the removal of the heat

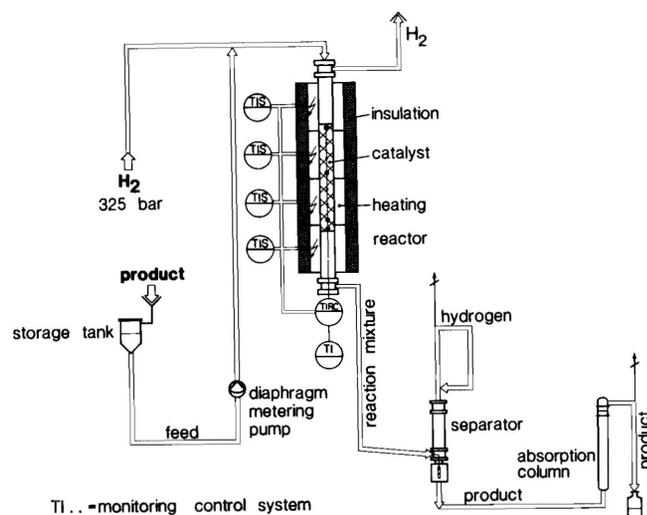


Figure 8. Trickle-Bed Reactor of Refinery Pilot Plant

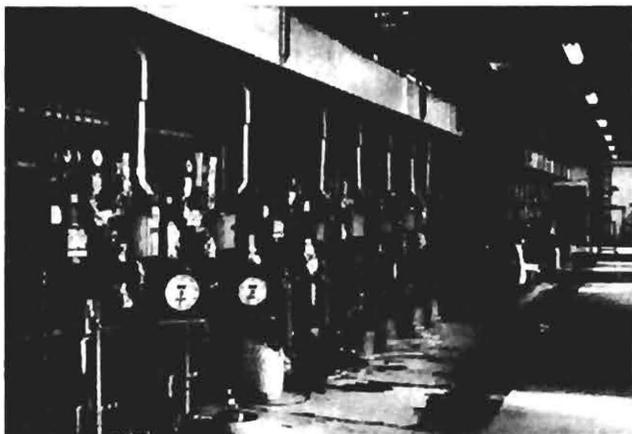


Figure 9. Pilot Plant for Testing Hydrocracking-Catalysts Using Trickle-Bed Reactors in Block Furnaces

of reaction. These reactors are generally operated adiabatically.

Figure 9 shows a pilot plant that contains a number of trickle bed reactors for carrying out life tests on hydrocracking catalysts and evaluating data for plant design.

4.2.2 Suspension Reactor

There are a number of types of suspension reactor for three-phase systems [16]. They all possess the common feature that the catalyst is suspended in the reaction liquid.

In suspension reactors, the particle size of the catalyst is limited only by filtration ability. In contrast to a fixed bed, concentration and temperature gradients can be substantially avoided. Other advantages of suspension reactors include good heat dispersion and the fact that catalysts having a short life can easily be replaced. The problems with suspension reactors are separating the catalyst and throughput limitation.

The simplest type of suspension reactor, and one which is widely used in organic chemistry, is the agitated-bed reactor. For example, agitated-bed autoclaves are generally operated batchwise, and the amount of catalyst used is from 1 to 5 %, based on the weight of reactants used.

5. DIFFERENTIAL REACTOR

It has already been mentioned that the kinetic data for measurements in an integral reactor are falsified by physical phenomena, such as heat and mass transfer.

In order to eliminate these transport effects and to be able to operate under strictly isothermal conditions, kinetic investigations have been carried out in differential reactors [6, 7, 12–15, 29–33].

5.1 Differential Reactor with Single Pass

In its simplest form (Figure 10), a differential reactor of this type consists of a tube reactor with a small catalyst bed through which the reaction mixture passes only once [6, 7]. The length of the catalyst bed is such that contact times are very short and conversions can therefore be kept in a differential range. It is therefore possible to assume that the concentrations of the reactants, and hence the reaction velocities, are constant at every point in the reactor. By analyzing the inlet and exit streams of the differential reactor, it is possible to determine the average composition in the reactor and to calculate the reaction rate directly from this.

