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STRATEGIES FOR MULTIPHASE REACTOR SELECTION

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Abstract—The central theme addressed in this paper is: how do we arrive at the "ideal" reactor configuration meeting most closely with the process requirements? The problem of reactor selection is analyzed at three strategy levels. Decisions are made at each strategy level using the reactor "wish" list. Combination of the individual decisions yields the final, ideal, reactor configuration. The three strategy levels are:

Strategy level I: "Catalyst" design strategy. At this strategy level the ideal catalyst particle size, shape, porous structure and distribution of active material are determined. For gas–liquid systems, the appropriate decision concerns the choice of gas-dispersed or liquid-dispersed systems, and the provision of the appropriate ratio between liquid-phase bulk volume and volume of liquid-phase diffusion layer.

Strategy level II: Injection and dispersion strategies. (a) Reactant and energy injection strategy: injection strategies examined include one-shot (batch), continuous, pulsed injection, reversed flow operation, and staged injection (in time or space), and the use of dispersionless contacting by keeping the reactants separated by a barrier (membrane). (b) Choice of the optimum state of mixedness for concentration and temperature: the proper choice of state of mixedness can influence selectivity and product properties. (c) Separation of product or energy *in situ*: product removal *in situ* helps to increase conversion by driving the reaction to the right and preventing undesirable side reactions. Removal of energy *in situ* by use of evaporating solvents has the function of a thermal flywheel. (d) Contacting flow pattern: here there is a choice between co-, counter- and cross-current contacting of phases.

Strategy level III: Choice of hydrodynamic flow regime. Here the choice between the various "fluidization" regimes, e.g. dispersed bubbly flow, slug flow, churn-turbulent flow, dense-phase transport, dilute-phase transport, is made on the basis of the interphase mass transfer characteristics, heat transfer, mixing, etc.

Combination of the decisions reached at the three strategy levels will yield the most suitable reactor configuration. In this paper it is argued that a systematic approach to reactor selection may lead to novel and innovative reactor configurations with a potential edge over existing and conventional technologies.

INTRODUCTION

For carrying out multiphase reactions (gas–solid, gas–liquid, gas–liquid–solid, liquid–liquid, gas–liquid–solid, liquid–liquid–solid, . . .), the number of reactor configurations that are possible is extremely large. Therefore, there is a need to give careful consideration to the choice of the "ideal" reactor configuration that meets fully with all the process "musts" and, to the maximum possible extent, the process "wants". The process "musts" could be:

- operability within technology feasible reaction coordinates of temperature, pressure and residence time,
- safe operation and freedom from runaways,
- environmental acceptability, and
- feasibility of scale-up to economically justified size.

The process "wants" could be the following:

- maximum possible conversion of the feedstocks,
- maximum selectivity of reaction to desired products,
- easy operability,
- lowest capital and operating costs, stemming from, e.g.
  - —low pressure drop,
  - —effective utilization of reactor space,
  - —simple constructions, etc.

This paper considers both two- and three-phase reactor selection strategies (see Fig. 1).

Typically, in the petroleum and petrochemical industry, even small percentage improvements, say of the order of 0.5% with respect to selectivity can be

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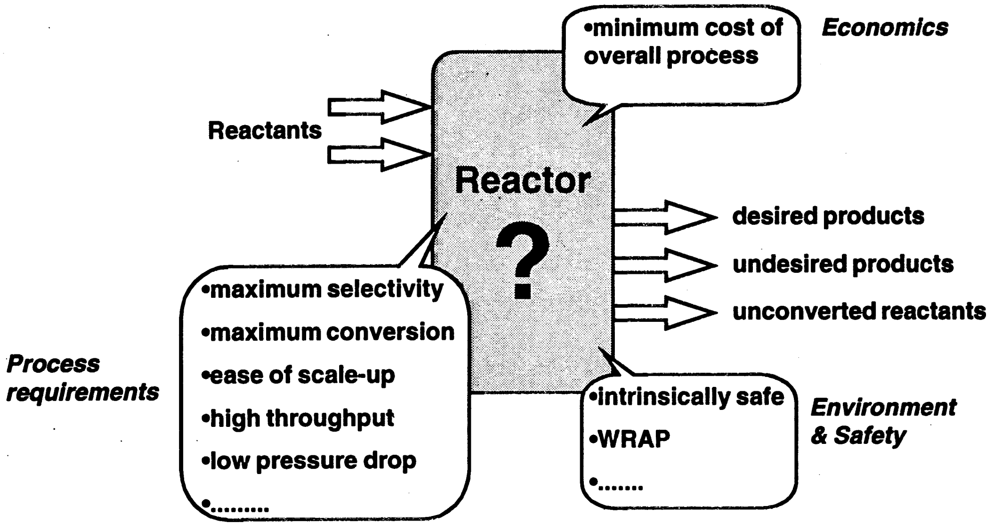


Fig. 1. The problem of reactor selection to meet the desired process requirements and constraints. The reactor has to meet with several "musts" and "wants".

extremely significant. For example, improvement of gasoline selectivity in Fluid Catalytic Cracking (FCC) operations by 0.5% would mean an increased revenue of US$2.5 million per day on a global basis. Improved yield and selectivity can be crucial for process licensers. A 1% selectivity advantage in the manufacture of ethene oxide (obtained by air oxidation of ethene) could be significant enough for a process licenser to gain a marketing edge over a competitor. For the ethene oxide producer, a 1% selectivity improvement signifies an increased revenue of the order of US$1 million per year. While the major process improvements will no doubt stem from improved reaction "chemistry" and catalyst design, there is further scope for effecting improved performance by clever choice of the reactor configuration. In the FCC riser reactor, improved feed atomization, better gas–solids contacting at inlet (e.g. by pre-fluidization with steam), and closer approach to plug flow of gas and catalyst phases are known to lead to great economic benefits. For ethene oxide manufacture, if it is possible to develop a packed bed reactor that operates under substantially isothermal conditions, the result will be significant selectivity advantages due to suppression of the undesirable combustion reaction.

In the Shell Middle Distillates Synthesis (SMDS) process which converts natural gas to synthetic hydrocarbons via advanced Fischer–Tropsch synthesis, the synthesis reactor configuration chosen for the first commercial unit in Malaysia, started up in 1993, was the multi-tubular downflow trickle bed with catalyst inside the tubes (Sie *et al.*, 1991); see Fig. 2(a). Because of the enormous exothermicity of the synthesis reaction and the relatively poor heat transfer, a very large heat transfer area is required. The reactor volume and weight are largely governed by the installable heat transfer area in a vessel of given volume. Use of the bubble column slurry reactor [see Fig. 2(b)] provides much better heat transfer characteristics (an improvement of a factor of about five over fixed bed units) and could lead to considerably lower reactor volumes. However, the anticipated scale-up problems with bubble column slurry operation were of overriding concern for Shell, who decided to adopt the fixed bed technology mainly due to a quicker development scenario which allowed them to meet the time plans of the business. The lead time for development of processes in the petroleum and petrochemical industries is usually of the order of a decade and for first-of-a-kind-technology such as the SMDS process there is an incentive to adopt a sure, safe and quicker process development route. It is interesting to note that other companies, e.g. Sasol and Exxon, have more recently opted for the slurry reactor configuration. These companies apparently did not consider the long lead time for development of the bubble column slurry reactor to be an insurmountable problem.

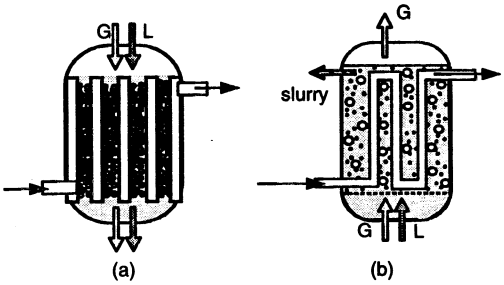


Fig. 2. Reactor types used for Fischer–Tropsch synthesis of hydrocarbons. (a) Multitubular trickle bed reactor, (b) bubble column slurry reactor.

The above discussions serve to underline the importance not only of choosing the reactor with the promise of the best performance but also for the need to anticipate scale-up difficulties. The approach advocated in this article is to attack the problem of reactor selection in a systematic structured manner.

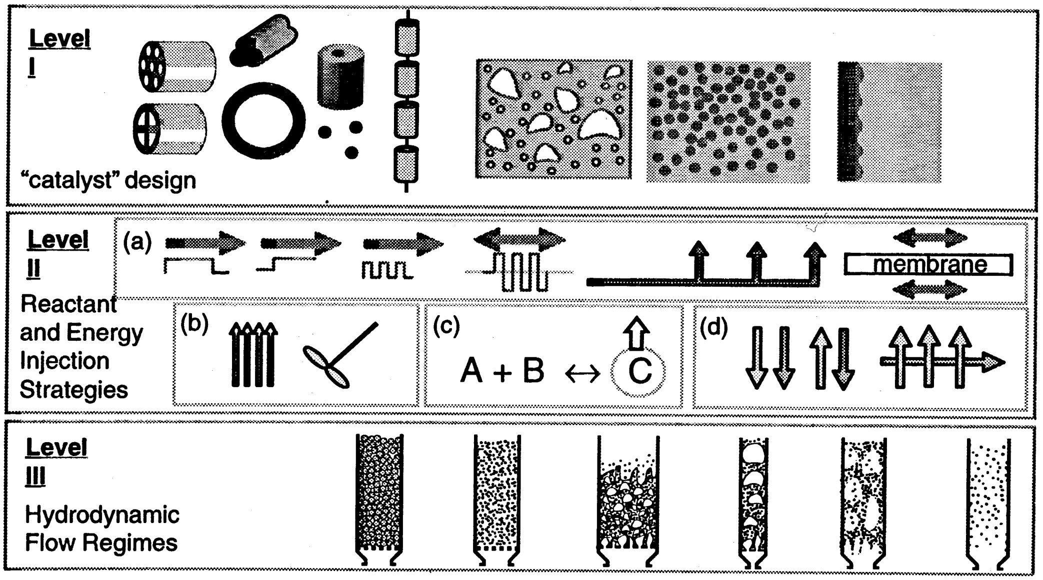


Fig. 3. Three-level strategy for multiphase reactor selection.

The reactor selection problem is analyzed at three strategy levels as pictured in Fig. 3, and at each of these levels "decisions" are made on reactor sub-sets or attributes.

At Strategy level I, the optimal "catalyst" design is developed. This involves determining the particle size, shape, porous texture, etc. For a gas–liquid system this would involve choosing an appropriate value of the parameter β = (bulk liquid volume)/(volume of liquid diffusion layer).

At Strategy level II, a decision is made on the ideal manner in which reactants and energy are injected into the reactor, the ideal state of mixedness with respect to concentration and temperature, whether to remove products *in situ*, and the desirability of employing dispersionless contacting by separating the phases by a barrier.

The choice of the hydrodynamic flow regime is considered at Strategy level III. A combination of the choices made at each strategy level will lead to the final reactor configuration. Compromises need to be made if incompatible sub-sets are chosen. It will be demonstrated here, with the help of several examples, that the structured, systematic approach may reveal several novel reactor configurations and operating strategies.

Each of the three strategy levels will now be considered in detail.

STRATEGY LEVEL I—"CATALYST" DESIGN

Gas–solid (catalyst) systems

Whilst the choice of "fluidization" regime (Strategy level III) sets limits for suitable sizes and shapes of catalyst particles via demands on fluidizability, suspensibility, pressure drop, flowability, etc., at this first strategy level the possibility of varying the catalyst morphology will be considered, so as to meet process demands dictated by reaction and diffusion in an optimal way. The interplay between chemical kinetics and rates of diffusion of reactant or product molecules can be influenced by variation of catalyst size, shape and porous texture. The distribution of active material inside the catalyst particles can be an additional variable in designing optimal catalysts, in particular when diffusion-limited poisoning reactions occur.

