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Three-phase catalytic reactors

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Abstract

This article aims at presenting both the general aspects and one working example of the so-called three-phase catalytic reactors. Being a contribution at a Seminar on Catalytic Reactors the purpose is essentially didactic in showing the problems met and how a few of them can be investigated and solved. Only trickle bed and slurry reactors are considered the most important, probably, among the class of three-phase reactors. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

There are several definitions of “multiphase reactors”. In principle, all reactors in which more than one phase is present may be defined as multiphase. However, this specification is generally devoted to systems in which two fluid phases (gas–liquid, liquid–liquid) are at least present, or to three-phase systems (gas–liquid–solid). In the following we will focus our attention on gas–liquid reactors, in which the solid phase is a heterogeneous catalyst. A deeper information on these reactors can be drawn from some books published in the 1980s [1–3].

A fundamental division of three-phase reactors may be made by whether the solid phase is present as a fixed bed or suspended in the liquid.

The former class covers fixed bed reactors with cocurrent or countercurrent gas–liquid flow (trickle-

bed reactors, submerged upflow reactors). The catalyst is usually in the form of porous pellets (3–6 mm) or extrudates (1–2 × 3–6 mm), poured randomly into the reactor.

The second class is mainly represented by slurry stirred reactors and slurry bubbling reactors. Here the catalyst is in the form of small particles, porous or not porous, with a size of the order of 50–200 μm or even less, suspended in the liquid by the fluid motion.

The reactors of the first class operate as continuous ones and are generally used for hydrogenation processes like:

- hydrotreating of mineral oils;
- hydrogenation of α -methyl styrene to cumene;
- hydrofinishing of lubricating oils;
- hydrogenation of caprolactone to hexanediol;
- hydrogenation of alkylantraquinone to alkylhydroquinone.

Slurry-type reactors are frequently used as semi-continuous or batch reactors; they are more flexible and are widely employed in specialty processes. The

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stirred reactors are also employed as multipurpose reactors in the fine chemical industry. Bubbling slurry reactors are particularly employed in fermentation processes; here the solid phase is represented by the biomass, which acts as a biocatalyst in the production of enzymes or other products.

The choice of a suitable reactor is strictly connected with the requirements and characteristics of the process and the engineering aspects. Slurry reactors, either continuous or batch, require separation of the catalyst that represents a cost and a further time of operation; moreover, abrasion of the catalyst with generation of very fine particles may occur. Stirred reactors have a high liquid holdup and a low (mass of catalyst/mass of liquid) ratio. As a consequence, they are particularly interesting for highly exothermic reactions (temperature control of these reactors is not a difficult task); on the other side, a negative aspect is represented by the occurrence of possible homogeneous side reactions. As batch reactors they must be employed when particular policies of reactants feed and temperature are adopted.

Continuous fixed bed reactors are generally employed for high throughputs and simple reactions. A limitation, in certain cases, is represented by temperature control, since they operate in an adiabatic mode. Difficulties may also arise from fluid phases distribution, which may give rise to poor performance or even hot spots and sintering of the catalyst.

2. Fixed bed reactors

2.1. Hydrodynamic regimes

Fixed bed reactors are mostly employed with cocurrent flows of gas and liquid to avoid the hydrodynamic limitation of flooding. Downward flows (trickle-bed reactors) are much more widely used than upward flows, because pressure drop is much less (in upflow, instead, hydrostatic head of the liquid must be overcome). In trickle-bed reactors, the liquid trickles down over the packing in the form of film or rivulets. The gas flows cocurrently in the void space.

Depending on the relative flow rate of the two phases, several regimes have been set up [4,5].

At low liquid and gas flow rates, the two phases flow with a low hydrodynamic interaction (low interaction regime, trickling regime); the pressure drop has the same order of magnitude as that arising from gas flow alone through a dry packing [5]. An increase of the liquid flow rate, at a constant gas flow rate, leads first to the pulsing flow, characterized by the formation of alternate slugs – liquid-rich and gas-rich slugs – travelling along the reactor (pulsing regime); the pressure drop increases remarkably, and shows a fluctuating behaviour. These fluctuations are due to the formation of liquid bridges in the packing channels caused by the thickness of the liquid film and the waves on it generated by the gas flow interaction. These bridges stop the gas in the channels, the pressure behind them increases and finally the liquid is blown up; then, the process is repeated.

A further increase of the liquid flow rate at relatively low gas flow rates can give rise to a bubbling flow, where the liquid is the continuous phase and the gas is carried along the reactor as bubbles. On the other hand, at high gas flow rates and low liquid flow rates, the spray regime exists, where the liquid is carried by the gas in the form of droplets.

Fig. 1 represents a map of these regimes for liquids and gas similar to water and air, respectively; it is certainly not exhaustive because the physical properties of the liquid (mainly the foaming characteristics) have important effects not yet mapped.