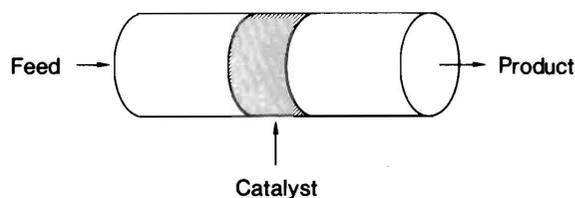


Figure 10. Differential Reactor with Single Pass

Other advantages of investigating kinetic processes in a fixed-bed differential reactor are the elimination of effects owing to radial velocity gradients and the elimination of axial diffusion, so that plug flow can be assumed. The catalyst particles should be very fine since otherwise channeling can occur. Heat and mass transfer limitations both within the catalyst particle and between the catalyst particles have to be taken into account. However, these can be minimized by the same techniques as were given for the integral reactor.

The major disadvantage of the differential reactor with a single pass of the reactants through the catalyst bed is the low accuracy of the analytical method in determining small concentration differences in highly dilute reaction mixtures.

Where only small errors are present in the compositional analysis, this reactor is well-suited to determining the activity and selectivity of the catalyst.

Deficiencies in the analytical method in the case of simple differential reactors can be eliminated by means of two reactor types that differ in construction:

- (1) a recycle-differential reactor; and
- (2) a continuous stirred-gas reactor.

5.2 Recycle-Differential Reactor

As shown in Figure 11, in the recycle-differential reactor the reaction mixture is circulated outside the heated inner reactor space by means of a suitable pump. Suitable units are diaphragm pumps and radial or axial blowers [6, 34].

The bulk of the gas mixture is circulated and is mixed with a small amount of fresh reactants during each pass.

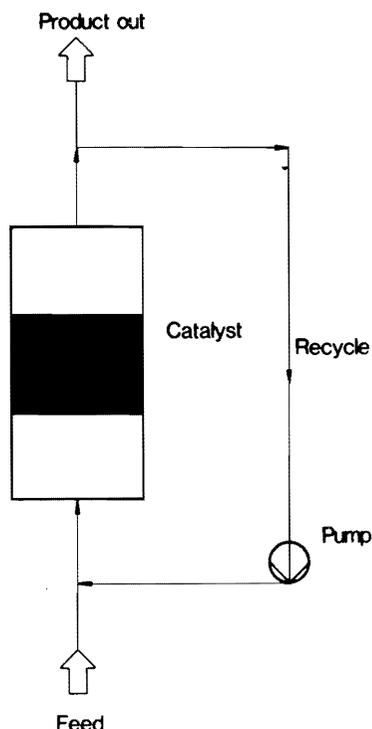


Figure 11. Recycle-Differential Reactor [6]

The advantages of this reactor type are as follows.

- (1) The required recycle/feed ratio of 10–15 can be achieved with relatively low investment.
- (2) The reaction system is virtually isothermal.
- (3) High flow velocities over the catalyst particles substantially eliminate all external mass transfer effects. By varying the recycling velocity, it is possible to determine the velocity above which external mass transfer can be neglected.
- (4) High recycling velocity ensures plug flow through the catalyst and avoids effects owing to possible heterogeneity in the catalyst bed.
- (5) A recycling apparatus facilitates the evaluation of reaction kinetics measurements.

Recirculation pumps present a critical problem in that they have to maintain a high flow velocity and must not contaminate the reaction mixture. Moreover,

the fact that the pump units have to withstand high temperatures and pressures means that they are often expensive.

The major disadvantage with respect to kinetic measurements is the fact that this design involves a large amount of dead space in the recycle. This disadvantage is overcome in continuous stirred-gas reactors because of their compact design.

5.3 Continuous Stirred-Gas Reactor

In the continuous stirred-gas reactor, the pump unit and the reactor form a single unit. Stirred gas reactors are in theory basically similar to recycle reactors [6, 12–15, 29, 34].

Although all stirred reactors have the same fundamental characteristics, they can still be classified into various groups, depending on whether the catalyst is fixed or agitated, and on the arrangement of the catalyst and of the stirring device.

There are a large number of continuous stirred-gas reactor types [34]. Of these types, the Carberry reactor and (particularly) the Berty reactor are important.

5.3.1 Carberry Reactor

In the case of the Carberry reactor (Figure 12), the catalyst bed is rotated during catalyst testing [6, 12, 15, 34].

The catalyst is mounted in a basket that rotates at high speed in the reaction mixture. If the reactor is properly designed, gradient-free conditions can easily be achieved.