Effect of particle size. Intraparticle diffusion limitation occurring with relatively fast reactions and slowly diffusing reactant molecules may result in incomplete utilization of the catalyst as the interior is not reached by the reactant molecules. This effect has been the subject of many chemical engineering studies and is relatively well understood. Utilization is expressed as the effectiveness factor η, which for a given particle geometry is a function of the generalized Thiele modulus:

$$\phi_{\text{gen}} \equiv \frac{V}{SA}\sqrt{\frac{k_m \rho_p}{D_{\text{eff}}}}$$

in which (V/SA) is the volume/external surface area ratio of the catalyst. For a given conversion rate, the external surface determines the flux density for diffusion of reactants to the catalytic surface inside the catalyst volume. The ratio (V/SA), which has the dimension of length, can be considered to be a measure of the average diffusion distance necessary to penetrate the particle. The relation between η and ϕ_{gen} is shown in Fig. 4. As a general rule, the particle size choice should aim at high effectiveness, so as to make good use of catalyst materials and reactor volume, and for improved activity. There are exceptions to this general rule, however, as will be discussed later.

Pore diffusion limitation is not uncommon in industrial fixed bed catalytic processes, particularly in classical processes which use relatively large catalyst

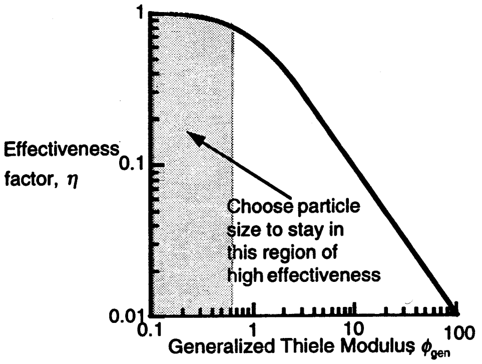


Fig. 4. Effectiveness factor as a function of the generalized Thiele modulus for a first-order reaction.

particles (pellets of 5–15 mm diameter). Simple calculations comparing the time needed for diffusion over a given distance inside the particle with the maximum time available for the reaction, show that for practical reaction rates as apply to most processes, and typical diffusivities in gas- or liquid-filled pores of catalysts, diffusion limitation will generally occur with particles having a diameter of a few millimeters. In the case of very fast reactions or very slow diffusion, as in the case of so-called conformational-type diffusion inside zeolite pores, pore diffusion limitation will occur with particles of even much smaller dimensions.

Figure 5 shows effectiveness factors of some catalysts in gas-phase reactions as a function of catalyst size. It can be seen that in these processes catalyst utilization is far from complete for fixed bed catalysts of practical sizes, i.e. above 3 mm. In such gas-phase reactions the diffusivity inside the catalyst particles is usually a Knudsen-type diffusion or a surface diffusion, and hence depends on the gas pressure and the pore texture.

In catalytic processes where liquid is present, the catalyst pores are likely to be filled with liquid and the low diffusivity in the liquid phase may increase the likelihood of diffusion limitation. Figure 6(a) shows the effect of particle size on the performance of a Co/Mo/alumina catalyst for hydrodesulfurization of a gas oil in trickle flow, demonstrating the occurrence of diffusion limitation. Figure 6(b) shows effectiveness factors of a series of catalysts of different particle sizes having the same composition. It can be seen that utilization of the catalyst is reasonably complete only with particles having a diameter of less than 1 mm. Catalyst utilization is far from complete for catalysts of relatively large size (pellets of 5–15 mm diameter and length) as used in classical hydrogenation processes before, and shortly after, World War II. Currently, extrudates of about 1.5 mm size are used for hydroprocessing, achieving effectiveness factor values close to unity.

Another example of the occurrence of diffusion limitation caused by the presence of liquid in the catalyst pores is depicted in Fig. 7. This figure shows the effectiveness factor as a function of the Thiele modulus for a number of Fischer–Tropsch catalysts operated under different conditions. The experimental results are in very good agreement with the theoretical curve calculated for the case that the reaction rate obeys first-order kinetics in hydrogen (as has been verified experimentally), while the limiting factor is the rate of diffusion of hydrogen as reactant in the liquid hydrocarbon product which fills the pores. The excellent fit demonstrates that as far as catalyst effectivity is concerned, its dependence on catalyst morphology may be established on the basis of first

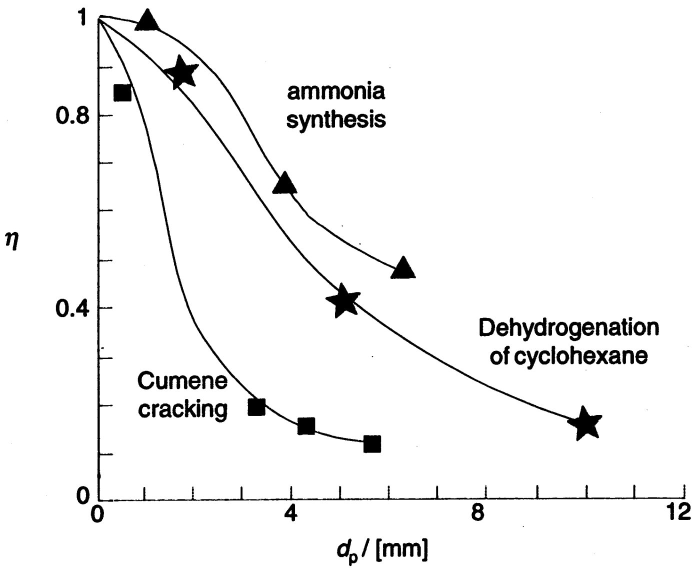


Fig. 5. Effectiveness factors in some gas-phase fixed bed processes. Data from: Corrigan and Garver (1953), Weisz and Schwegler (1955) and Bokhoven and Van Raayen (1954).

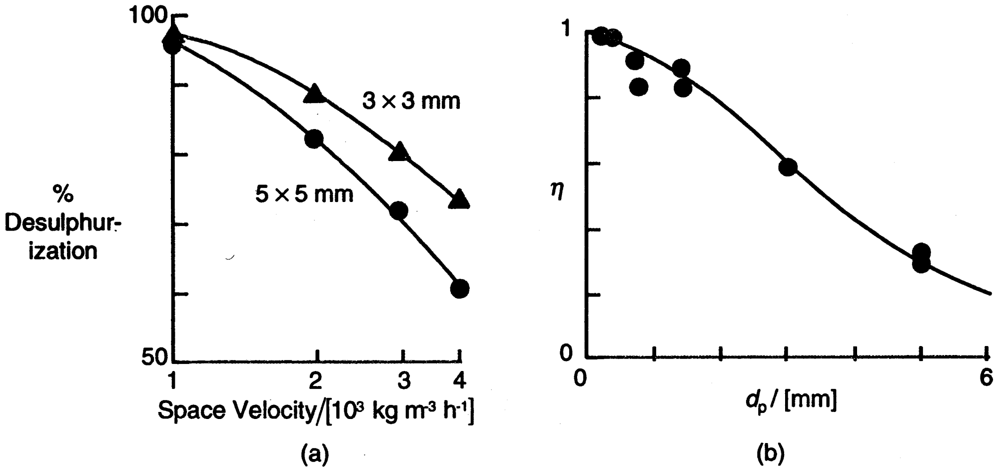


Fig. 6.(a) Effect of catalyst particle size in trickle-flow hydrodesulfurization of Kuwait straight run gas oil over a Co/Mo/alumina catalyst. (b) Utilization of catalyst as a function of particle size in hydrodesulfurization of Kuwait straight run gas oil over a Co/Mo/alumina catalyst. Adapted from Le Nobel and Choufour (1959).

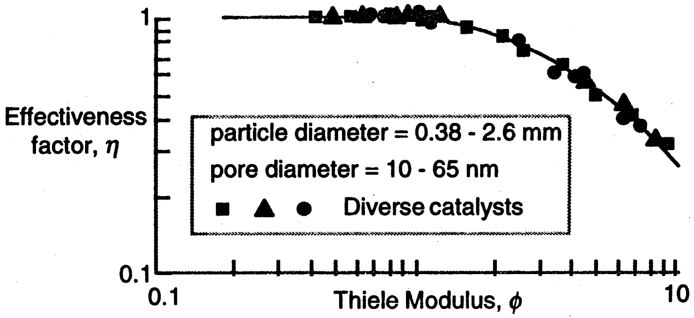


Fig. 7. Effectiveness factors as a function of the Thiele modulus for Co-type Fischer–Tropsch Catalysts. Adapted from Post *et al.* (1989).

principles if the reaction kinetics and the mechanism of diffusion are known.

Geometry of catalyst particles. The geometric factor which governs the utilization of catalyst particles from a given catalytic material is in first approximation the ratio between external surface area and volume of the particle, (SA/V, cf. expression of the generalized Thiele modulus). For geometrically similar shapes the (SA/V) is inversely proportional to a characteristic dimension, e.g. the diameter d_p. Hence, for such similar shapes the (SA/V) multiplied with the diameter d_p is a dimensionless constant which is characteristic for the shape. Figure 8 compares the (SA/V) of some catalyst shapes currently used in fixed bed reactors in a plot of the above dimensionless constant against the length over diameter ratio (L/d_p). It can be seen that rings, hollow extrudates and more sophisticated shapes such as "wagon wheels" and "miniliths" offer a greater surface-to-volume ratio than the more common cylindrical tablets and cylindrical extrudates of the same outside diameter and length. Since pressure drop and effective radial heat conductivity in packings are mainly determined by the outside diameter of the particles, these shapes are advantageously used in gas-phase operated adiabatic fixed bed reactors or non-adiabatic tubular reactors. For liquid-phase processes they are less advantageous since the hollow space is likely to be filled with relatively stagnant liquid. Extrudates with a clover leaf cross section, namely trilobe or quadrulobe extrudates, offer a greater surface-to-volume ratio than cylindrical extrudates of the same maximal outside diameter, and retain their advantage also in liquid-phase operation. It can be seen that round, disk-shaped tablets of a length-to-diameter ratio below 1, have a greater surface area than cylindrical extrudates of the same diameter with a ratio above 1. Notwithstanding this, extrudates have largely superseded tablets in most fixed bed processes. This is because reduction of the diameter of pressed tablets to values much lower than 5–15 mm, as used in classical fixed bed processes, results in rapidly escalating manufacturing costs (the number of particles for a given weight of catalyst increases with the third power of the linear dimension). Extrudates, however, can be produced at little extra cost at diameters below 1 mm.

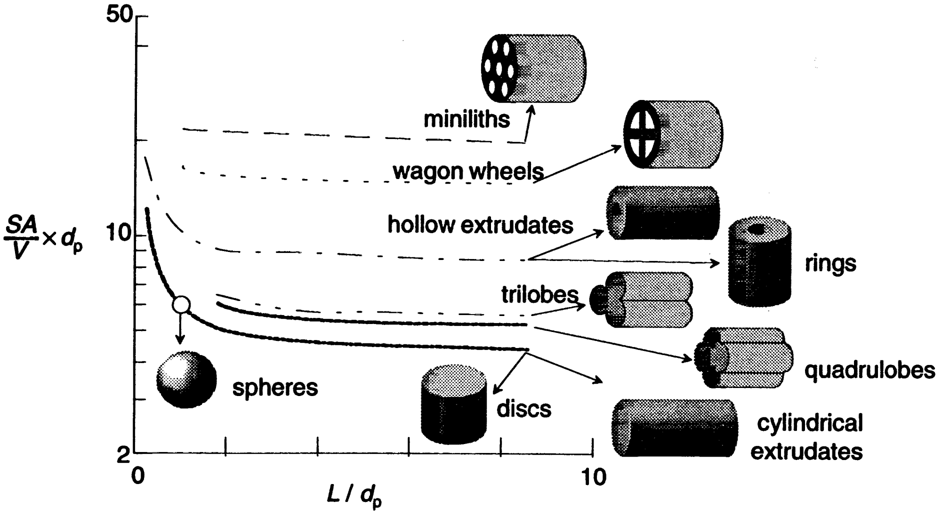


Fig. 8. Surface area over volume ratio of shaped catalyst particles.

