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Chapter 7

Laboratory scale plants for catalytic tests

Luigi Cavalli, Antonella Di Mario

Research and Development, Montecatini Tecnologie, Via Fauser, 50, 28100 Novara, Italy

1. Introduction

Generally speaking, laboratory-scale plants consist of a series of equipment arranged together with the purpose of investigating some critical aspects of the operations of chemical processes.

Naturally, a laboratory-scale plant is projected and built after the research hypothesis becomes concrete, the project feasibility is ascertained and the presence of an economical return is verified. The experimentation with a laboratory-scale plant represents, now more than ever, a strictly required step in the development of a new process or of a new product. In fact, the industrial chemical plants have become more and more complex and large to obtain economies of scale. However all this has increased the risk to be run for an industrial achievement. The laboratory-scale plant, if correctly projected, allows the critical aspects of the process to be defined and, at the same time, points out solutions that can appreciably decrease risks.

High flexibility and low working cost are important aspects in the arrangement of a laboratory-scale plant.

As a particular case a laboratory-scale plant can be projected and used for catalytic tests. In this case the objective of the experimentation is the evaluation, as wide as possible, of catalyst performances. This allows to obtain data and information for catalyst industrial use in a new process or, when a consolidated process is concerned, to make comparisons with other commercial products and therefore to establish the economical advantage available from the choice of a new catalyst.

2. Types and size of laboratory plants

The laboratory plants for catalyst testing can be defined on the basis of the step of catalyst research they are used for. The various sections of the plant are dimensioned on the basis of the reactor volume which in turn depends mainly on catalyst size.

The first research step consists usually of the development of catalyst chemical composition. In this case reactor volumes typically of 1–10 ml and catalyst size of 0.1–1.0 mm are used. The resulting microplants or miniplants are described and discussed in paper 5.

During the scale-up of catalyst manufacturing process the catalytic tests are performed on final catalyst size. This requires much larger reactors with volume mostly in the range 100–1000 ml. The related plants are usually defined semi-scale or semi-technical plants. They will be specifically discussed in this paper.

Plants of larger size (pilot plants) are employed, using the catalyst that will be charged in the industrial reactor, to study the influence of process variables on catalyst performances. A

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special case is represented by the so called side-stream plants paralleling the industrial reactor to use the same feed.

The use of pilot plants in process scale-up is discussed in paper 13.

3. Basic arrangement of a semi-scale plant for catalytic tests

A semi-scale plant for catalytic tests consists mainly of four different sections.

3.1. Storage of reactants

For gaseous reactants this section consists of cylinders containing compressed or liquefied gases, with on–off valves and devices for gas feeding at constant pressure.

Liquid reactants are stored in glass or steel reservoirs having sufficient capacity for the length of the catalytic test.

3.2. Feed of reactants

Gaseous reactants are fed to the reactor from the cylinders of the storage section through stainless steel tubing. Their flow rate is usually measured by rotameters or, preferably, by the more costly mass-flow meters, which easily lend themselves to automatic flow control.

Liquid reactants are usually fed by volumetric pumps.

When a gas-phase reaction is concerned, liquid is fed to the catalytic bed through an electrically heated evaporator. Moreover in this case an effective mixing of different flows is very often required, unless a gaseous mixture is previously prepared in the cylinders. This can be accomplished by right-angle tubing connections and by subsequent abrupt increase of tube diameter for a certain length.

Mixing of liquid flows is not frequent, as the mixture is done, whenever possible, in the storage reservoirs.

3.3. Reactor

In semi-scale plants for fixed bed and fluid bed processes the reactors are mostly constructed in stainless steel. Glass is sometimes used for slurry reactors at atmospheric pressure. For high pressure slurry processes commercial autoclaves are available.

In all the above-mentioned cases the reactor is equipped with a thermocontrolled electrical heating system. The heat exchange is provided by either a circulating or static fluid, wherein the reactor is immersed (water, oil, molten salts). In other cases a high-conductivity metal block (copper is recommended) tightly fixed to the reactor can be used. In the latter case suitably different resistances can be placed along the reactor to obtain better isothermicity.