The data used for Fig. 1 were all taken at atmospheric pressure. A recent paper by Wammes et al. [6] shows a certain influence of pressure (tests till 2 MPa were performed); these data were in qualitative agreement with the trickle flow-pulsing flow transition diagram proposed by Talmor [7].

The regimes of interest in commercial units are the trickling flow and the pulsing flow near the transition between these two regimes. Pilot and bench-scale reactors are instead operated in the trickling flow at very low flow rates per unit area. This causes problems in scale-up as will be shown later on.

Also two phase upflow through a packed bed gives rise to several regimes [8], but only the one where the gas is bubbling in the continuous liquid phase is of practical interest. Upflow bubbling reactors may be employed for a highly exothermic reaction because of the relevant holdup of liquid.

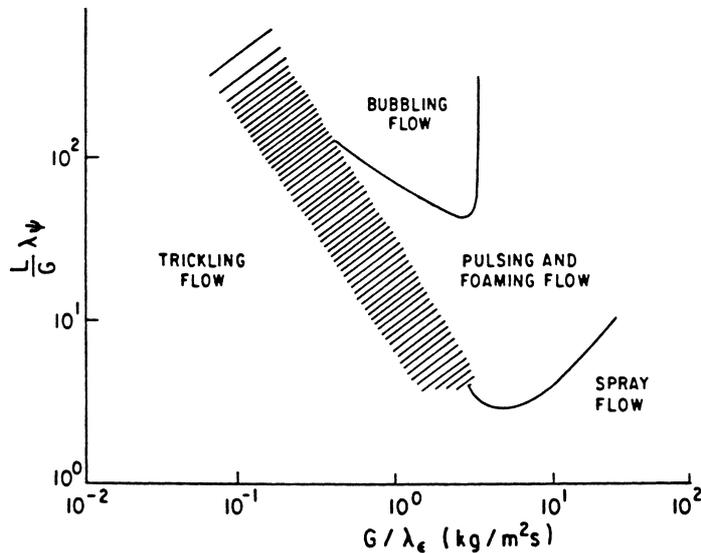


Fig. 1. Flow regime maps for trickle-bed reactors.

2.2. Micro- and macrokinetics

Microkinetics is generally described in terms of a series of elementary kinetic steps. The reaction is assumed to occur only in the porous solid catalyst uniformly wetted by the liquid. The kinetics inside the pellet may be affected by diffusion phenomena in the pores (assumed to be filled completely by the liquid) according to the Thiele modulus. These effects are classically taken into account by the catalyst effectiveness factor η . Intrinsic kinetics and effectiveness factor are determined in laboratory bench reactors (slurry or basket-type reactors), and great care must be devoted in order to define them accurately.

The determination and the use of this kinetic information is complicated by the fact that the reaction heat is released into the pellet and this may eventually lead to temperature gradients inside the catalyst. However, it was demonstrated [9] that when the pores of the catalyst are full of liquid, the temperature gradients can be ignored even in the presence of a highly exothermic reaction.

The reactants are supplied to the catalyst from the liquid; at steady state, for each reactant, the following equation can be written:

$$-k_s(c_{As} - c_{Al}) = \frac{V_c}{A_c} R_A(c_{As}) \quad (1)$$

where k_s is the liquid–solid mass transfer coefficient and $R_A(c_{As})$ is the kinetic rate inside the pellet at the interface liquid–solid concentration c_{As} .

The gaseous reactant is transferred to the liquid phase by a two-step phenomenon: gas-to-liquid interface transport and liquid interface-to-bulk liquid transport. Generally, the gas phase resistance is very weak and ignored; the gas–liquid mass transport flux (per unit reactor volume) is written as follows:

$$j_A = -(k_1 a)(c_{Al} - c_A^*) \quad (2)$$

where c_A^* is the liquid concentration in equilibrium with the gas phase.

Macrokinetics refers to the distribution of reactants in the reactor, and concerns the reactor model.

The complete, heterogeneous model assumes:

- the three phases are separated and continuous;
- the solid is in contact with the liquid only;
- the particles are uniformly wetted;
- the plug flow-axial dispersion model is adopted for the fluid phases.

For a bimolecular reaction between a gaseous reactant A and a liquid (nonvolatile) reactant B:



the model is written as follows:

gas phase:

$$-D_g \frac{d^2 c_{Ag}}{dz^2} + \frac{d(v_g c_{Ag})}{dz} + (k_1 a)(H c_{Ag} - c_{Al}) = 0, \quad (3)$$

liquid phase:

$$-D_l \frac{d^2 c_{Al}}{dz^2} + \frac{d(v_l c_{Al})}{dz} - (k_1 a)_A (H c_{Ag} - c_{Al}) + (k_s a)_A (c_{Al} - c_{As}) = 0 \quad (4a)$$

$$-D_l \frac{d^2 c_{Bl}}{dz^2} + \frac{d(v_l c_{Bl})}{dz} + (k_s a)_B (c_{Bl} - c_{Bs}) = 0, \quad (4b)$$

solid phase:

$$(k_s a)_A (c_{Al} - c_{As}) / \nu_A = (k_s a)_B (c_{Bl} - c_{Bs}) / \nu_B = (1 - \epsilon_0) R(c_{As}, c_{Bs}) \quad (5)$$

where $R(c_{As}, c_{Bs})$ is referred to as catalyst volume.