Pressure drop, reactor productivity and strength of catalyst particles. As discussed above, the problem of diffusion limitation can be alleviated by choosing smaller catalyst particles of a shape that has a high (SA/V) ratio. The main limiting factor for reduction of particle size in a fixed bed reactor is generally the pressure drop over the bed. Figure 9 shows the general relation between pressure drop and reactor productivity for extrudates of different shape and size. This figure shows trends rather than quantitative data, since the latter depends on several factors such as properties of reactant fluids, aspect ratio of the bed, axial versus radial flow, etc. The demand for a minimum desired reaction rate within a maximum allowable pressure drop determines suitable sizes and shapes of catalyst particles for a given case. For instance, for the case depicted, it can be seen that cylindrical extrudates need not be considered, but that wagon wheels in a certain range of sizes can be used. Trilobe extrudates of a specific size are marginally applicable for this case. The superiority of wagon wheel and trilobe extrudates over cylindrical extrudates with respect to the reaction rate–pressure drop relation is caused by the higher surface area to volume ratio of the former types of extrudates. However, these types of extrudates also have their drawbacks so that they may not be the preferred type under all circumstances.

Figure 10 shows the relationship between manufacturing costs and surface-to-volume ratio for the

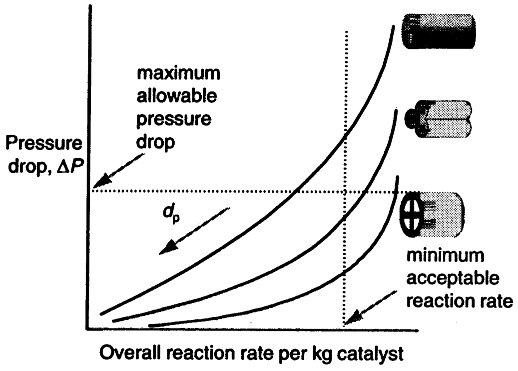


Fig. 9. Relation between reactor productivity and pressure drop for some types of fixed bed catalysts.

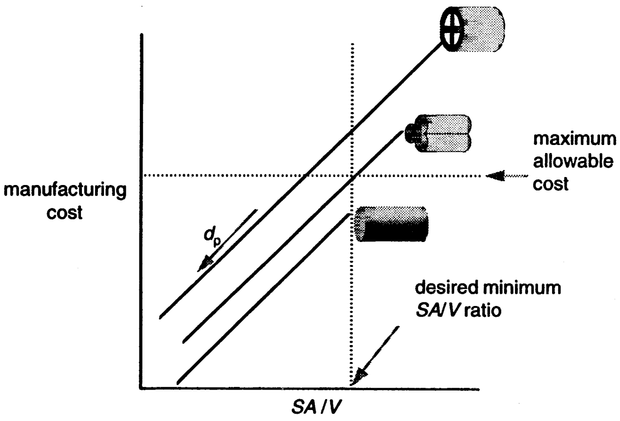


Fig. 10. Relation between reactor manufacturing cost and surface/volume ratio of some fixed bed catalysts.

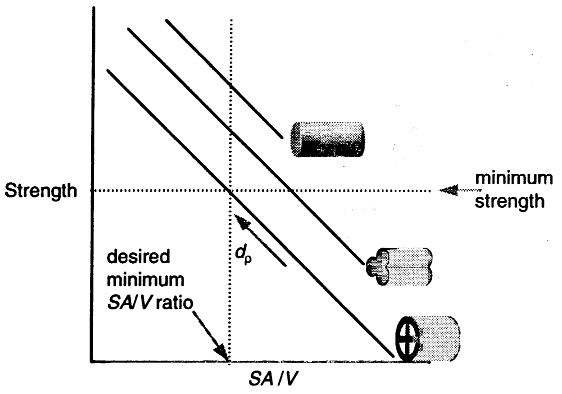


Fig. 11. Strength versus surface-to-volume ratio of some fixed bed catalysts.

different types of extrudates. It can be seen that, in general, the simple cylindrical extrudates are the cheapest to manufacture. The figure shows that to satisfy the specifications on minimum (SA/V) ratio and maximum allowable costs, as indicated in this figure for a hypothetical case, both trilobe and cylindrical extrudates may be considered. Of these two, cylindrical extrudates present the more economic solution, while trilobe extrudates are merely acceptable.

Strength of catalyst particles is in most cases an important factor in fixed bed processes. Particles should be able to withstand the forces exerted on them by the weight of the bed above, and by the pressure drop. This strength is generally measured either on a single catalyst particle, giving the so-called side-crushing strength (SCS), or measured by exerting a pressure on a small bed of particles, giving the so-called bulk-crushing strength (BCS). Figure 11 shows the relationship between catalyst strength (either SCS or BCS) and (SA/V) ratio for extrudates of some different shapes and different sizes. It can be seen that extrudates of the more sophisticated shapes are, in general, less strong. Minimum requirements on strength and (SA/V) ratio as indicated in this figure for a hypothetical case, can be satisfied by all three types of extrudates. Whereas the requirements are amply fulfilled by trilobes and cylinders, this is only marginally so in the case of wagon wheels.

Effect of diffusion limitation on selectivity. Diffusion limitation not only affects the apparent activity of a catalyst, but can also affect selectivity. The best-known effect of diffusion limitation is a negative one. This applies to a case of consecutive reactions $A_1 \rightarrow A_2 \rightarrow A_3$, where A_2 is the desired product. Diffusion limitation reduces the chances of the intermediate product A_2 escaping from the catalyst particle so that the selectivity of its production will be lowered due to increased chances of A_2 being further converted to unwanted product A_3.

A good example of the influence of intraparticle diffusion on selectivity is the partial hydrogenation of edible oils to modify their melting behavior and their taste stability. Edible oils consist of esters of mainly unsaturated acids and glycerol. Hydrogenation of oils is the reaction of hydrogen with unsaturated triacylglycerol molecules over a nickel-based catalyst. For example, the hydrogenation of trioleoylglycerol (Ol_3) to tristearoylglycerol (St_3) occurs according to the following consecutive steps: $Ol_3 \rightarrow StOl_2 \rightarrow St_2Ol \rightarrow St_3$ where $StOl_2$ and St_2Ol represent the partially hydrogenated products. With respect to product properties like melting behavior, selective hydrogenation giving the maximum concentration of intermediates $StOl_2$ and St_2Ol is required. The selectivity can be influenced by proper choice of the pore size and particle size of the catalyst; see Fig. 12 (Colen *et al.*, 1988).

In contrast to the above case, diffusion limitation can also have positive consequences. An example of the use of diffusion limitation as a means of steering the formation of products towards a desired molecule is the selective production of *p*-xylene by disproportionation of toluene. The principle is shown schematically in Fig. 13. The selective formation of *p*-xylene from toluene depends on the differences in diffusion rates between the isomeric xylenes in ZSM-5 zeolite. *p*-Xylene diffuses much faster than the two other xylenes, while the feed molecule toluene and the

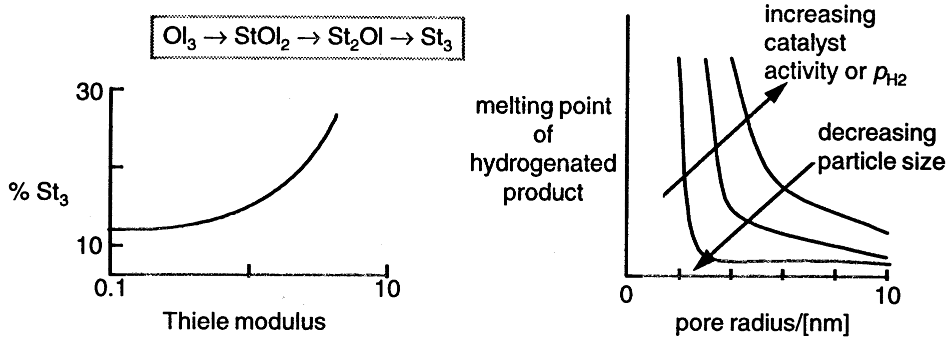


Fig. 12. Influence of intraparticle diffusion on selectivity of intermediate product in a consecutive reaction sequence. The reaction considered is the hydrogenation of trioleoylglycerol (Ol_3) to tristearoylglycerol (St_3), which proceeds through the partially hydrogenated intermediates StO_2 and St_2Ol. By tailoring the catalyst with respect to particle size and pore size the diffusional influence can be altered to obtain a product with the desired property, such as melting point. Adapted from Colen *et al.* (1988).

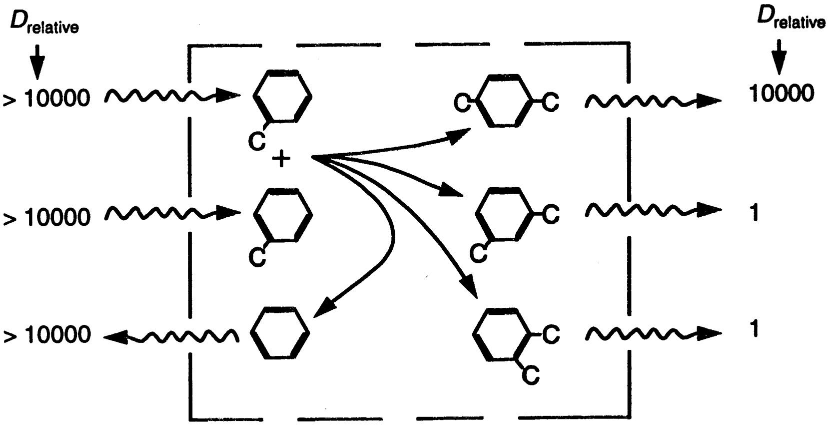


Fig. 13. Schematic representation of the role of diffusion in production of *p*-xylene by disproportionation of toluene. Adapted from Weisz (1980).

by-product benzene diffuse even faster. Without diffusional control, the relative proportions of the xylene isomers will correspond to the thermodynamic equilibrium between them. As the diffusion of the xylene molecules becomes more limiting, the differences in diffusivity of the isomeric xylenes gain importance, resulting in increased selectivity to the *para*-isomer.

Effect of diffusion limitation on a catalyst deactivation. If the catalyst deactivates as a consequence of the occurrence of a reaction which is subject to diffusion limitation, regulated access of the catalyst particle to the poison-generating molecules by tailoring catalyst morphology offers a means to control catalyst life. This principle forms the basis for catalyst design for hydroconversion of metal-containing residual oils (Sie, 1980). In this process, the deposition of contaminant metals (Ni, V) as sulfides on the catalyst surface deactivates it for the main reactions, the hydrodesulfurization and hydrocracking of the oil molecules. The metals originate from large molecular complexes (asphaltenes) which because of their size diffuse very slowly into the catalyst particles. Since the breakdown of these molecules which releases the metals is pore diffusion limited, deposition of the metal sulfides occurs in an outer zone of the particle, leaving the inner core unpoisoned.

The penetration depth of metal-containing asphaltenic species into the catalyst particle determines the size of the unpoisoned inner core of the catalyst particle, and thereby its residual activity for the desired reactions, hydrodesulfurization and hydrocracking of the non-asphaltenic oil molecules. Equally important is the effect of penetration depth on catalyst life: in the course of time, metal sulfides continue to be deposited in the peripheral zone and eventually fill the pore volume in this area completely, which means the end of catalyst life. As the zone is broader and involves a larger proportion of the particle, it takes more time to completely deactivate the catalyst. Figure 14 shows that for different catalysts used in hydrodesulfurization of a given residual oil feed, the maximum metal uptake capacity is proportional to the effectively used pore volume for metal deposition (Sie, 1993).

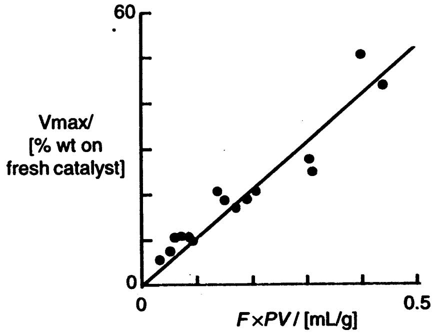


Fig. 14. Correlation between vanadium uptake capacity with effective pore volume in residue hydroprocessing. *F* is the effectiveness factor for storage of metals deposits in the pore volume of the catalyst particle. Adapted from Sie (1993).