For strongly exothermic slurry reactions a cooling coil is sometimes inserted in the autoclave to avoid large temperature increases.

3.4. Products recovery and analysis

For gaseous systems the exit gases are usually analysed on-line and then vented (through a suitable abatement device, when required). When liquid components are involved, on-line analysis can be employed, but the connecting tubes must be carefully heated. Liquids are then condensed in a cooling trap and the gases vented as before. Otherwise off-line analysis is done on the condensed liquid and on-line analysis, if required, on the gases leaving the trap. Gas-chromatography is the most frequently used analytical technique in semi-scale plants. Acid–base titration, HPLC, IR spectroscopy are also sometimes used.

4. Basic criteria for projecting a semi-scale plant

As previously mentioned, the projecting of the semi-scale plant is an important step in the work for the development of new or improved catalysts. In fact the evaluation of the catalytic properties (activity, selectivity, life) allows not only the comparison of different catalysts, but also gives information useful for the prediction of catalyst behaviour in the industrial reactor.

It is obvious that the data obtained must be accurate and reliable, that is possible only after correct projection of the whole plant. Isothermicity of the catalytic bed should be considered the main requirement for obtaining reliable data, therefore every effort should be devoted to approach this goal. This is not a problem for fluid-bed reactors, but it is for fixed-bed and slurry ones, as many catalytic reactions of industrial interest are strongly exothermic, more rarely endothermic.

In practice, in fixed-bed reactors the circulation rate of the thermostating fluid should be as high as possible, while, for metal-block reactors, different electrical heating sections should be provided, each of which having its own controller. This arrangement allows tuning the electrical input of the various sections during reactor operation, to compensate for the temperature gradients in the catalytic bed.

In slurry reactors the addition, as previously mentioned, of a cooling coil could be beneficial, but the regulation of coolant flow rate is very critical.

In fixed beds catalyst dilution with some inert material, preferably with high heat conductivity and with the same size, could contribute to decrease temperature gradients.

The output data of catalyst testing in a semi-scale fixed bed plant consist usually of a set of conversion curves as function of space velocity for different temperatures. As reaction rate strongly varies with temperature, the plant should have facilities for changing reactants flow rates in a very wide range.

A slurry reactor, where the output is given by a curve of conversion versus time, should be provided with a fast and reliable system for liquid sampling during the run. A high-speed stirring system is also required, to decrease temperature gradients and improve mass transfer.

A fixed bed reactor should have a diameter at least 5 times larger than catalyst pellet size, to ensure a correct fluodynamic regime. The height/diameter ratio of the catalytic bed should be at least 10, to minimize back diffusion phenomena. Therefore sufficient length should be provided for the reactor.

An axial thermocouple well is always recommended to record the temperature profile during the run. When geometrical constraints do not allow this, two thermocouples should be placed just before and after the catalytic bed.

Where possible, the catalytic tests should be carried out in the same operating conditions as the industrial reactor. But in several cases the conversion in such conditions is so high that catalysts with different activities cannot be discriminated. In such cases making activity tests at lower temperatures is compulsory, as there are practical limits to the increase of space velocity.

To the contrary, selectivity tests have to be performed at the same temperature and conversion levels of the industrial reactor.

Sometimes it is necessary to make life tests in a relatively short time period (accelerated life tests). When catalyst decay is due to sintering, this is accomplished by heating the catalyst, in reactant medium or not, at a temperature much higher than that of the process for a predetermined length of time. Obviously the heating system should be projected in order to do this. When catalyst decay is due to poisoning, facilities for poisons feed together with reactants should be provided. It is recommended that a separate plant is dedicated for poisoning tests.

When the catalytic tests concern the improvement of a catalyst used for a consolidated process, it is advisable to project the semi-scale plant on the basis of scaling-down the industrial plant. The significance of semi-scale data will be thus improved.

Finally it should be remembered that catalyst testing on real-size pellets can be advantageously performed in gradientless high conversion reactors (Carberry and Berty reactors), which are commercially available.

Information about the equipment for measurement and regulation of temperature, pressure, flow rate and about analytical techniques has been already given in paper 5 for small-scale laboratory plants and holds also for semi-scale plants.