Allowance is made for variation of the gas and liquid superficial velocities.

The model as described by Eqs. (3–5) does not take into account heat effects and temperature distribution; these will be considered later on. Even with this simplification, the model is rather complex, nonlinear, affected by several hydrodynamic parameters.

Axial dispersion effects are usually ignored in commercial units because of the low axial gradients of concentrations; however, the liquid axial dispersion coefficient should be considered in bench and pilot reactors. Several data exist on D_l , but they are in poor agreement. A useful survey of literature on the topics can be found in a recent paper by Iliuta et al. [10].

The reason for the scatter of the data is due to the complexity of the liquid hydrodynamics. A simple piston-dispersion model is generally considered to be not suitable for simulating the response curve in dynamic experiments carried out in order to characterize the hydrodynamics of the liquid; a PDE model (piston-dispersion-exchange with dead zones) has given better results. So, data of D_l obtained either with PD or PDE models can be found in the literature. Furthermore, the mathematical method adopted to identify the parameters of the hydrodynamic model have a remarkable effect on the obtained values of the parameters [11,12]. The final result is a considerable scatter of data. This would suggest to design pilot units

and program experiments in order to have low axial gradients of concentration and minimize the effects of axial dispersion.

As for mass transfer coefficients, both gas-to-liquid and liquid-to-solid, a very good presentation of data and correlations can be found in the book edited by Gianetto and Silveston [3]. Also in this case, there is a wide scatter of data because of the variety of packing examined, and most of all, because of the important role of the physical properties of the liquid, which are difficult to take into consideration (surface tension, foaming, wettability of the solid). An interesting paper by Mazzarino et al. [13] points out the effects of surfactants in a gas-liquid-solid reaction. For this reason, the correlations of $(k_1 a)$ covering a wide range of operating conditions are usually expressed as a function of pressure drop or energy dissipation [14,15]. This way of correlating data may be interesting from a scientific point of view, but it is not so for design purposes because it shifts the problem to pressure drop calculation, i.e. to another problem not well solved as yet.

For trickle-bed reactors at very low liquid velocities ($0.05\text{--}0.5 \text{ mm s}^{-1}$), the data of $(k_1 a)$ by Goto and Smith [16] and Turek and Lange [17] can be employed. For $(k_s a)$ in such conditions, the data by Goto et al. [18] may be suggested. As concerns upflow reactors, Visser et al. [19] succeed in modelling a bench scale reactor for hydrogenation of styrene to ethylbenzene by using, for $(k_1 a)$, the correlation proposed by Snider and Perona [20], and for $(k_s a)$, the one by Specchia et al. [21].

A considerable simplification of the model is often adopted, especially for hydrotreating reactions of mineral oils where the so-called pseudo-homogeneous model is employed. In this model, there is no distinction between the phases; all the kinetic phenomena are lumped into a homogeneous rate equation, generally a power law equation. Only the liquid concentrations are considered, and a plug flow model is adopted so that the disappearance of a liquid reactant is described as follows:

$$v_l \frac{dc_{Al}}{dz} = R'(c_{Al}) = -k_v c_{Al}^n \quad (6)$$

This model is adopted to interpret pilot data when the overall reaction is a combination of different parallel and series reactions as in hydrodesulphuration

or demetallation of oils. The simplification of the reaction path implies a simplification of the reactor model.

Sometimes, several reacting compounds in such processes can be grouped into two classes: refractory compounds and non-refractory compounds; the kinetic model considers two reactions in parallel with independent kinetic constants and activation energy. Eq. (6) is then transformed as follows:

$$v_1 \frac{dc_{NR,1}}{dz} = -k_{NR} c_{NR,1}^n \quad (7a)$$

$$v_1 \frac{dc_{R,1}}{dz} = -k_R c_{R,1}^m \quad (7b)$$

An example of the application of this approach to desulphuration and demetallation reactions can be seen in the paper by Iannibello et al. [22].

2.3. Solid–liquid contacting effectiveness

The heterogeneous model described before assumes a complete and even wetting of the catalyst pellets; accordingly, the reactants are supplied to the catalyst from the liquid phase only, and react in liquid filled pores only.