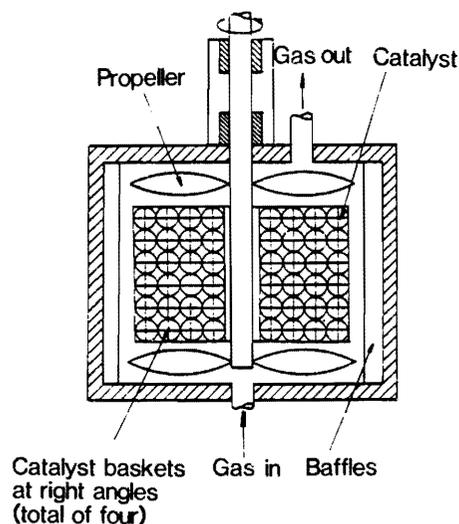


Figure 12. Rotating Basket Reactor: Carberry reactor

However, the fact that the temperature in the catalyst bed cannot be measured directly is a disadvantage. Although the gas phase is thoroughly mixed, the actual speed of the gas over the catalyst particles is not known with complete certainty. Moreover, this reactor is unsuitable for relatively small catalyst particles. These disadvantages can be overcome if a fixed catalyst bed is used, as in the Berty reactor.

5.3.2 Berty Reactor

At present, the Berty reactor is probably the most widely-used gradient-free reactor in industrial laboratories [6, 13, 15, 34], although other differential reactors are frequently employed and described in the scientific literature.

Integrated into the apparatus shown in Figure 13 is a Berty reactor. This apparatus was used to study the kinetics of phosgene formation over active carbon. Analysis was carried out by means of an IR spectrometer.

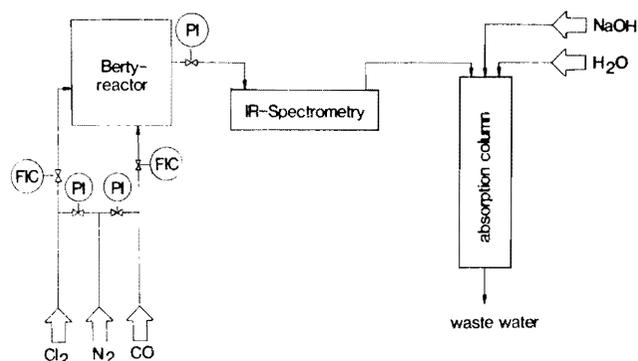


Figure 13. Flow Diagram of Catalyst Testing Apparatus with a Berty Differential Reactor

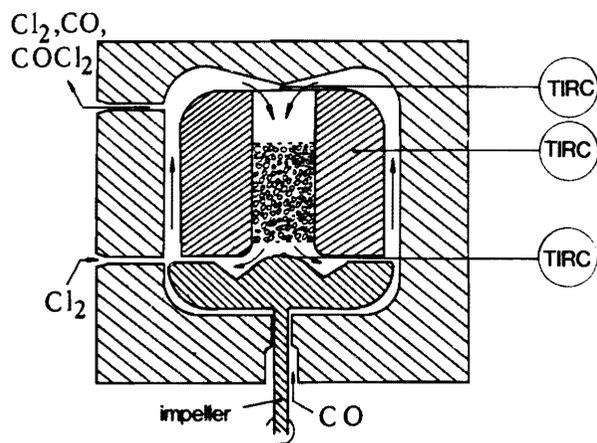


Figure 14. Continuous Stirred-Gas Reactor: Berty Reactor

The construction of such a reactor is shown schematically in Figure 14. An impeller is located in the lower part of the reactor. It sucks the recycle mixture through the central tube, which contains the catalyst, mixes it with the fresh starting materials, and passes the mixture round through the external space. The mixture then flows through the catalyst from top to bottom. An amount of gas corresponding to the feed of fresh gas is taken off through a lateral outlet.

The most important characteristics of this reactor are:

- (1) that the actual temperature of the catalyst can be measured directly;
- (2) that the ratio of free volume to catalyst volume is small; and
- (3) that the reactor can be operated under completely isothermal conditions.

Although differential reactors can be used for the determination and evaluation of kinetic data without falsification by heat and mass transfer processes, these reactors have not displaced the integral reactor, which is still widely used in the laboratory. Problems of a constructional nature and other complications result in long development times for differential reactors and high funding.

Another disadvantage of the gradient-free reactor is that it does not provide any information on the effects of transport processes on velocity, selectivity, or poisoning in the catalytic reaction. Such effects occur in industrial practice and are often critical.

5.4 Single-Pellet Diffusion Reactor

The smallest laboratory reactor unit is the single-pellet diffusion reactor [7, 35–37]. A single catalyst pellet is mounted in the reactor, and the arrangement corresponds in principle to a continuous fixed-bed reactor. The reactants are converted over this catalyst pellet, and the reaction products are identified directly downstream from the reactor outlet by means of GC or, as shown in Figure 15, by means of IR spectrometry.