By variation of the catalyst morphology, i.e. changing catalyst size and shape or the porous texture, one can precisely regulate the relative depth of metal penetration and thereby control the life of the catalyst and its activity for the main reactions. This is illustrated in Fig. 15 which shows the effect of average pore diameter on the performance of a series of similarly shaped catalysts for hydrodesulfurization of a Middle East atmospheric residue. Catalyst activity in this plot has been defined as the second-order rate constant for sulfur removal at half of the useful catalyst life. It can be seen that activity decreases as accessibility for asphaltenes increases with larger pore diameters. This is because the active inner core of the catalyst becomes smaller. Catalyst life, which is also shown in this plot, becomes longer as accessibility increases, because a larger proportion of the catalyst pore volume becomes available for storage of metal deposits. From Fig. 15, it can be seen that even relatively small changes in average pore diameter (1 nm) can have significant effects. Control of average pore size of the catalyst support (which can be done,

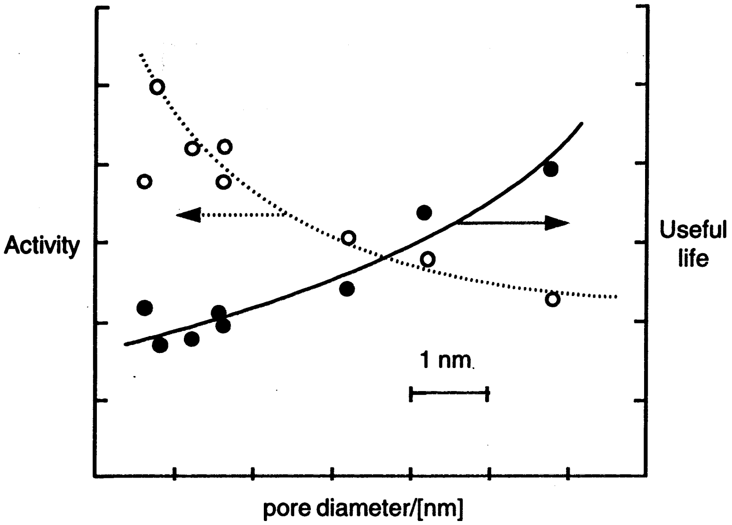


Fig. 15. Effect of average pore diameter on the performance of catalysts for the hydrodesulfurization of atmospheric residue of a Middle East crude oil. Catalysts studied belong to a series of Co/Mo/alumina catalysts of identical shape and size having sharp unimodal pore size distributions. Adapted from Sie (1993).

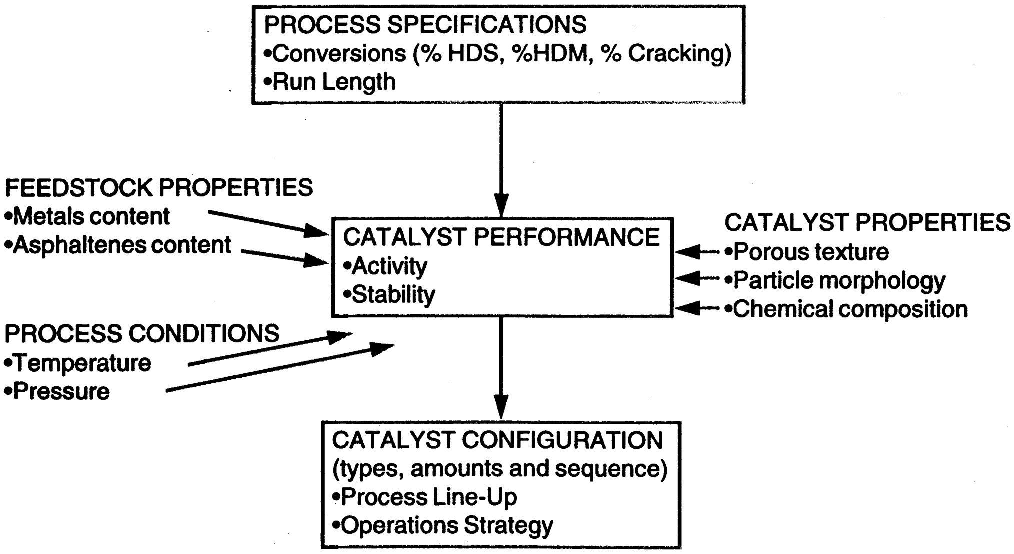


Fig. 16. Relationships between process, feedstock and catalyst parameters determining the choice of hydroprocessing catalysts. Adapted from Oelderik *et al.* (1989).

for instance, by hydrothermal treatment) thus offers a means of adjusting catalyst performance for a given duty.

In a fixed bed process for hydroprocessing of residues, the removal of metals from the oil stream will cause a decrease in their concentration in the direction of the stream. Therefore, the balance between activity and tolerance for metals deposition will not be the same in different parts of the reactor or reactor train. Thus, it is advantageous to use a combination of different catalysts rather than just one: a highly metals-tolerant catalyst upstream (which can cope with the relatively high concentration of metal contaminants in the feed) and a highly active catalyst in the downstream part. The latter catalyst will have a low tolerance for metals deposition, but this tolerance suffices since metals concentration in the oil has already been lowered. Ideally, a large number of catalysts designed for a gradually sliding balance between activity and metals tolerance should be placed in series. With such a multicatalyst combination, definition of an optimal catalyst is not straightforward since the desired activity and life of a catalyst depend on its position in the reactor train, on feedstock characteristics, on target conversion level and desired onstream time, etc., as is shown in Fig. 16. However, when a process model is available which has been validated with sufficient practical data, it becomes possible to predefine catalyst parameters for a desired duty.

An example of catalyst design assisted by a computerized process model is shown in Fig. 17. It

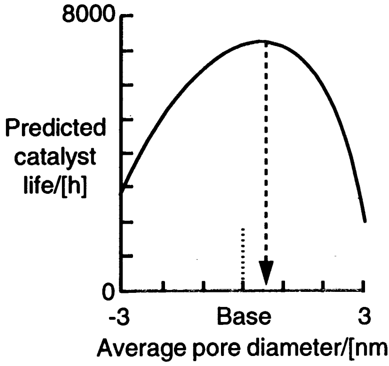


Fig. 17. "Computer-aided design" of catalyst porous texture. Predicted life as a function of the average pore diameter of a tail-end catalyst in the hydroconversion of an Arabian Heavy vacuum residue at 60% conversion. Adapted from Oelderik *et al.* (1989).

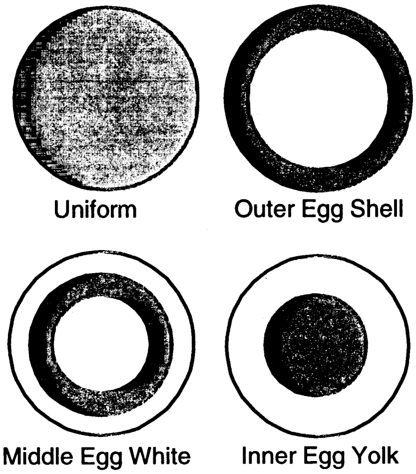


Fig. 18. Different activity distributions in a catalyst pellet.

can be seen that catalyst life passes through a maximum at a certain value of the average pore diameter. At smaller diameters, the catalyst deactivates faster because the relatively shallow outer layer available for deposition of metal sulfides becomes more rapidly filled. At larger diameters, the activity of the catalyst is relatively low (as a consequence of the relatively small unpoisoned inner core) so that higher temperatures have to be applied to reach the process specifications. The smaller span of operating temperatures thus shortens the operating cycle.

It can be seen that, in this example, the experimentally tested base case is not far from the calculated optimum situation, but this is of course not always true. This possibility of designing catalysts is especially important in residue hydroprocessing since actual life tests require runs of several thousands of hours, so that catalyst optimization by way of empirical testing is not likely to achieve an optimum result within a reasonable amount of time and effort.

Spatial distribution of activity within catalyst pellets. In the absence of diffusion limitation, it is a common policy to uniformly load the support pellet with catalytically active species, in order to maximize the catalytic activity per unit volume of catalyst bed. If the effectiveness factor is significantly lower than unity, it is obvious that the catalytic agent may be saved by leaving the inner core free from it, without losing overall activity. However, non-uniform distributions of activity within a catalyst pellet can have additional advantages besides savings in active material. Different possible activity distributions are shown in Fig. 18. The problem of optimal activity distributions has been studied theoretically by several authors for various cases of single, parallel and consecutive reactions, in the presence or absence of extraparticle mass transfer limitation and for non-isothermal cases; see, e.g. the recent review of Gavriilidis and Varma (1993).

Non-uniform activity distributions can have particular advantages when the main reaction is accompanied by an irreversible poisoning reaction (Becker and Wei, 1977). In the case of a diffusion-limited poisoning reaction, where the poisoning occurs in an outer shell (pore-mouth poisoning) it can be advantageous to concentrate the active component in a layer inside the pellet. When the bare support is capable of adsorbing the poison, the active components inside are thus protected from it. The main factors determining the best type of activity distribution are the Thiele moduli for the main reaction and the poisoning reaction. Figure 19 presents a catalyst selection chart on this basis.

Intraparticle heat effects. Intraparticle heat transport can also have an effect on selectivity when the selectivity of the desired reaction is strongly dependent upon temperature and when significant amounts of heat are generated by the reaction itself or by accompanying reactions. A temperature profile over the catalyst particle with a peak at the interior, as a result of the difficulty of removing locally generated heat, may give rise to deterioration of selectivity. In this case, one could opt for shortening the path of intraparticle heat conduction by choosing small particles or shapes such as rings, miniliths, etc., depending opon the allowable pressure drop. Another solution is to locate the catalytic active material at the outside of the particles, i.e. apply an egg-shell-type catalyst. The latter approach is illustrated in Fig. 20 for the oxidation of ethene to ethene oxide: a strongly exothermic reaction which is accompanied by an even more exothermic unwanted reaction, namely total combustion to carbon dioxide and water. The latter reaction, which lowers the selectivity to desired ethene oxide, has a higher activation energy than the desired one. Therefore, intraparticle temperature gradients are detrimental to selectivity.

Mechanical transport properties of catalyst particles. Aside from intraparticle mass and heat transport effects as discussed above, the mechanical transport

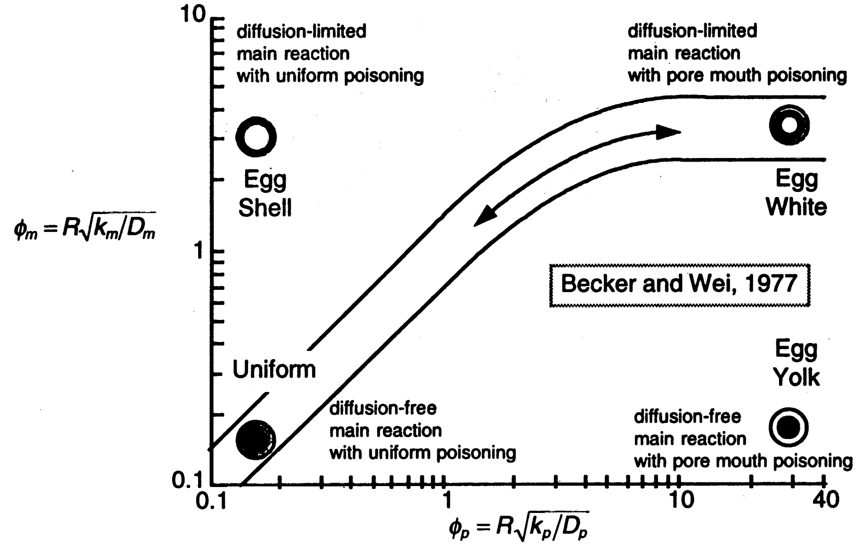


Fig. 19. Catalyst selection chart for four catalyst designs for a catalytic reaction accompanied by a poisoning reaction. Criterion: longest catalytic life with effectiveness of 0.4 or higher. Adapted from Becker and Wei (1977).