Actually, the situation is much more complicated, especially in trickle-bed reactors. At low liquid flow rates as those adopted in pilot and bench-scale reactors (much less than 1 mm s^{-1} of superficial velocity), the catalyst is unevenly contacted by the liquid so that its outlet surface is partially in contact with flowing rivulets, partially in contact with dead zones, and partially covered by a very thin film (Fig. 2). The reactants supply rate is uneven due to the different thicknesses of the liquid film and transport efficiency in the different zones; this may cause an uneven penetration of the reactants into the pellet, and result in an apparent internal diffusivity less than the actual one [23].

As a consequence, the reaction rate may be more affected by diffusion phenomena and may be slower than that in an evenly wetted particle.

This phenomenology has been verified for quasi-isothermal reactions, when the liquid reactant is the key one and not volatile, and a contacting effectiveness η_E (less than one), or partial wetting, has been introduced [24,25]. In addition to the experimental data available, Mills and Dudukovic [26] proposed an

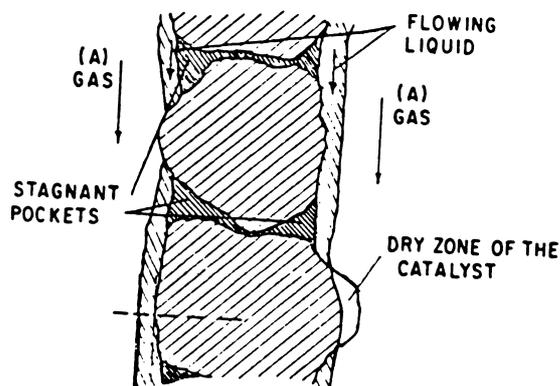


Fig. 2. Distribution of the liquid over the packing in a trickle-bed reactor.

equation for η_E in terms of Reynolds, Weber and Froude numbers, that has received some indirect validation [22]. η_E depends on many variables, but mainly on the liquid superficial velocity; at $v_1 \geq 4 \text{ mm s}^{-1}$, η_E is 1; at $v_1 < 1 \text{ mm s}^{-1}$, it becomes smaller than 0.8 and decreases as the liquid velocity decreases.

This gives rise to a problem in scaling up, since in pilot or bench reactors the contacting effectiveness plays a considerable role, while in commercial units it is almost 1.

The contacting effectiveness can be introduced in the two models presented before; Eq. (5) of the heterogeneous model is modified as follows:

$$(k_s a)_A (c_{A1} - c_{As}) / \nu_A = (k_s a)_B (c_{B1} - c_{Bs}) / \nu_B \\ = (1 - \epsilon_0) \eta_E R(c_{As}, c_{Bs}). \quad (8)$$

The pseudo-homogeneous model is written in the following way:

$$v_1 \frac{dc_{A1}}{dz} = -\eta_E k_v c_{A1}^n = -k_{app} c_{A1}^n. \quad (9)$$

Indeed, it was the increase of k_{app} vs. v_1 in pilot and commercial trickle-bed reactors that first gave rise to the problem of liquid–solid contacting effectiveness [24].

When the key reactant is the gaseous one, things are different. Indeed, the gaseous reactant is fed more efficiently to the catalyst through the unwetted zones so that a decrease of the liquid velocity may lead to an increase of the apparent reaction rate; the reason being that in this way the unwetted zones

increase and the supply of the gaseous reactant will increase [27,28].

2.4. Heat transfer

The effects of the heat generated by the reaction on the reactor performance must be considered at three levels:

- intraparticle temperature gradients;
- interphase heat transport;
- temperature distribution in the reactor.

Intraparticle gradients of temperature depend on two parameters:

$$\beta = \frac{c_{As}(-\Delta H_r)D_{eff}}{\lambda_{eff}T_s} \quad (\text{Prater number}), \quad (10)$$

$$\gamma = E/RT_s \quad (\text{Arrhenius number}) \quad (11)$$

Solid–fluid temperature differences are instead governed by the Biot number of the particle:

$$(Bi)_p = h_s d_p / \lambda_{eff} \quad (12)$$

It was demonstrated [9] that the gradients inside a pellet with pores filled by the liquid are very weak due to the low value of D_{eff} and the (relatively) high value of λ_{eff} . Moreover, if the particle is in contact with flowing liquid, $(Bi)_p$ is quite high because of the high value of the heat transfer coefficient. This means that if the particle is evenly and effectively wetted, there are no temperature gradients and the reaction at the particle level occurs isothermally.

However, at low liquid velocities, thermal instability can take place in trickle-bed reactors because of the uneven liquid distribution at the particle scale. Stagnant liquid zones with very poor liquid renewal are very ineffective for heat transfer. The heat generated near these zones may give rise to a remarkable increase of temperature that may eventually lead to evaporation of the liquid. In the dry zone then, a much faster gas phase reaction can take place that enhances evaporation and increases the local temperature. A hot spot so generated can extend to all parts of the reactor in particular operating conditions. This phenomenon has been observed at the bench scale by Germain et al. [29] and Hanika et al. [30,31].