5. Safety systems

In the project of the semi-scale plants due attention must be paid to the choice of materials, especially for the reactor, taking into consideration on the basis of working temperature, pressure and of the nature of corrosive agents, if any.

In several cases the reactants can form explosive mixtures, when combustion supports (such as oxygen) and combustible compounds (organic compounds, hydrogen, carbon monoxide, ammonia, etc.) are mixed together. For each mixture the explosive limits must be taken into account and the experiments planned so that the gaseous mixtures are always outside such limits. Automatic safety devices should ensure gas flow interruption when the explosive limits are reached. In any case suitable rupture disks must be inserted in plants with explosion risks. In the more risky cases suitable screens and also remote control devices can be installed.

When flammable compounds are used, (for instance, hydrocarbons), losses must be prevented by careful control of the tightness of the whole plant before starting every run.

When toxic compounds are involved, special attention should be given to projecting reactants storing and products collecting sections. The threshold limit values should be well known by the operators and the compounds monitored in the ambient atmosphere.

If the compounds used are toxic only if ingested, their DL50 values should be known.

It should also be remembered that in Italy operators using toxic gases must possess special permission given by National Health Service.

6. Automation systems

The function of a control system is to measure the value of a variable and then produce a counter response to limits its deviation from reference point. In an automatic control system, the operator is replaced in the control loop by a device known as the automatic controller.

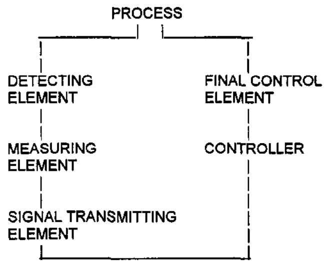
A process automation has some basic benefits:

the process, whether it is being carried out on a bench-scale, a semi-scale or a full production scale, can be run continuously without operator's attention. This reduces manpower requirements and labour costs. The reduction in operators results, also, in a decrease of human errors.

adherence to optimum conditions results in an improvement in overall process quality.

safety in operation is increased as warnings of abnormal conditions is provided and automatically corrective actions taken. In addition, automatic control eliminates the need for operators to be in the vicinity of hazardous equipment or conditions.

The basic layout of an automatic control loop is shown:



A good control depends both on the accuracy of the measuring system and on its speed of response. If a time lag is present, it is made up of 3 contributing factors: the lag inherent in the process, the response lag associated with the detecting element and the lag associated with signal transmission. After the signal transmission, the controller is the fundamental element in a control loop. It receives information continuously from the measuring devices and sends a signal back to the final control element.

The controller compares the value of a measured variable to its established value to produce an output signal that maintains this value constant. The signal produced by the controller can be either pneumatic or electronic.

Controllers are chosen on the basis of required actions:

on–off control action: a control mechanism having only two values of output;

proportional control action: the controller output signal is proportional to the deviation;

proportional-plus-reset control action: the controller output signal is proportional to the time integral of the deviation;

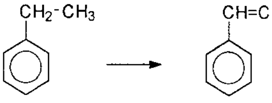
rate control action: the controller output signal is proportional to the rate of deviation change.

7. Practical examples of semi-scale plants

The herein described semi-scale plants have been built with the purpose of using them to make catalytic tests on real-size catalysts, in particular in the development of improved catalysts for already existing processes.