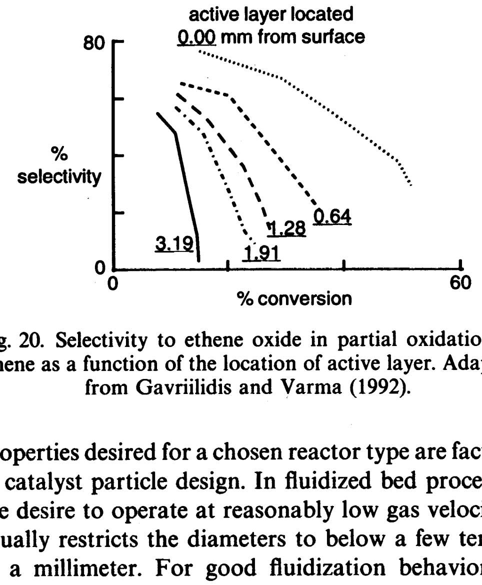


Fig. 20. Selectivity to ethene oxide in partial oxidation of ethene as a function of the location of active layer. Adapted from Gavriilidis and Varma (1992).

properties desired for a chosen reactor type are factors in catalyst particle design. In fluidized bed processes the desire to operate at reasonably low gas velocities usually restricts the diameters to below a few tenths of a millimeter. For good fluidization behavior in a bubble fluidized bed, catalyst particles in the form of microspheres with a certain size distribution, e.g. in the range of 30–150 μm, are preferred. Microspheroidal catalyst particles in this size range can be prepared by spray drying of a hydrogel or slurry containing the catalytic material.

Fluidized bed reactors are very often applied when there is a need to cycle catalyst particles between the reactor and a regenerator (in case of fast catalyst deactivation of the catalyst during the reaction) or a heater (in case heat has to be supplied). Rapid transport of catalyst between vessels implies subjecting the particles to strong attrition forces and possible thermal shocks; the attrition resistance is therefore an important criterion. The microspheroidal form, as already mentioned, is a favorable shape to reduce mechanical attrition.

However, when the catalytic material is inherently weak, special means are required to bring attrition resistance to the required level for a practical process. A way in which this can be achieved is illustrated by the development of the catalyst for the recently commercialized Du Pont fluid bed butane oxidation process to produce maleic anhydride. The vanadium phosphate (VPO) used as catalyst is too weak to withstand the forces associated with the cycling between the fluidized bed regenerator and the dense phase riser reactor where gas velocities up to 1 m s^{-1} prevail. Attrition resistance is imparted to the VPO catalyst by spray drying this material together with a silica hydrogel under conditions which allow silica to migrate to the outer regions, thus encapsulating the active VPO catalyst into a porous silica shell whose pore openings allow reactant and product molecules to diffuse into and out of the particle; see Fig. 21.

In slurry processes the particle size is often determined by the desired catalyst concentration to obtain acceptable reaction rates on the one hand, and maximum allowable slurry viscosity on the other. At the same solids concentration, finer particles give rise to higher slurry viscosities. Other factors which have an impact on the choice of particle size are the settling velocity (one may either want to avoid settling at the velocities applied or to have rapid settling for slurry thickening), filterability of the slurry, or separation possibility by hydrocyclones, sieve bends, or other separating equipment.

Separation of solid catalyst from liquid by the separation methods mentioned above is difficult or impossible for very fine catalyst particles. Such catalyst particles, e.g. smaller than 1 μm, may be desirable for reasons of catalyst effectiveness with fast reactions. Another advantage of such fine particles is that due to the fast reaction, and their presence in

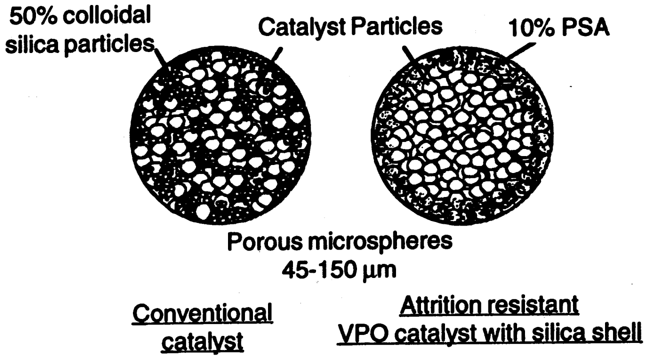


Fig. 21. Attrition resistant VPO catalyst with silica shell as used in the Du Pont butane oxidation process. After Contractor *et al.* (1987).

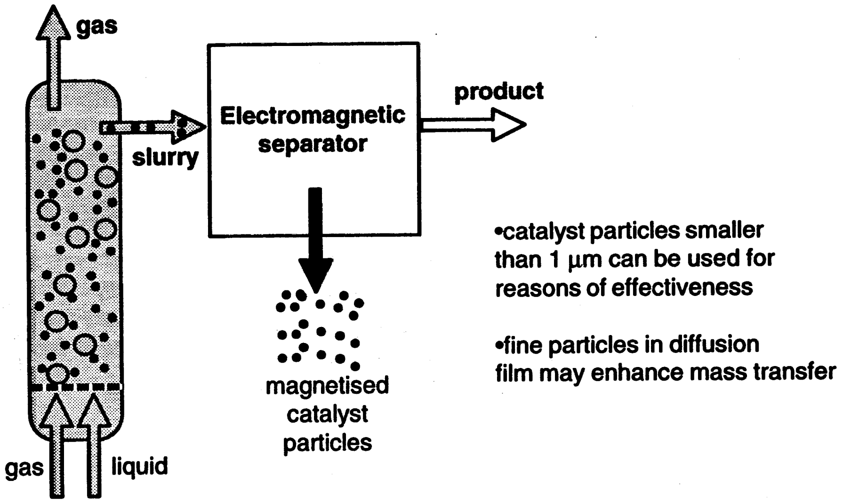


Fig. 22. Conceptual reactor system using extremely fine particles for fast reactions.

or near the diffusion film, they may significantly enhance the gas–liquid mass transfer. A possible way to use ultrafine particles in a slurry bubble column and yet avoid the solid–liquid separation problem is to make the particles magnetizable, so that they can be removed from the liquid with an electromagnetic separator; see Fig. 22.

Another conceptual way of improving the separation possibilities between catalyst and liquid is to encapsulate the catalyst by a porous shell rather similar to the butane oxidation catalyst discussed above; see Fig. 23. This technique may even be applicable to homogeneous catalysts: if the metal organic complex synthesized from components small enough to pass through the pores of the shell is too bulky to diffuse out of the shell, a situation is obtained akin to the well-known ship-in-a-bottle. In this concept, there is not only a diffusion barrier for the active catalyst, but there may also be a diffusion limitation. In the case of a hydroformylation reaction, which is of a negative order in CO, such a diffusion barrier may be beneficial.

In moving bed processes, smooth movement of the catalyst poses demands on flowability and additional requirements have to be met on attrition resistance and crush strength. Uniformity of size may also be important for moving bed catalysts. Since the particles are free to move, undesired segregation may occur when particles appreciably different in size are present (note that the mass of a particle is proportional to the third power of its diameter). As a result of movement, smaller particles may tend to occupy the space left by the larger ones, thus decreasing the permeability of the packing.

Structured packings and monoliths. In the catalytic treatment of flue gases to reduce atmospheric pollutions, e.g. of sulfur and nitrous oxides, very large volumes of gas at relatively low (near atmospheric) pressure must be handled, which calls for reactor designs with very low pressure drop. In addition, the chance of plugging by particulates (soot or ash) in the gas should be minimal. Figure 24 shows various catalyst configurations meeting with these requirements.

In the parallel-passage reactor, particles of a catalyst or a regenerable adsorbent are enclosed in wire screen envelopes which are mounted in a parallel fashion. Gas flows in the empty passages between

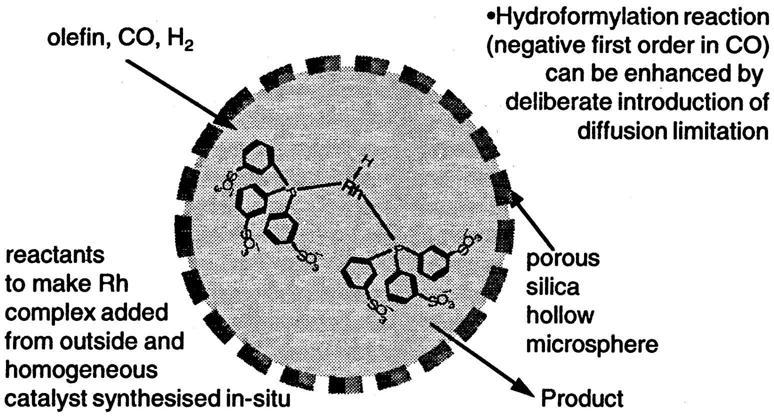


Fig. 23. Concept of an encapsulated (homogeneous) catalyst. The homogeneous catalyst is encapsulated inside a porous hollow microsphere. The complex is synthesized *in situ* and cannot diffuse out due to the small pore size, say of the order of 1 nm. These spheres are dispersed inside the reactor. Deliberate introduction of diffusional limitation for CO to the ligand has potential beneficial effects.

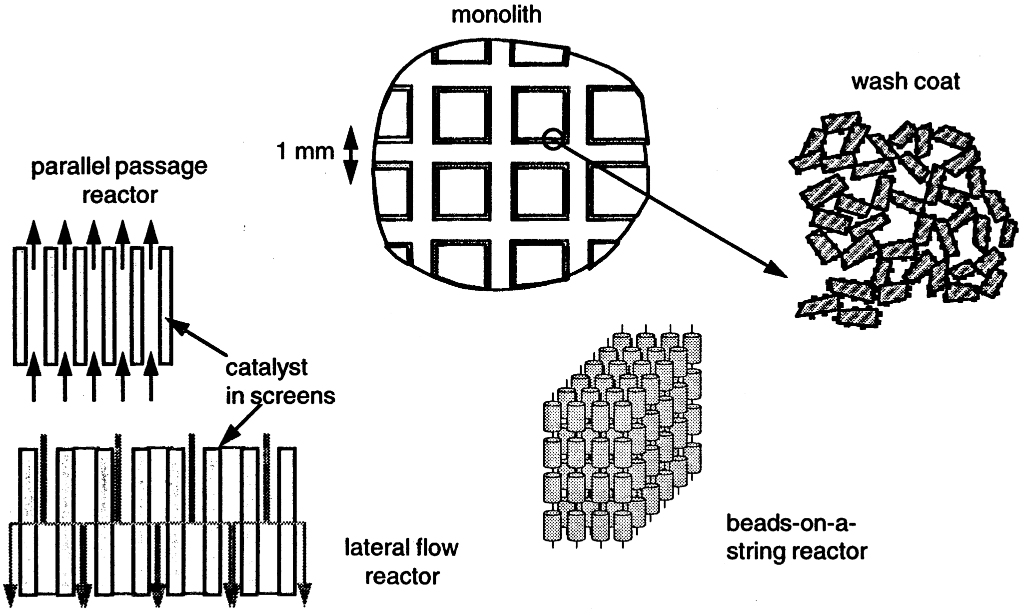


Fig. 24. Catalyst configurations for low-pressure drop applications.

adjacent envelopes. The straight, unobstructed gas channels give rise to a low-pressure drop and good tolerance to plugging by dust. Pollutant molecules are transported to the catalyst or adsorbent by lateral diffusion. This type of reactor has been applied in the Shell Flue Gas Desulphurization (SFGD) process (Dautzenberg *et al.*, 1971) which is based on the use of a regenerable copper adsorbent. A commercial SFGD unit for cleaning flue gas from refinery furnaces has been built and operated in Japan. A more recent application of the parallel-passage reactor is the selective catalytic reduction of NO_x with ammonia to N_2 with a vanadium-on-silica-type catalyst (Goudriaan *et al.*, 1989).

In applications where flue gases are relatively free of particulates, such as flue gases from gas-heated furnaces, dust tolerance requirements are less and the lateral-flow reactor is an option. In this reactor, which is in essence a fixed bed reactor with a very large cross section over volume ratio, gas flows through the catalyst layers rather than alongside. This type of reactor has been applied also for selective catalytic reduction of NO_x (Samson *et al.*, 1990).