The distribution of the temperature in the reactor is essentially caused by a convective mechanism. Gas

and liquid are assumed at thermodynamic equilibrium, i.e. equal temperature, gas phase saturated by the liquid. Assuming a piston flow model, the distribution of temperature is given by the following equation:

$$\frac{d}{dz} [(v_1 \rho_1 c_{p1} + v_g \rho_g (\omega_1 c_{p1} + \omega_{Cg} c_{p1})) T] + \frac{d}{dz} (v_g \rho_g \omega_{Cg} \lambda_C) = (-\Delta H_r) |R_A(c_{As}, c_{Bs}) / \nu_A|. \quad (13)$$

The gas phase has been considered as constituted partly by an uncondensable gas I, with a mass fraction ω_1 , partly by vapour of a liquid component C (mass fraction in the gas: ω_{Cg} ; vaporization heat: λ_C). The vapour partial pressure of C is calculated by vapour–liquid equilibrium relationship. Hence, two further equations are needed: a mass balance of C and a gas–liquid equilibrium equation:

$$v_{1,0} \rho_{1,0} \omega_{C,0} = v_1 \rho_1 \omega_{C1} + v_g \rho_g \omega_{Cg} \quad (14)$$

$$\omega_{Cg} = f(\omega_{C1}, \dots, T). \quad (15)$$

The vaporization of part of the liquid caused by the reaction heat is a way to control the temperature rise for highly exothermic reaction; to this aim, a volatile solvent is added to the liquid reactants. Care must be taken to avoid formation of dry zones due to evaporation because this will give rise to gas phase reactions and enhance heat generation rate. In other words, the mass flow rate of the volatile solvent must be suitably higher than that evaporated by the reaction heat.

Another temperature control policy is recycling of a cooled part of the outlet liquid flow either at the inlet or along the reactor. In this way, however, the liquid reactants are diluted and the reaction rate depressed. For this reason, injection of cold gaseous reactants along the reactor may be better; of course, the heat capacity of the gas is low so that this method can be adopted only for middle conditions of reaction heat.

Less frequent, although efficient, is intercooling of fluids between two sections of the reactor by heat exchangers.

The model and the considerations are valid for upflow and downflow reactors. Upflow reactors, however, generally do not give rise to serious problems of temperature control, while care must be taken with trickle-bed reactors. Here, a high liquid superficial velocity ($>4 \text{ mm s}^{-1}$) and good liquid distribution is required for good temperature control in commercial units. That notwithstanding, sometimes hot spots

occur due to occlusion of some packing channel by fine particles. Downstream this occlusion, a dry catalyst zone is formed, and gas phase reactions may take place with an increase in the rate of generation of heat. This may eventually result in an enlargement of the dry zone, because of evaporation of liquid, an increase of temperature and sintering of the catalyst.

2.5. Nontraditional fixed bed reactors

To improve the performance of fixed bed reactors, new reactors have been proposed; among them, trickle-bed reactors (periodically operated), monolith two-phases reactors and structured catalyst reactors can be cited.

In a trickle-bed reactor (periodically operated) the liquid feed is periodically changed between two extreme values (the minimum flow rate is generally null) with a square wave form. When the liquid flow is cut off, the bed partially drains. This thins out the liquid film surrounding the particles with an increase in the transport flux for the gaseous reactant. When the liquid flow rate is fixed at the maximum value, there is an efficient transport of the liquid reactants and products to and from the pellets. Interesting results were obtained with this operating method in the case of oxidation of SO_2 to SO_3 over carbon catalyst [32] and for hydrogenation of α -methylstyrene [33]. No commercial application of this operating way has been performed until now. It may be observed, however, that unsteady reactors, when properly used, give surprising results; hence, the periodic operations of fixed bed reactors must be considered a proposal worth to consider.

Use of monolith reactors for two-phase reactors is more mature from a technological point of view. The hydrogenation of alkylanthraquinone in hydrogen peroxide production is a commercial example of the application of monolith reactors for two-phase reaction (Eka Nobel–Akzo Nobel). Several studies exist on the topics starting from the pioneering work of Mazzarino and Baldi [34]; Irandust and Andersson [35] and Cybulski and Moulijn [36] are the authors of wide reviews on the application of monolith reactors for gas and gas–liquid reactions. The essential behaviour of this type of reactor is a lower pressure drop in comparison to trickle-bed and upflow reactors with comparable and even higher mass transfer coefficients.