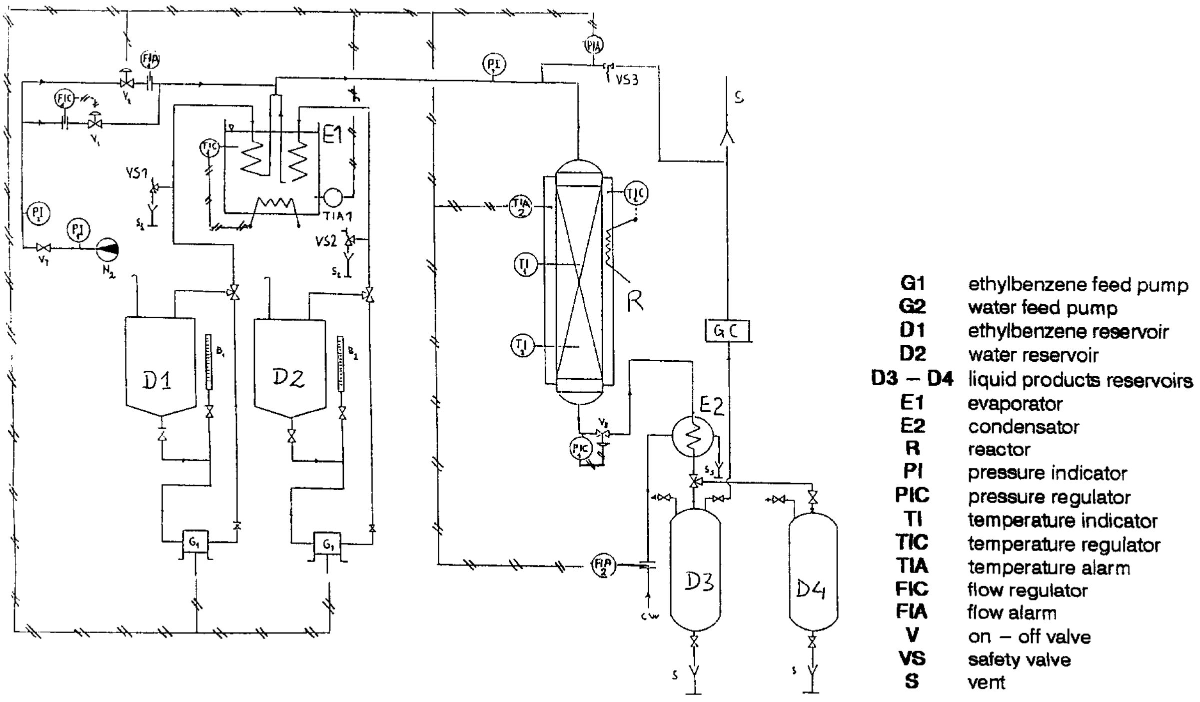
7.1. Dehydrogenation of ethylbenzene to styrene (endothermic fixed bed)

Styrene is mainly produced by ethylbenzene dehydrogenation according to the reaction:



The main characteristics of this industrial process are the following:

Radial adiabatic reactor:usually 2 in series
Width of catalyst layer: typically 70–80 cm



G1	ethylbenzene feed pump
G2	water feed pump
D1	ethylbenzene reservoir
D2	water reservoir
D3 – D4	liquid products reservoirs
E1	evaporator
E2	condensator
R	reactor
PI	pressure indicator
PIC	pressure regulator
TI	temperature indicator
TIC	temperature regulator
TIA	temperature alarm
FIC	flow regulator
FIA	flow alarm
V	on – off valve
VS	safety valve
S	vent

Fig. 1. Styrene from ethylbenzene dehydrogenation semi-scale plant.

Temperature range: 600–650°C
Pressure range: 0.5–1.5 atm
LHSV: 0.5 h^{-1}
Steam/oil ratio: 1.5–2.0 by weight
Catalyst charge: 100–200 tons
Catalyst: Fe_2O_3 + K_2CO_3 + promoters, (Fe_2O_3 is reduced to Fe_3O_4 in working conditions)
Catalyst shape: cylindrical extrudates = 3–5 mm