Monoliths are also applied in selective catalytic reduction of NO_x because of their low pressure drop and tolerance to plugging by dust, due to the presence of straight parallel channels through which the gas flows in the laminar regime. The inner walls of the channels are provided with a layer of catalytically active material (wash coat). Because the diameter of the channels is rather small, mass transfer by radial diffusion in the gas to the gas–catalyst interface can be sufficiently fast. These monoliths form the elements of a commercial reactor, which consists of a stack of monolith blocks.

The features of low pressure drop and dust tolerance are also of importance in the application of monoliths in automotive exhaust catalysis. For this application, monoliths offer the additional advantages of minimal volume for the required catalytic conversion (which gives flexibility in mounting a catalytic exhaust converter in a car) and minimal mass. The latter is important since it minimizes the heating-up time and thus the extra emissions during the cold-start period when the temperature is still too low for the catalyst to be active.

The perspectives for use of monoliths in heterogeneous catalysis are analyzed by Cybulski and Moulijn (1994).

Gas–liquid systems

For a gas–liquid system with reaction within the liquid phase there are fundamentally three different modes of gas–liquid contact: (1) gas bubbles dispersed in liquid (as encountered in bubble columns), (2) liquid droplets dispersed in gas (e.g. tray operating in the spray regime), and (3) a thin flowing liquid film in contact with a gas (e.g. gas–liquid contacting in a packed column or wetted-wall column); see Fig. 25.

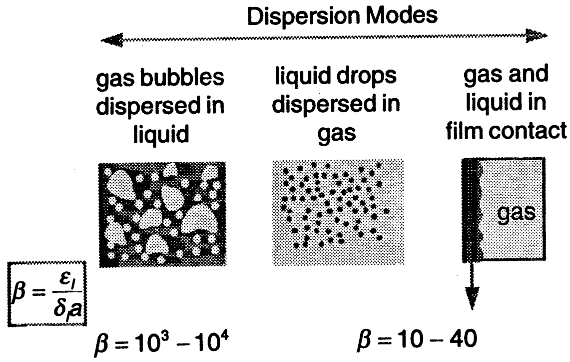


Fig. 25. Three fundamental procedures for contacting gases and liquids. β is the ratio of the liquid-phase volume to the volume of the diffusion layer within the liquid phase.

The hydrodynamic and mass transfer characteristics for any system are reflected by the parameter β which is the ratio of the liquid-phase volume to the volume of the diffusion layer. The first major decision for a gas–liquid system is the choice for this parameter β; this choice is analogous to the particle size decision for the catalyst. The value of β lies in the range 10–40 for liquid sprays and thin liquid films, whereas $\beta = 10^3$–10^4 for gas bubbles in liquid. The choice with regard to β depends on the relative rates of chemical reaction and mass transfer within the liquid phase, portrayed by the Hatta number. The choices for β are summarized in the Enhancement factor–Hatta number diagram of Fig. 26, which is equivalent to the Effectiveness factor–Thiele modulus diagram of Fig. 4. The overall aim is to choose the value of β such that the reactor volume is effectively utilized. Thus, for slow liquid-phase reactions the aim should be to increase the bulk liquid volume at the expense of interfacial area. A high value of β is achieved by dispersing the gas in the form of bubbles (e.g. bubble columns and tray columns operating in the froth regime). To give an example, air oxidation of cyclohexane (in the liquid phase) is a slow reaction usually carried out in bubble contactors.

In the fast pseudo-first-order reaction regime, the reaction occurs predominantly in the diffusion film close to the gas–liquid interface and a contactor with a low value of β should be chosen (e.g. spray towers and packed columns). Furthermore, in the fast pseudo-first-order reaction regime, the rate of transfer is independent of the liquid-phase hydrodynamics; there is no need to spend energy for increasing turbulence in the liquid phase. An example of process operating in the fast pseudo-first-order reaction regime is absorption of carbon dioxide in aqueous caustic solutions; this is usually carried out in packed columns. The liquid phase flows down the column in thin liquid rivulets. If the gas–liquid reaction corresponds to the instantaneous reaction rate regime, once again efforts should be made to maximize the interfacial area at the expense of bulk liquid volume. In contrast to the fast pseudo-first-order reaction

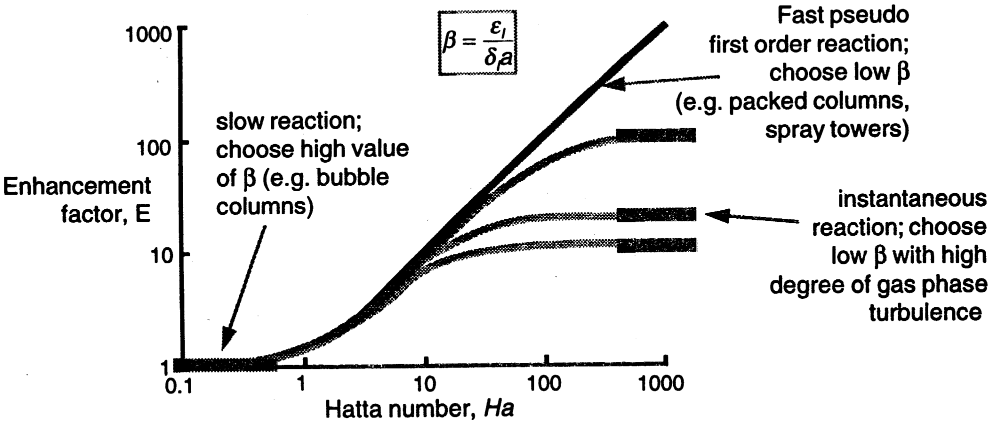


Fig. 26. Enhancement factor for gas–liquid reactions as a function of the Hatta number; adapted from Trambouze *et al.* (1988). This diagram is also valid for liquid–liquid contacting.

regime, it generally pays to attempt to enhance the degree of turbulence in both the liquid and gas phases. Contactors that satisfy these requirements include tray columns operating in the spray regime and venturi scrubbers. The sulfonation of aromatics using gaseous sulfur trioxide is an instantaneous reaction and is controlled by gas-phase mass transfer. In the commercially used thin-film sulfonator, the liquid reactant flows down a tube as a thin film (low β), in contact with a highly turbulent gas stream (high k_g). A thin-film contactor is chosen in place of a liquid droplet system due to the desire to remove heat from the liquid phase; this heat is generated due to the highly exothermic sulfonation reaction. Chlorination of *p*-cresol follows a consecutive reaction sequence and the selectivity towards the intermediate monochloro product is influenced by mass transfer limitations within the liquid phase. Increasing the liquid-phase mass transfer coefficient, by increasing the bubble size (Teramoto *et al.*, 1970) or the stirrer speed in a stirred vessel (Pangarkar and Sharma, 1974), increases the selectivity towards the intermediate product.

Considerations of intrinsic process safety often dictate the choice of β; it is often desired to minimize the hold-up of one of the hazardous reacting components in the reactor.

Gas–liquid–solid systems

Here, both the solid particle size and the ratio β need to be chosen. The considerations leading to the choices for these parameters are the same as above. If, from a transport–reaction analysis, particle sizes smaller than 1 mm are chosen, slurry operations would need to be considered. On the other hand, if particle sizes larger than say 2 mm are allowable there is extra flexibility in choosing fixed bed (e.g. trickle beds) or three-phase fluidized operations. The choice between fixed beds and three-phase fluid bed operations can be further narrowed down by additional analysis at Strategy levels II and III.

Liquid–liquid systems

Assume that the reaction takes place in one of the phases, say L2. The ideal choice for the parameter $\beta_{L2} \equiv \varepsilon_{L2}/\delta_{L2}a$ is dictated by the same considerations as for gas–liquid systems; cf. Fig. 26. To achieve high values of β_{L2} we should disperse phase L1 in the form of drops in the continuous phase L2. Low values of β_{L2} could be achieved by dispersing L2 in the form of drops in the continuous phase L1. Thin liquid film flow, as encountered in gas–liquid systems (cf. Fig. 25), though not impossible, is unusual in liquid–liquid systems.

Sometimes, practical considerations override the decisions arrived at from a transport–reaction analysis. It is thus advisable to disperse corrosive liquid so as to reduce contact with the reactor walls. Hazardous liquid mixtures are usually dispersed so as to reduce their hold-up, even if this is contrary to conclusions reached from a transport–reaction analysis.

STRATEGY LEVEL II—INJECTION AND DISPERSION STRATEGIES

Four different sub-levels of this strategy are considered.

II(a) Reactant and energy injection and phase dispersion strategy

For each reactant to the reactor there are several injection strategies to choose from: (1) one-shot (i.e. batch), (2) step function (continuous feed), (3) pulsed feed injection, e.g. using square wave functions, and (4) staged injection of the feed, in the sense of time or space.

Batch vs continuous operation. One of the most important decisions the chemical technologist has to make is whether to use continuous or batch processing (Gonzalez and Larder, 1984). The parameters that determine this choice include scale of operation, supply and availability of raw materials, capital and operating costs, maintenance and labor requirements, environmental problems, product quality, operability and safety. Since the continuous processes were developed at the beginning of the century, conventional wisdom has held that batch manufacture is better for high-value products with low outputs (such as fine chemicals), whereas continuous processing is more advantageous for high-volume products of low value (such as petrochemicals).

The desire to operate under intrinsically safe conditions requires that the inventory (hold-up) of reactants in the reactor be minimized. Wiederkehr (1988) presents an example of the production of "Carbol", a key product in the synthesis of a vitamin. In view of the reaction conditions (long reaction times, heterogeneous nature of reaction medium, reaction under pressure), a continuous reaction seemed to be feasible only with great difficulty, but Hoffman–La Roche nevertheless decided to go for a continuous reaction, mainly for reasons of safety.

Another example is the production of peroxy esters (e.g. *tert*-butyl peroxy 2-ethyl hexanoate), based on the reaction between the corresponding acid chloride and the hydroperoxide in the presence of NaOH or KOH, which are highly temperature sensitive and violently unstable. Batch operations to produce even 1000 t per annum are found to be unsafe. A continuous reactor was found to overcome most of the problems and claims have been made for producing purer chemicals at lower capital and running costs (Kohn, 1978). The continuous reactors produced 7–10 times more material per unit volume compared to batch processes, and since the amount of hazardous product present in the unit at any given time is so small, protective barrier walls were unnecessary.

Pulsed reactant injection. Continuous processes have been typically operated at steady state. This has been viewed as desirable due to the relative ease of this type of operation. Despite its ease, steady-state operation is not necessarily the optimum mode of operation and varying one or more variables periodically can significantly enhance the process performance (e.g. Douglas, 1967; Horn and Lin, 1967; Ray, 1968; Bailey *et al.*, 1971; Rigopolous *et al.*, 1988; Hatzimanikatis *et al.*, 1993). The simplest mode of periodic operation consists of a pulsed operation since it simply amounts to switching a process variable between two values. When the reaction kinetic is non-linear or when the reaction sequence involves series or parallel reactions proceeding with different reaction orders, the use of pulsed concentrations can lead to conversion or selectivity advantages. One example of the use of the pulsed injection strategy is in the production of diamines by hydrogenation of nitriles, e.g. succinonitrile. Hydrogenation of nitriles to diamines proceeds via the intermediate imines, which are extremely reactive. Under hydrogen depletion conditions inside the catalyst, these imines will react to produce undesirable by-products. Manna *et al.* (1992) showed that by using asymmetric oscillations or pulsations at very low frequencies of the inlet concentration of the dinitrile, a significant improvement of yield and selectivity to diamines can be obtained.

Periodic flow reversal. Recently, stemming from the pioneering work of Matros and co-workers (Boreskov and Matros, 1983; Matros, 1985) there has been considerable interest in the cyclic operation of catalytic reactors with periodic flow reversal; see Fig. 27. In fixed bed operation with periodic flow reversal, the fore and aft parts of the catalyst bed act as regenerative heat exchangers for feed and effluent, allowing weakly exothermic reactions to be operated autothermally at high reaction temperatures. The catalytic combustion of undesired components, e.g. volatile organic compounds, in air, are well suited for this way of operation (Eigenberger and Nieken, 1988; Vanin *et al.*, 1993). Reverse flow operation has also been successfully used, on an industrial scale, for oxidation of SO_2 (Matros, 1985; Silveston *et al.*, 1994) and, on a pilot scale, for production of synthesis gas from the catalytic partial oxidation of natural gas with air (Blanks *et al.*, 1990). Reversed flow operation for methanol synthesis has been extensively investigated by Froment and co-workers (Van den Bussche *et al.*, 1993).