Sometimes a better selectivity is also attained. This is due to the particular hydrodynamics occurring during gas–liquid flow in the small channels of the monolith. First of all, the reactor operates with upward flow; secondly, the best regime is the one where alternate slugs of gas and liquid take place because there is an enhancement of mass transfer from gas to solid during the period of thinning of the liquid film (Fig. 3). The disadvantages are cost of the monolith and uneven distribution of gas and liquid. This is one of the most delicate problems and particular care must be dedicated in creating a suitable gas–liquid dispersion before entering the monolith [37].

Structured packed beds have the advantage of a lower frictional pressure drop than the usual random one [38]. Application to gas–liquid reactions have been proposed recently by Mazzarino et al. [39,40] by using a Katapak–Sandwich catalyst, where the catalyst beads are retained between two wire-mesh sheets, which can be shaped to obtain a macroscopic open cross flow structure. Upward flow was adopted. The major advantage of this packing lies in the fact that very small beads of catalyst can be used in order to avoid reaction limitation due to internal diffusion. There is a good renewal of the liquid around the particles, and sufficiently high mass transfer coefficients can be obtained. On the other hand, high values of liquid axial dispersion were measured, and only upward flow can be adopted. Anyway, this or similar packings may be suitable in certain cases.

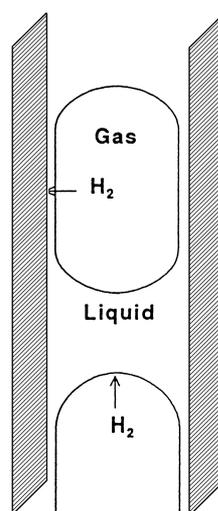


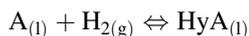
Fig. 3. Slug gas–liquid in a channel of a monolith.

3. A working example of slurry reactor design and rating

As quoted before, slurry reactors constitute one type of three phase unit where one gas reactant and a solid catalyst are dispersed in a continuous liquid phase where a second reactant showing a reduced, if any, volatility is present.

In order to get, a little bit, in depth into the problem, putting into evidence its many facets and the involved phenomena as well as the way to take them into consideration aiming at a soundly based and reliable model for rating and for designing purposes, we shall work out an illustrative example for an industrial hydrogenation reaction.

The chemical reaction can be put into the form:



where the hydrogenated product is also a nonvolatile species.

For the purpose of clarity we shall consider the problem in its simplest form; this means that the basic phenomena will be accounted directly, and modelled in the proper way whilst for secondary ones, assumptions will be made, whose validity has to be checked afterwards.

A number of industrial cases can be schematized as follows:

- A pressurized stream of pure hydrogen is fed to the reactor, sparged and broken up into bubbles under vigorous stirring so that a hydrodynamic bubble regime takes place and a rather complete mixed liquid phase exists.
- Absolute pressure range is 0.1–1 MPa.
- The volumetric power dissipation is lower than 1 kW m^{-3} .
- A porous catalyst having size in the 10^1 – $10^2 \mu\text{m}$ range is used for a catalyst load amounting up to 5 – 6 kg m^{-3} of liquid phase. Generally speaking both the stirrer speed and the specific power are high enough so as to completely suspend the solid particles within the reactor.

These assumptions correspond to a scheme of perfect mixing for the liquid–solid suspension; whilst, as for the bubble phase, the extent of mixing can vary from the plug flow to the uniform gas phase behaviour,

the latter one seeming to be the most appropriate one for industrial units.

In any case the gas phase reactant, H_2 , has to overcome a number of rate steps before reacting with the catalyst particle. They are:

1. Absorption into the liquid phase by mass transfer through the bubbles area.
2. Diffusion from the gas–liquid interface into the bulk liquid phase.
3. Diffusion from the bulk liquid phase to the catalyst surface (external diffusion).
4. Diffusion through the pore structure of the catalyst while reacting with the liquid co-reactant on the active sites.

Hydrogen participates in all the four steps, the liquid co-reactant and the product, taken as not volatile, are involved in the last two steps, one in the reverse order from the other.

Moreover, for process units where the liquid phase reactant constitutes essentially the liquid phase, its concentration does not vary in a significant way so that in looking for the rate determining step as well as for the importance of each individual resistance, only H_2 has to be accounted for or considered as the key reactant.

Modelling the steps just described enables one to establish the links relating the reaction microkinetics to the global rate law (macrokinetics) as depending on the parameters affecting each step.

This can be done in terms of rates of disappearance of hydrogen per unit volume of liquid phase for each considered step, namely:

(1) *Absorption rate*. For almost pure hydrogen there is no practical resistance, therefore the interface hydrogen concentration is in equilibrium with the gas phase partial pressure according to the Henry's law.

$$P_{H_2} = H_E C_{H_2}^i,$$

where P_{H_2} is the partial pressure of H_2 (Pa, atm), H_E the Henry constant ($\text{Pa m}^3 \text{ kmol}^{-1}$) and $C_{H_2}^i$ is the liquid phase concentration of H_2 at the gas–liquid interface (kmol^{-3}).