Investigations in this type of reactor are very useful for formulating dynamic model equations. This is an area in which process engineers are active. However, each catalyst pellet is an individual entity and differs from other pellets with regard to porosity, surface properties, acidic centers, etc. When this method is used, the catalyst chemist therefore has to investigate a large number of individual pellets in a tedious series of measurements and to evaluate the results statistically

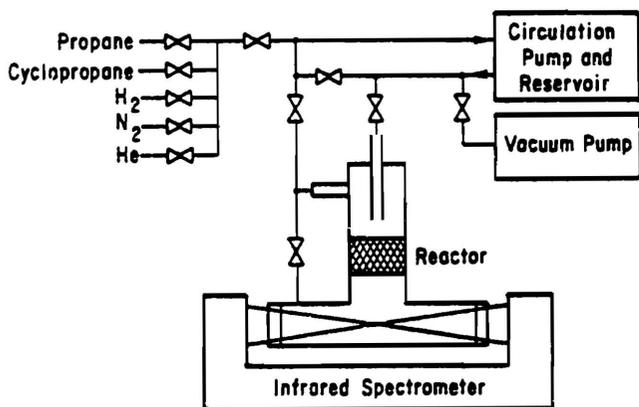


Figure 15. Flow Diagram of a Single-Pellet Diffusion Reactor System [35]

in order to be able to make accurate statements on the catalytic properties.

The single-pellet diffusion reactor is therefore used to a greater extent for academic work in universities and national research institutes than in the laboratories of industrial catalyst researchers.

6. MINIPLANT TECHNOLOGY

As the name implies, a miniplant is a complete production plant in miniaturized form, including the reactor and the processing stage. Pilot plants are very expensive to set up and operate, and they can be replaced by cheaper miniplants for many purposes.

The core of the miniplant is assembled in the laboratory. Such a core can comprise simply the reactor itself. Such compact apparatus can easily be installed in a fume hood, for example.

If promising results should be obtained, it will be necessary to add processing stages and to improve the instrumentation, in other words to complete the miniplant. This can be done by transferring the compact unit comprising the reactor and instrumentation to another laboratory containing a complete permanently-installed processing system (Figure 16).

Combining individual units to form a complete plant saves assembly and dismantling time and therefore saves money. The reactor unit of the miniplant is in the foreground in Figure 16, and the distillation column for processing the reaction products is in the background.

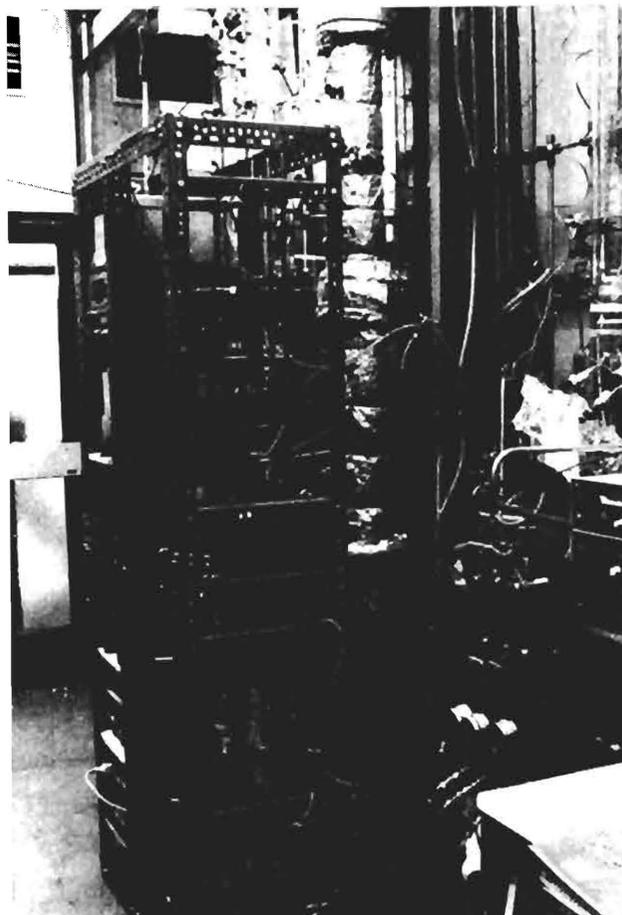


Figure 16. Miniplant with Reactor and Distillation Column

7. CONCLUSION

This paper gives an overview of the scale of catalyst testing and also demonstrates the wide variety of experimental techniques employed.