Controlled (*staged*) *injection of reactant.* Consider the co-dimerization of propene and butene to produce heptenes. This reaction is accompanied by two competing, undesirable reactions: dimerization of propene to hexene, and dimerization of butene to octene. The propene dimerization reaction proceeds extremely rapidly and in order to suppress the formation of hexenes, a staged injection of propene into the reactor should be adopted, with all the butenes at the beginning of the operation (Trambouze *et al.*, 1988).

In the chlorination of propene to allyl chloride the undesirable side reactions to 1,3-dichloropropane (DCP) and 1,3-dichloropropene ($DCP^=$) can be reduced by employing staged injection of chlorine (see Fig. 28), a strategy which has surprisingly not been suggested in the literature (Biegler and Hughes, 1983; Seider *et al.*, 1990). In the sulfuric acid alkylation of *iso*butane, staged injection of the olefin feed to the cascade of stirred reactors is employed because of selectivity considerations and improved octane number of the product (Lerner and Citarella, 1991); see Fig. 29.

For polymerization of ethene in a simple tubular reactor, ethene conversion of 20–25% is normally achieved. However, on subsequent addition of cold gaseous monomer and initiator, and applying tubes with increasing diameters, conversion of up to 35% is possible (Gerrens, 1982); see Fig. 30.

In the hydroprocessing of oils in trickle bed reactors, staged injection of cold hydrogen gas between the catalyst beds not only compensates for hydrogen consumption but also serves to limit the temperature rise in the reactor.

Controlled addition of one of the reactants through a membrane maintains its low concentration and thus limits side reactions or subsequent reactions of the product. Controlled addition can thus also be used to prevent catalyst deactivation by the latter reasons; see Fig. 31(a). Another possibility is the addition of one reactant through a membrane so that a higher

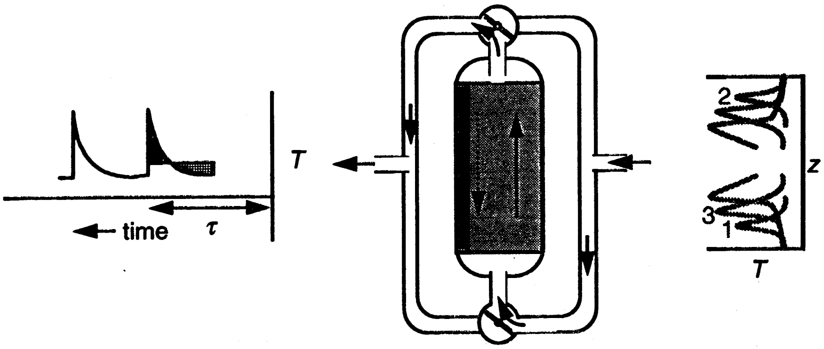


Fig. 27. Reverse flow strategy for catalytic combustion of volatile organic compounds in a fixed bed reactor.

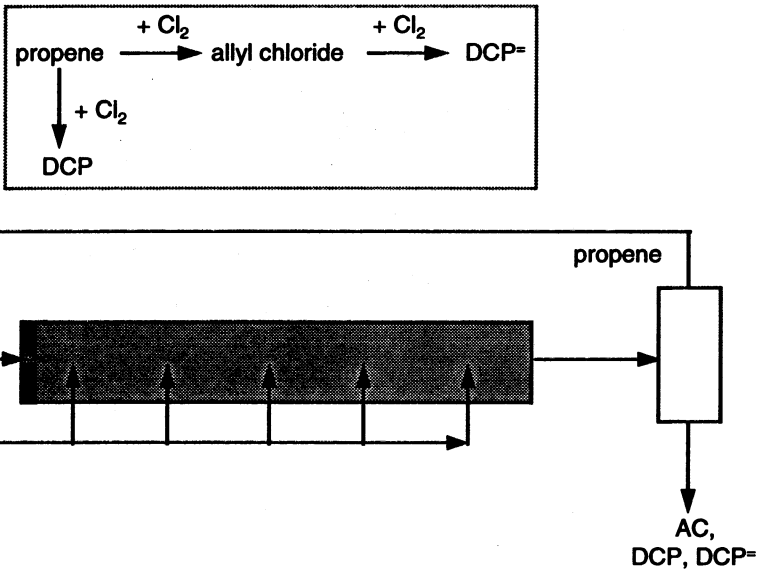


Fig. 28. Staged injection strategy for chlorination of propene to allyl chloride.

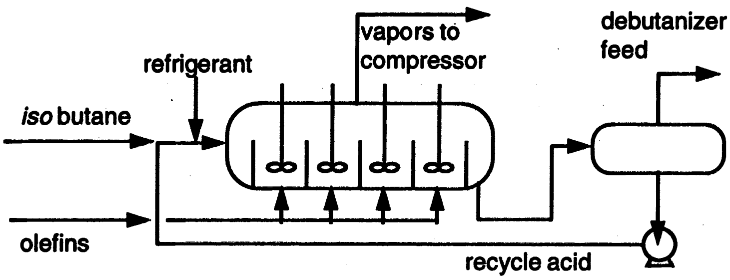
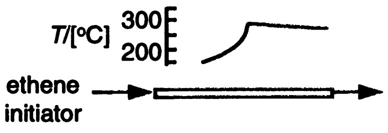
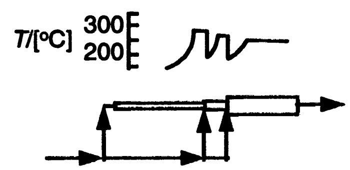


Fig. 29. Staged injection of olefins improves selectivity in the alkylation of *iso*butane. Adapted from Lerner and Citarella (1991).



(a) simple tube reactor



(b) Tube reactor with distributed feed

Fig. 30. Staged injection of ethene gas and initiator in polymerization. Adapted from Gerrens (1982).

concentration of the reactant can be obtained on the catalyst surface [Fig. 31(b)]. This may yield higher conversions when the surface concentration of the reactant is limited because of competitive adsorption. In addition, a more uniform concentration can be obtained on the catalyst surface than in a standard tubular reactor. A membrane can also be used to prevent a poison from reaching the catalyst site [Fig. 31(c)]. Falconer *et al.* (1993) list several examples where controlled addition of reactant is beneficial.

In the examples considered above, one of the reactants was introduced in a progressive, staged manner. Pursuing this line of attack, the benefits in keeping the two reactants completely segregated from each other and allowing them to meet only on active catalytic sites should be examined. The active components of the catalyst could be incorporated within a non-permselective ceramic membrane with the reactants on either side. Figure 32 shows a schematic diagram of such a catalytic membrane reactor for carrying out the Claus reaction (Sloot *et al.*, 1990)

$$2H_2S + SO_2 \leftrightarrow \tfrac{3}{8}S_8 + 2H_2O.$$

This novel reactor type has specific advantages for chemical processes requiring strict adherence of the feed rates to the reaction stoichiometry. The reaction plane within the catalyst membrane would shift in such a manner that the molar fluxes of the reactants across the membrane are always in the stoichiometric ratio; this allows greater flexibility of the reactor to

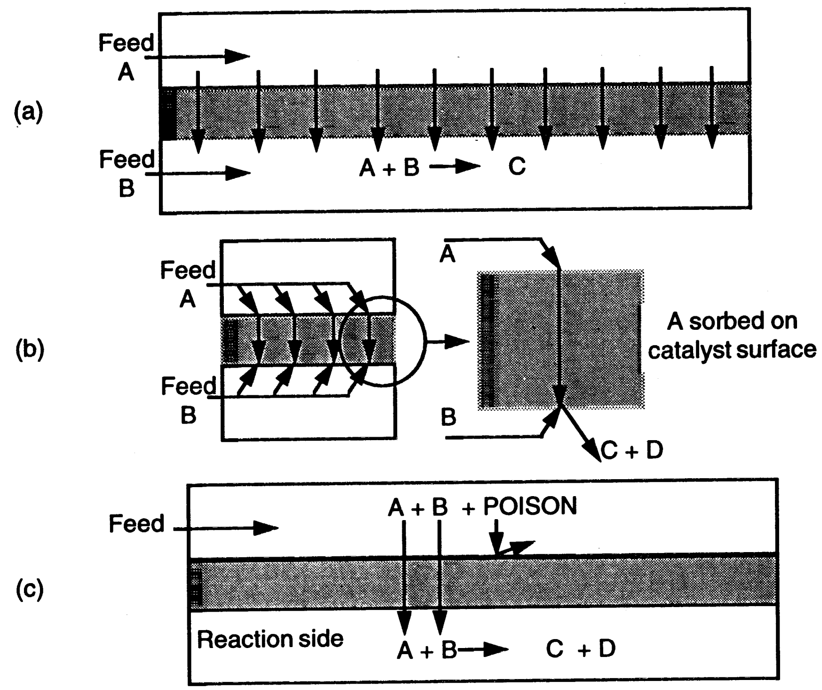


Fig. 31. Dispersionless contacting strategies. (a) Progressive addition of A through a porous membrane wall. (b) Injection of reactants A and B on opposite sides of a catalytic membrane wall with reaction within the catalyst plane. (c) Selective exclusion of a poison from the reaction zone by selective permeation through a membrane. Adapted from Falconer *et al.* (1993).

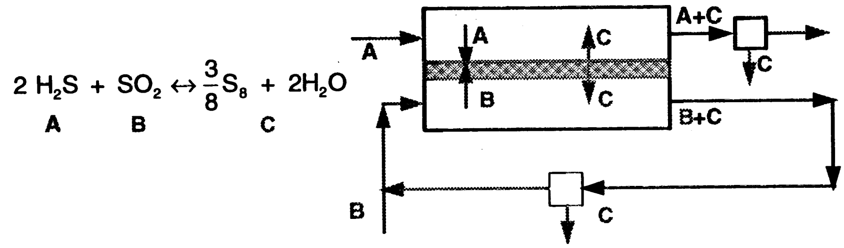


Fig. 32. Catalytic membrane reactor for carrying out the Claus reaction: $2H_2S + SO_2 \leftrightarrow 3/8S_8 + 2H_2O$. Adapted from Sloot *et al.* (1990).

feed rates of hydrogen sulfide and sulfur dioxide. The practical feasibility of this novel concept has been demonstrated by Sloot *et al.* (1990). This concept has also been suggested by Van Swaaij and co-workers (see Sloot *et al.*, 1990) for catalytic reduction of nitric oxide with ammonia in flue gas; by keeping the reactants separated and allowing reaction only within the membrane it will be possible to cope with varying ratios of the concentration of nitric oxide and ammonia, while ensuring stoichiometry at the reaction side and avoiding significant slip of reactants in the treated flue gas without the need for accurate dosage of ammonia.

Another class of processes where it is advantageous to keep the reactants separated from each other, except on catalytic sites, is partial oxidation of light hydrocarbons (e.g. methane, ethene, propene, or butene). Flammability considerations usually restrict the feed mixture composition. By adopting the concept of a multitubular cooled catalytic membrane reactor, with the reactants kept separate, it should be possible to avoid any flammability constraint; see the schematic in Fig. 33. This concept has been demonstrated by Veldsink *et al.* (1992). Lafarga *et al.* (1994) used a similar reactor concept for methane oxidative coupling. Oxygen supply is by permeation through the walls and this helps to maintain the oxygen concentration in the reactor at a low level. Improved hydrocarbon selectivity is obtained in this membrane reactor compared to a conventional packed bed reactor.