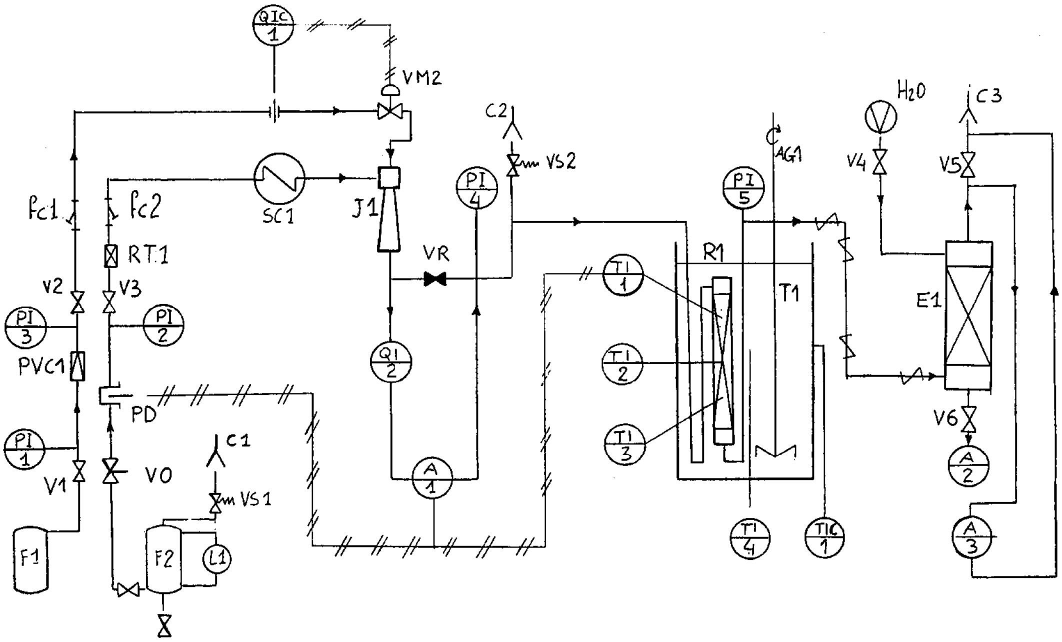
Semi-scale reactor compliance with industrial conditions is the most common choice. Therefore industrial temperature, pressure, LHSV, steam/oil ratio are adopted.

Temperature values lower by some tens of °C are usually required to keep conversion not too close to equilibrium. With the usual volume of semi-scale reactors (100–1000 ml) the presence of external diffusion phenomena have to be expected. Whether they can hinder or not catalyst evaluation is a matter of experimentation.

Typical operating conditions night be the following: LHSV = 0.5 h^{-1}; S/O = 1.5; $P = 0.5$ atm (by dilution with nitrogen); $T = 550–600$°C.

In Fig. 1 a scheme of the semi-scale plant is shown.

Ethylbenzene and water are sent from the reservoirs to the evaporator by a piston pump. The two flows are mixed together and, if necessary, nitrogen added, then they reach the downflow reactor. Exit gases are condensed by a heat exchanger and liquids are collected in reservoirs. Gases are analysed on-line by GC and vented. Reactor heating is ensured by 10 electrical resistances.



F1	Air	PD	Benzene feed pump	AG1	Stirrer
F2	Benzene	V	on – off valve	T1	Molten salts bath
L1	Level indicator	VR	Throttle valve	E1	Scrubber
PCV1	pressure reducer	VM	Automatic valve	TIx	Temperature indicator
fc	Filter	VS	Safety valve	TIC	Temperature regulator
RT1	Back pressure valve	C	Vent	A1	On line benzene analyzer
SC1	Evaporator	QI	Rotameter	A2	Liquid effluents analysis
QIC	Mass flowmeter	J1	Mixer	A3	Gaseous effluents analysis
		R1	Reactor		

Fig. 2. Maleic anhydride from benzene semi-scale plant.

The plant is equipped with various safety systems. In the case of coolant fluid flow interruption in the heat exchanger, excessive reactor heating or overpressure in the reactor feed line, nitrogen is introduced into the plant. Simultaneously the reactor heating is interrupted.

Prior to the run the catalyst is reduced and stabilised in situ in appropriate conditions. As the reaction is fairly endothermic, a minimum temperature is encountered along the catalytic bed.

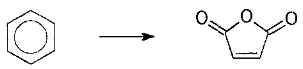
To have a correct comparison between different runs, heating is regulated so that the exit temperatures are always the same.

The following type of data were obtained for the experimental runs: conversion/T, selectivity/T, conversion/selectivity, conversion/(S/O), selectivity/(S/O), pressure and LHSV being constant. Conversions in the range 50–70% and selectivities in the range 85–95% are usually obtained. By complex kinetic models the rate constant can be calculated.