The chemistry of heterogeneously catalyzed reactions involves not only the catalyst test itself, but also a large number of spectroscopic and chemical investigations. It should be emphasized that the study of catalysts requires a great deal of time and money.

It is perhaps therefore appropriate to conclude with a quotation from Beakland [38] that summarizes the philosophy of industrial catalyst research:

‘Commit your blunders on a small scale and make your profits on a large scale’.

REFERENCES

- [1] J. M. Smith, 'Kinetics and Reactors – The Engineer's Dilemma', *Canadian Journal of Chemical Engineering*, **48** (1970), pp. 142–146.
- [2] Ch. N. Satterfield, *Heterogeneous Catalysis in Practice*, Chemical Engineering Progress Symposium Series. New York: McGraw-Hill, 1980.
- [3] R. Krabetz and W. D. Mross, 'Katalyse, heterogene, und Katalysatoren', in *Ullmanns Encyklopädie der technischen Chemie*, 4th Edition, Vol. 12. Weinheim: Verlag Chemie, 1977, pp. 517–569.
- [4] A. M. R. Difford and M. S. Spencer, 'Catalyst Test Reactor Types and Examples of Their Applications', *American Institute of Chemical Engineers Journal Symposium Series*, **143**, Volume 70 (1974), pp. 42–48.
- [5] V. W. Weekman, Jr., 'Laboratory Reactors and Their Limitations', *American Institute of Chemical Engineers Journal*, **20** (1974), pp. 833–840.
- [6] L. K. Doraiswamy and D. G. Tajbl, 'Laboratory Catalytic Reactors', *Catalysis Review—Science and Engineering*, **10** (1974), pp. 177–219.
- [7] E. G. Christoffel, 'Laboratory Reactors and Heterogeneous Catalytic Processes', *Catalysis Review—Science and Engineering*, **24** (1982), pp. 159–232.
- [8] L. Forni, 'Experimental Devices in Chemical Kinetics', *La Chimica e L'Industria*, **63** (1981), pp. 13–19.
- [9] K. Kochloeff, 'Anwendung von Mikroreaktoren bei der Entwicklung und Prüfung von technischen Katalysatoren', *Chemische Technik*, **4** (1975), pp. 443–448.
- [10] F. Trifiro and J. Pasquon, 'Experimental Reactors for the Study of Catalyzed Heterogeneous Reactions', *La Chimica e L'Industria*, **51** (1969), pp. 944–950.
- [11] E. Grundke, 'Mikroreaktor-Anlage zur Untersuchung heterogen-katalytischer Prozesse', *Chemische Technik*, **22** (1970), pp. 14–21.
- [12] J. J. Carberry, 'Designing Laboratory Catalytic Reactors', *Industrial Engineering Chemistry*, **56** (1964), pp. 39–46.
- [13] J. M. Berty, 'Reactors for Vapor-Phase Catalytic Studies', *Chemical Engineering Progress*, **70** (1974), pp. 78–84.
- [14] A. Golebiowski and K. Stolecki, 'Differentialreaktor für kinetische Untersuchungen katalytischer Reaktionen', *Chemische Technik*, **29** (1977), pp. 454–455.
- [15] J. Nelles, H. Jankowski, R. Adler, B. Kubias, and Ch. Salzer, 'Experimentelle und Auswertungsmethoden zur reaktionstechnischen Untersuchung heterogen-gaskatalytischer Prozesse, Teil III', *Chemische Technik*, **30** (1978), pp. 555–559.
- [16] H. J. Joschek, 'Reaktoren für Gas-Flüssig-Fest-Reaktionen', in *Ullmanns Encyklopädie der technischen Chemie*, 4th Edition, Vol. 3. Weinheim: Verlag Chemie, 1977, pp. 494–518.
- [17] H. P. Hortig, 'Gaskatalyse in Festbettreaktoren' in *Ullmanns Encyklopädie der technischen Chemie*, 4th Edition, Vol. 3. Weinheim: Verlag Chemie, 1977, pp. 465–479.
- [18] W. Frey, 'Gasreaktionen an festen Katalysatoren im Fließbett', in *Ullmanns Encyklopädie der technischen Chemie*, 4th Edition, Vol. 3. Weinheim: Verlag Chemie, 1977, pp. 480–493.