(2) *Rate of diffusion from the gas/liquid interface*.

$$|R_{H_2}| = K_L a (C_{H_2}^i - C_{H_2}^b) \quad (\text{kmol m}^{-3} \text{ s}^{-1})$$

where K_L is the mass transfer coefficient in the liquid phase (m s^{-1}), a the gas/liquid surface area ($\text{m}^2 \text{ m}^{-3}$)

and $C_{H_2}^b$ is the bulk liquid phase hydrogen concentration (kmol m^{-3}).

(3) *Rate of transport to the catalyst surface.*

$$|R_{H_2}| = K_C a_C m_C (C_{H_2}^b - C_{H_2}^s) \quad (\text{kmol m}^{-3} \text{ s}^{-1})$$

where K_C is the liquid phase transfer coefficient for catalyst particles (m s^{-1}), a_C the specific surface area of catalyst particles ($\text{m}^2 \text{ kg}^{-1}$), m_C the catalyst loading (kg m^{-3}) and $C_{H_2}^s$ is the liquid phase hydrogen concentration at the catalyst surface (kmol m^{-3}).

(4) *Rate of diffusion and reaction within the catalyst particle.*

$$|R_{H_2}| = m_C \eta R_s \quad (\text{kmol m}^{-3} \text{ s}^{-1})$$

where η is the effectiveness factor (dimensionless) and R_s is the microkinetic reaction rate at the surface conditions ($\text{kmol kg}^{-1} \text{ s}^{-1}$).

Due to the virtual constancy of the liquid coreactant, one can often assume that the microkinetic rate law is linear in H_2 concentration; that means

$$R_s = K C_{H_2}^s$$

where K is the first order kinetic constant ($\text{m}^3 \text{ kg}^{-1} \text{ s}^{-1}$).

According to the first order kinetics, the dependence of the effectiveness factor on the Thiele modulus is described by the classical expression

$$\eta = \frac{3}{\phi^2} (\phi \coth \phi - 1)$$

$$\phi = \frac{D_p}{2} \sqrt{\frac{K \rho_p}{D_{H_2, \text{eff}}}}$$

Having as limit values

$$\eta \rightarrow 1, \quad \phi \rightarrow 0,$$

$$\eta \rightarrow \frac{3}{\phi}, \quad \phi \rightarrow \infty$$

the above equations can be put into the form

$$\frac{|R_{H_2}|}{K_L a} = C_{H_2}^i - C_{H_2}^b$$

$$\frac{|R_{H_2}|}{m_C K_C a_C} = C_{H_2}^b - C_{H_2}^s$$

$$\frac{|R_{H_2}|}{m_C \eta K} = C_{H_2}^s$$

Summing up and rearranging one gets

$$\frac{C_{H_2}^i}{|R_{H_2}|} = \frac{1}{K_L a} + \frac{1}{m_C} \left(\frac{1}{K_C a_C} + \frac{1}{\eta K} \right)$$

which gives us the macrokinetic rate law as a function of each individual step and accounts for the relative weight of the “resistances” taken into consideration.

The role played by the catalyst charge is clearly shown as well as the ways by which physical diffusion phenomena and chemical reaction intervene in determining the global rate.

Of particular relevance appears to be the effect of catalyst particle size D_p included in the terms related to the transport to the catalyst surface

$$\left(\frac{1}{K_C a_C} \right)$$

and to the reaction with possible internal diffusion limitation

$$\left(\frac{1}{\eta K} \right)$$

$$a_C = \frac{6}{D_p \rho_p}$$

As a matter of fact the specific surface area of the catalyst particle is directly related to the size, while the mass transfer coefficient is usually estimated according to the law

$$Sh = \frac{K_C D_p}{D_{LH_2}} = 2 + 0.6 Re_D^{1/2} S_C^{1/3}$$

whence one gets

$$K_C a_C = \lambda_1 D_p^{-2} + \lambda_2 D_p^{-1.5}$$

and in an asymptotic form

$$\frac{1}{K_C a_C} = \alpha_1 D_p^{3/2} \div \sigma_2 D_p^2$$

From the other side, as for the chemical kinetic resistance corrected by the effectiveness factor, two asymptotic dependencies are to be considered:

$$\frac{1}{\eta K} = \alpha_3 D_p^0 \div \alpha_4 D_p$$

As a whole the resistance terms associated with the catalyst load

$$\frac{1}{K_C a_C} + \frac{1}{\eta K}$$

may show, against particle diameter, three regimes depending on the asymptotic slope; namely

$$r = \alpha D_p^n$$

where

- $n=0$: reaction within catalyst is the determining step,
- $n=1$: internal diffusion is the determining step,
- $n=1.5 \div 2$: external diffusion is the determining step.