The above-mentioned semi-scale plant has been proved to be effective and reliable in the evaluation of catalysts for styrene production in their real size.

7.2. Oxidation of benzene to maleic anhydride (exothermic fixed bed)

Maleic anhydride is industrially produced by either butane or benzene oxidation, in the latter case according to the reaction:



The main characteristics of this industrial process are the following:

reactor: multitubular
tubes number: 3000–12000
internal tube diameter: 16–27 mm
bed depth: 1600–3300 mm
temperature: 360–410°C
cooling agent: molten salts
pressure: 0.5–1.5 atm
space velocity: 2200–2600 h^{-1}
benzene content: 1.35–1.70% vol.
catalyst: $V_2O_5 + MoO^{3+}$ promoters on ceramic ring carrier

Also in this case, semi-scale reactor compliance with industrial conditions is the most common choice.

Therefore the industrial values of temperature, pressure, space velocity and benzene/air ratio are adopted.

The following test conditions are typical of semi-scale reactors:

internal tube diameter: 23 mm
bed depth: 600 mm
temperature: 360–410°C
cooling agent: molten salts
pressure: 0.5 ate
space velocity: 2400 h^{-1}
benzene content: 1.35% vol.

Prior to the run the catalyst must be activated in situ.

At standard space velocity and benzene/air ratio, the molten salts temperature is increased starting from 360°C until a stable hot spot of 450°C is reached.

A whole test allows conversion, selectivity and yield to be determined by a series of runs covering a temperature range of 360–410°C.

Conversions in the range 60–100% and yields by weight of 60–95% are usually obtained.

The comparison among the performances of different catalysts can be made by plotting conversion and yield or selectivity as function of temperature.

In Fig. 2 a scheme of a semi-scale plant is shown.

Air flowing from F1 is measured by means of the mass flowmeter QIC1. Benzene from F2 is measured by the pump PD and evaporated in SC1.

Air and benzene are mixed in J1 and checked by a on-line benzene analyser, then fed to the reactor A1, immersed into a thermostatic bath controlled by TIC1 and containing molten salts (Hitec mixture) stirred by AG1.

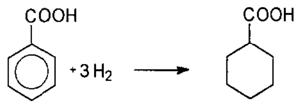
Pressure drop of the reactor can be obtained by PI4 and PI5.

Gaseous effluents are washed in the column E1 where maleic anhydride is converted in maleic acid and the solutions obtained analysed in A2. Permanent gases are analysed in A3 by GC analysis.

Some safety devices are present: if benzene/air ratio and/or reactor temperature become too high, the benzene feed is interrupted.

7.3. Hydrogenation of benzoic acid to cyclohexancarbossilic acid (slurry reactor)

In the manufacture of caprolactam, benzoic acid hydrogenation to cyclohexancarbossilic acid is the fundamental step (Fig. 3). The aromatic ring of the benzoic acid is hydrogenated under pressure in the presence of palladium catalyst in a series of 3 continuous stirred tank reactors at 170°C and 80 Atm, according to the reaction:

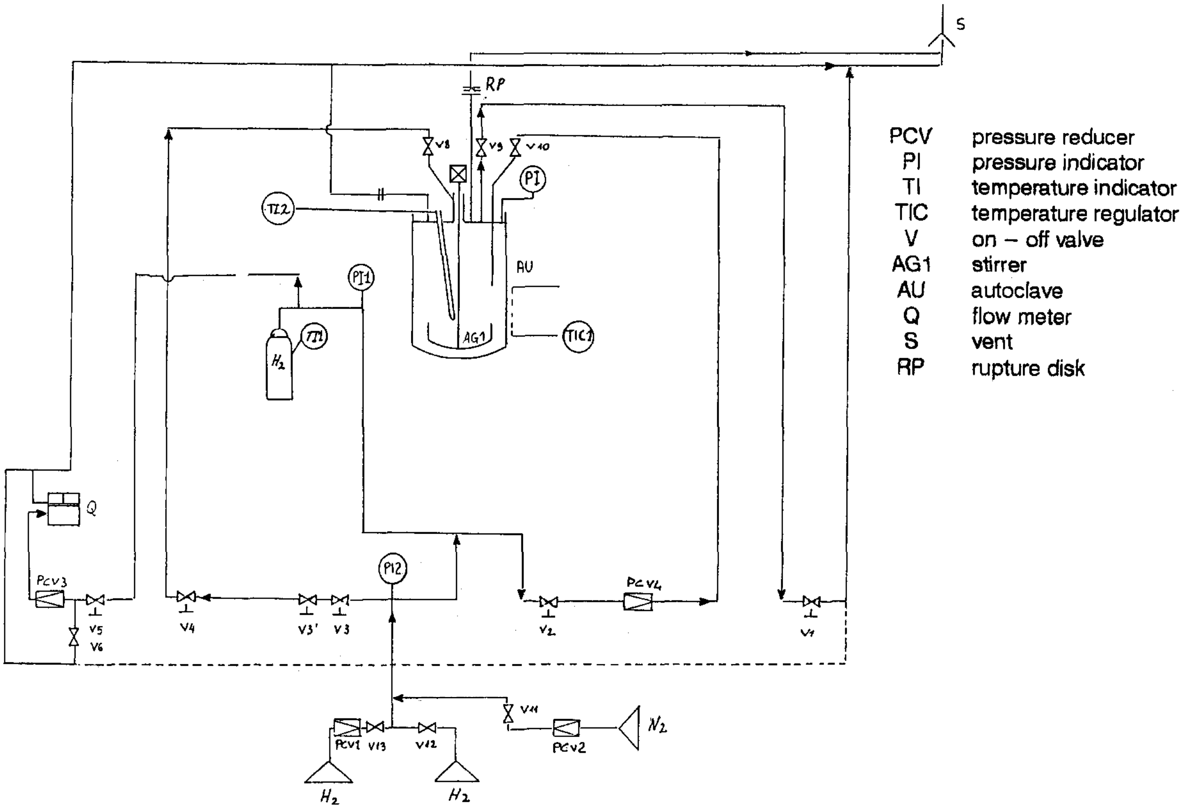


The reaction goes almost to completion (90%) in the first reactor.

In a semi-scale plant, the industrial first reactor can be simulated by an autoclave, but, in this case, the reaction is carried out as a batch process.

Preferred operating conditions are the same of industrial plant.

In this way a more realistic evaluation of catalysts performances can be carried out. Only the catalyst quantity utilised must be changed to



PCV	pressure reducer
PI	pressure indicator
TI	temperature indicator
TIC	temperature regulator
V	on – off valve
AG1	stirrer
AU	autoclave
Q	flow meter
S	vent
RP	rupture disk

Fig. 3. Cyclohexancarbossilic acid from benzoic acid semi-scale plant.

minimize the diffusive effects, because, if the same catalyst/benzoic acid ratio is used, the reaction rate would be too fast. To promote the mass transfer at the gas–liquid–solid interfaces a turbine stirrer with a stirring rate of at least of 400 rpm has been employed. Such stirring rate has been established by preliminary tests.

As heat transfer problems are unavoidable, it is convenient to start the reaction when the temperature inside the autoclave is some degrees lower than the reaction temperature, depending on autoclave volume. The temperature increases up to 170°C in a few minutes and remains constant until the end.

The pressure is kept constant in the autoclave during the runs.

To this purpose the autoclave is connected to a calibrated higher-pressure reservoir through a high-precision pressure reducer. To avoid overpressure phenomena that could occur, a security valve with a rupture disk has been included.

The following procedure is used for the test. Benzoic acid and catalyst are loaded in the autoclave and heated up to about 160°C without stirring. The reaction starts when the stirring is switched on and the hydrogen consumption is followed by the pressure decrease in the reservoir. The catalyst activity is expressed as reaction rate in the range 20–90% of conversion. The lower values are not considered because the temperature in this range is not constant. At the end of the run a sample of products analysed by GC to detect by-products.

The above-mentioned plant is useful to make catalyst tests both on laboratory scale and semi-scale. Moreover this type of semiscale plant can be used in the fatty acids hydrogenation and in many other hydrogenation reactions.

8. For further reading

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