- [19] R. Randhava, D. S. Goltermann, and E. D. Treworgy, 'Advanced Configurations for Catalyst Research', *Chemical Engineering Progress*, **11** (1983), pp. 52–58.
- [20] D. E. Mears, 'Tests for Transport Limitations in Experimental Catalytic Reactors', *Industrial Engineering Chemistry Process Design Development*, **10** (1971), pp. 541–547.
- [21] C. E. Schwartz and J. M. Smith, 'Flow Distribution in Packed Beds', *Industrial Engineering Chemistry*, **45** (1953), pp. 1209–1218.
- [22] M. S. Joffe, B. N. Kuznetsov, Yu. A. Ryndin, and Ju. I. Yermakov, 'Influence of Low-Valent Ions Bound to the Support on the Properties, of Dispersed Metal for (W+Pt)/SiO₂ Catalysts', *Proceedings of the 6th International Congress on Catalysis*, London, 1976, Vol. 1, pp. 131–138.
- [23] H. Bakemeier, H. Gössling, and R. Krabetz, 'Ammoniak' im *Ullmanns Encyklopädie der technischen Chemie*, 4th Edition, Vol. 7. Weinheim: Verlag Chemie, 1977, pp. 444–513.
- [24] V. Hlavacek and M. Kubicek, 'Modeling of Chemical Reactors. XXI. Effect of Simultaneous Heat and Mass Transfer inside and outside of a Pellet on Reaction Rate—I', *Chemical Engineering Science*, **25** (1970), pp. 1537–1547.
- [25] C. M. Merger and R. Aris, 'Revista Latinoamericana de Ingeniera', *Quimica Aplicada*, **2** (1971), pp. 149.
- [26] M. J. Smith, *Chemical Engineering Kinetics*, 2nd Edition. New York: McGraw-Hill, 1970.
- [27] P. Zehner and F. W. Hennecke, 'Wärmeübergang im konzentrischen Ringspalt', in *VDI-Wärmeatlas*, 2nd Edition. Düsseldorf: VDI-Verlag, 1974, pp. Gg. 1–6.
- [28] H. Suter, 'Phthalsäureanhydrid und seine Verwendung', in *Wissenschaftliche Forschungsberichte*, Vol. 1. Darmstadt: Steinkopf-Verlag, 1972, pp. 1–184.
- [29] C. D. Bennett, M. B. Cutlip, and C. C. Yang, 'Gradientless Reactors and Transient Methods in Heterogeneous Catalysis', *Chemical Engineering Science*, **27** (1972), pp. 2255–2264.
- [30] J. A. Mahoney, 'The Use of a Gradientless Reactor in Petroleum Reaction Engineering Studies', *Journal of Catalysis*, **32** (1974), pp. 247–253.
- [31] J. M. Berty, 'Testing Commercial Catalysts in Recycle Reactors', *Catalysis Review—Science and Engineering*, **20** (1979), pp. 75–96.
- [32] G. Luft, R. Römer, and H. Röder, 'Kreislaufapparaturen für reaktionskinetische Messungen', *Chemie Ingenieur Technik*, **45** (1973), pp. 596–602.
- [33] J. A. Mahoney, K. K. Robinson, and E. C. Myers, 'Catalyst Evaluation with the Gradientless Reactor', *Chemtech*, **12** (1978), pp. 758–765.
- [34] H. Jankowski, J. Nelles, R. Adler, B. Kubias, and Ch. Salzer, 'Experimentelle und Auswertungsmethoden zur reaktionstechnischen Untersuchung heterogen-gaskatalytischer Prozesse. Teil II', *Chemische Technik*, **30** (1978), pp. 441–446.
- [35] L. L. Hegedus and E. E. Petersen, 'The Single Pellet, Diffusion Reactor: Theory and Applications',

- Catalysis Review—Science and Engineering*, **9** (1974), pp. 245–266.
- [36] E. G. Christoffel and J. C. Schuler, 'Der Einzelkorndiffusionsreaktor als Laborreaktor zur Untersuchung heterogen-katalytischer Gasreaktionen', *Chemie Ingenieur Technik*, **52** (1980), pp. 844–845.
- [37] J. L. Hahn and E. E. Petersen, 'Poisoning Studies in a Single-Pellet Catalytic Reactor', *Canadian Journal of Chemical Engineering*, **48** (1970), pp. 147–150.
- [38] L. H. Baekland, 'Practical Life as a Complement to University Education—Medal Address', *Industrial Engineering Chemistry*, **8** (1916), pp. 184–192.

Paper Received 10 February 1985; Revised 4 May 1985.