The relevance of gas–liquid mass transfer limitation depends, moderately in the bubble regime, on the power dissipated per unit volume, and mainly on the amount of catalyst loaded into the reactor.

Such considerations must be taken in due account when investigating experimentally a stirred slurry reactor; the basic experimental factors, for a defined geometrical configuration, being fixed as:

- H_2 pressure,
- catalyst size,
- catalyst load.

3.1. Working example

A classical example taken by the literature [41,42] can illustrate very clearly the analysis to be performed in order to arrive at the determination of the rate law and at its controlling phenomena.

Isothermal runs were carried out on a pilot slurry reactor to hydrogenate an unsaturated fatty ester to the corresponding saturated one. Three of them can be summarized in Table 1.

By interpreting the last column

$$C_{H_2}^i / |R_{H_2}|$$

in terms of the law

$$\frac{C_{H_2}^i}{R_{H_2}} = \frac{1}{K_L a} + \frac{1}{m_C} \left(\frac{1}{K_C a_C} + \frac{1}{\eta K} \right) = r_b + \frac{1}{m_C} (r_C + r_r)$$

Table 1

Experimental runs for a hydrogenation reaction

Run	P_{H_2} (atm)	$C_{H_2}^i$ (kmol m ⁻³)	Catalyst size (μm)	Catalyst load (kg m ⁻³)	R_{H_2} (kmol m ⁻³ s ⁻¹)	$C_{H_2}^i / R_{H_2} $ (s)
1	3	0.007	40	5.00	10.420×10^{-4}	6.720
2	6	0.014	40	0.20	2.9670×10^{-4}	47.191
3	6	0.014	80	0.16	1.217×10^{-4}	115.068

one gets from runs 1 and 2 ($D_p=40 \mu\text{m}$)

$$r_b = \frac{1}{K_L a} = 5.0344 \text{ (s)}$$

by assuming that the mass transfer coefficient per unit volume is constant over the range of considered catalyst loads.

Furthermore,

$$(r_C + r_r)_{1,2} = \frac{1}{K_C a_C} + \frac{1}{\eta K} = 8.431 \text{ (s kg m}^{-3}\text{)}$$

From the last run ($D_p=80 \mu\text{m}$) one can therefore estimate the term relevant to external/internal diffusion and kinetic resistance r_C+r_r ; one obtains

$$\frac{(r_C + r_r)_3}{(r_C + r_r)_{1,2}} = \frac{17.062}{8.431} = 2.024 \cong 2$$

One can fairly argue that the controlling step shows a resistance increasing linearly with catalyst size at least over the size range investigated.

This corresponds, as previously said, to internal diffusion strongly limiting the reaction rate. In other words,

$$r_C + r_r \cong r_r = \frac{1}{\eta K}$$

and

$$\frac{C_{H_2}^i}{|R_{H_2}|} \cong \frac{1}{K_L a} + \frac{1}{m_C} \frac{1}{\eta K}$$

gives the rate law of hydrogen disappearance as a function of H_2 partial pressure, through the Henry law, of gas liquid volumetric mass transfer coefficient and of catalyst load.

No information is available to separate the effect of microkinetic reaction rate and of internal diffusion within the catalyst due to the apparent asymptotic value of efficiency against Thiele modulus. To such a goal runs with smaller particle size are required.

Conversely, within the range of experimental factors investigated, one can use the obtained rate law to predict the performance of an existing unit or to design it.

One has also to check the value and the reliability of the simplifying hypothesis previously quoted but not appearing explicitly in the obtained formula; such a consideration, however, applies for any design problem and demands for the attitude to criticize assumptions made on the base of the results obtained.

4. Notations

A_c	external area of a catalyst pellet
c_{Al}, c_{As}	concentration of A in the liquid bulk and at the solid–liquid interface
c_{Ag}	concentration of A in the gas
c^*	concentration in the liquid at equilibrium with the gas phase
c_p	specific heat
d_p	particle diameter
D_{eff}	intraparticle diffusivity
D_g, D_l	axial dispersion of gas and liquid
E	activation energy
h_s	particle–fluid heat transfer
ΔH_r	enthalpy of reaction
k_s	liquid–solid mass transfer coefficient
k_v, k_R, k_{NR}	reaction rate constants
$(k_1a), (k_s a)$	volumetric gas–liquid and liquid–solid mass transfer coefficient
j_A	gas-to-liquid mass flux per unit reactor volume
R_A	reaction rate of component A
R'_A	pseudo-homogeneous reaction rate
T	temperature
v_g, v_l	superficial gas velocity of gas and liquid
V_c	volume of one pellet
ϵ_0	bed void fraction
η_E	solid–liquid contacting effectiveness, wetting efficiency
λ_C	heat of vaporization of component C
λ_{eff}	intraparticle thermal conductivity
ν	stoichiometric coefficient
ρ_g, ρ_l	gas and liquid density
ω	mass fraction

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