The problem of incomplete wetting efficiency of a trickle bed reactor can be solved by the cross flow catalyst contactor concept of Schöön and co-workers (De Vos *et al.*, 1982) in which the gas and liquid phases are made to flow in separate channels, separated by flat catalyst "plates"; see Fig. 34. In order to obtain sufficient reaction capacity, the catalyst may contain a great number of parallel plates. In the study by Schöön, the plates were separated from each other by corrugated planes, forming a system of parallel

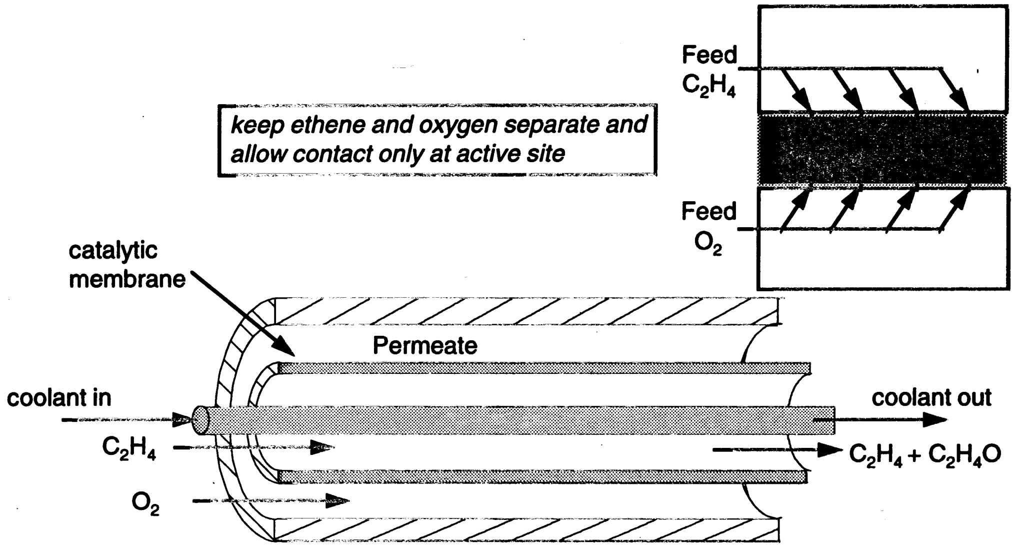


Fig. 33. Catalytic membrane concept for oxidation of ethene to ethene oxide. Adapted from Veldsink *et al.* (1992).

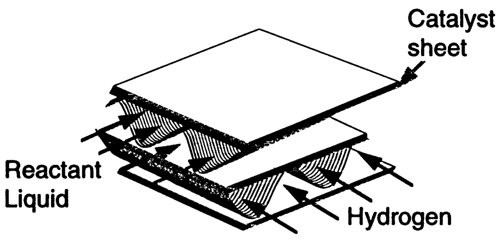


Fig. 34. Cross-current dispersionless contacting of gas (hydrogen) and liquid (oil) in a monolith reactor. Adapted from De Vos *et al.* (1982).

channels. The pressure drop of flow in the channels is negligible and the specific gas–liquid contact area is large.

Staged energy supply and removal. There is a complete analogy between staged reactant injection and staged energy supply, or removal, strategies. In a batch reactor, for example, the energy removal (supply) strategy can be programmed to keep the temperature constant. The energy removal can be by means of an evaporating solvent or the product itself. In a continuous flow reactor the temperature profile can be optimized by programmed energy removal by installation of, say, interstage cooling (heating). Commonly, heat is removed (supplied) by indirect heat exchange through installed surfaces within the reactor. Such heat transfer surfaces are conceptually similar to dispersionless contacting in the membrane systems discussed above.

II(*b*) *Choice of the optimum state of mixedness of concentration and temperature*

The optimum states of mixedness of concentrations and temperature within the reactor have to be decided upon separately. For an isothermal reaction within a single phase this decision is often governed by the desire to reduce the reactor volume required for achieving a specified conversion level. If it is desired to maximize the intermediate A_2 in a consecutive reaction scheme $A_1 \rightarrow A_2 \rightarrow A_3$ within a phase, plug flow conditions should be aimed for, i.e. "unmixed" concentration conditions within the reactor; this conclusion is analogous to the avoidance of intra-particle diffusion resistances (see Fig. 12).

For highly exothermic reactions the dilemma is usually: *to mix or not to mix?* From a concentration viewpoint it is usually preferable to approach plug flow conditions, i.e. concentrations should not be mixed along the reactor. But from the point of view of temperatures, a thermally well-mixed system would be preferred. Consider the specific example of the oxidation of ethene to produce ethene oxide. This highly exothermic reaction is conventionally carried out in a cooled multitubular packed bed reactor. Close to the inlet of the reactor there is a temperature peak (hot spot). At increasing temperatures there is loss of selectivity to ethene oxide because of the parallel reaction to combustion products. Figure 35 shows the simulated temperature and selectivity profile of an ethene oxide. From the point of view of maximum selectivity, it would be preferable to have a reactor concept in which the temperature is completely backmixed but the concentrations are unmixed (plug flow). The peak temperature can be "shaved" by a programmed energy removal strategy or a profiled axial catalyst activity; see Fig. 36. The energy flux removal near the inlet, "hot spot" zone needs to be higher than towards the exit of the reactor; this strategy is approached by using co-current single-phase coolant. Using lower activity catalyst in the initial hot spot zone will also lead to a selectivity improvement. Figure 36 shows that either of the above strategies leads to selectivity improvements of

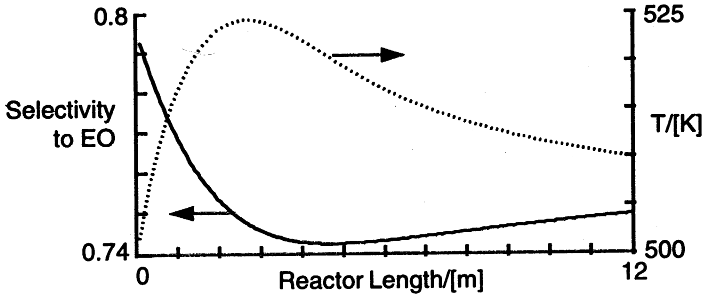


Fig. 35. Temperature and selectivity profiles for the exothermic reaction of oxidation of ethene to ethene oxide in a multitubular packed bed reactor. The simulations for the reactor temperature and selectivity were carried out using the kinetic data of Westerterp and Ptasinski (1984). The coolant temperature was constant along the length of the solvent; this was achieved by the use of evaporating water as a cooling medium.

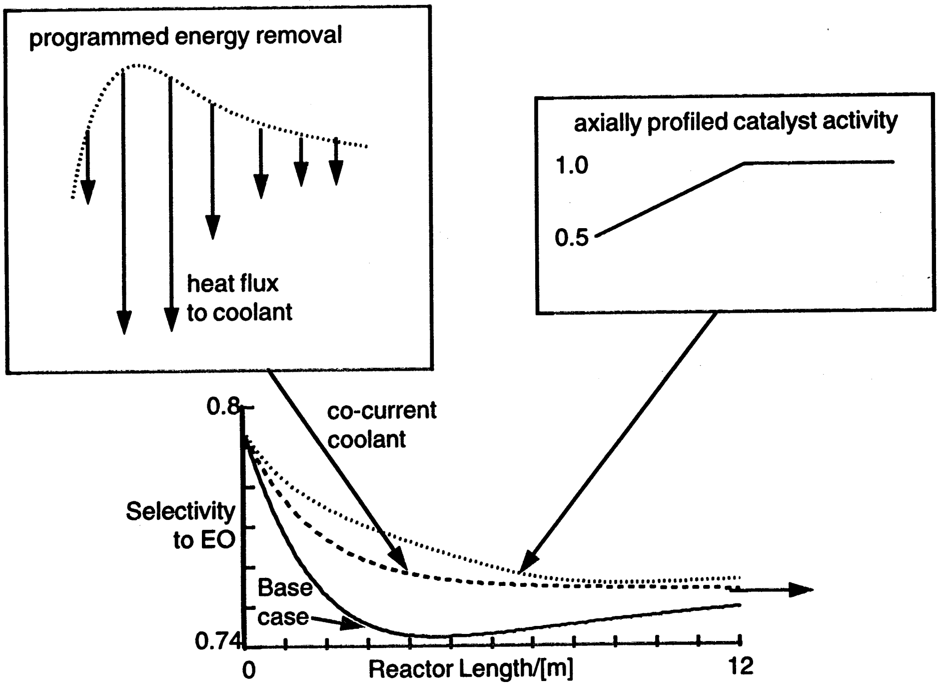


Fig. 36. Selectivity profiles for base case with constant coolant temperature, co-current coolant strategy and axially profiled catalyst activity strategy. The base case chosen in the calculations is one in which the coolant temperature is constant and the activity profile along the length of the reactor is at unity level.

the order of 0.5–1%, which can be commercially significant.

Another strategy for operating a packed bed reactor under near isothermal conditions is the use of the pancake reactor (Fig. 37), wherein the contact time is kept short by high severity operation. Heat removal at high temperatures is by use of molten salt (Blumenberg, 1992).

A well-mixed temperature in partial oxidation reactions can be achieved by circulating the catalyst and removing the heat externally. The Du Pont process for production of maleic anhydride by oxidation of butane uses the circulating fluid bed reactor concept (Contractor and Sleight, 1988); see also discussions below on Strategy level III. As discussed earlier, catalyst circulation is possible only if the attrition resistance is improved. Circulating dense-phase fluidized bed reactors have good potential for carrying out exothermic gas–solid reactions, especially with deactivating catalysts (see Gianetto *et al.*, 1990); this potential is as yet largely untapped. In the Exxon process for partial oxidation of methane to produce syngas, well-mixed temperature conditions are realized by opting for a bubbling fluid bed operation (Eisenberg *et al.*, 1994).

The degree of backmixing has a significant impact on product properties in a polymerization process. For polymerization of methyl methacrylate the standard deviation in diameter of the particles of the latex produced in batch, pulsed tubular and CSTR are compared in Fig. 38. A pulsed tubular reactor is to be favored over a CSTR for a controlled, narrow

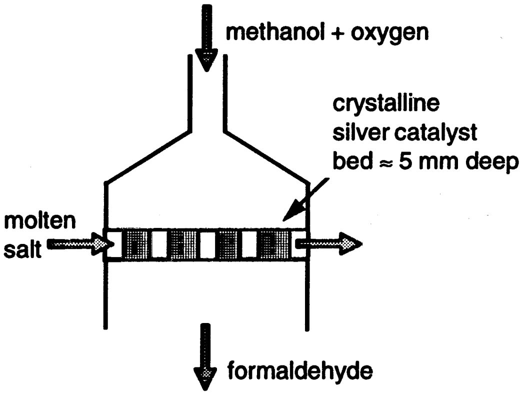


Fig. 37. Cooled pancake reactor concept of BASF for maintaining isothermal conditions in a multitubular reactor. Adapted from Blumenberg (1992).

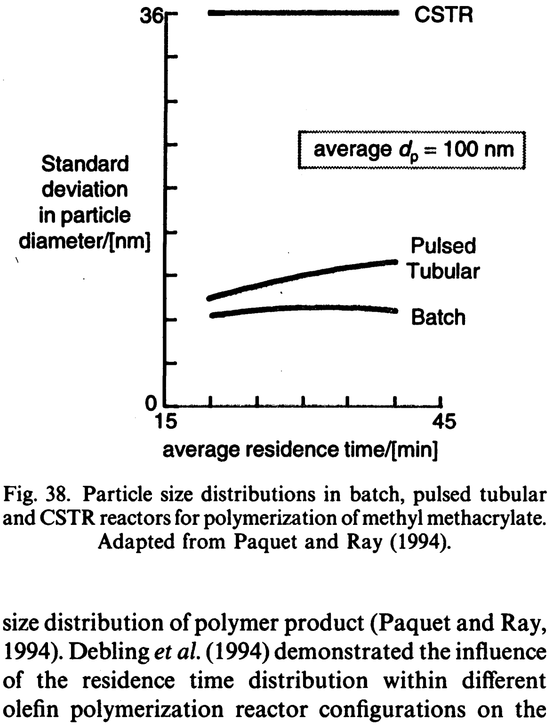


Fig. 38. Particle size distributions in batch, pulsed tubular and CSTR reactors for polymerization of methyl methacrylate. Adapted from Paquet and Ray (1994).

size distribution of polymer product (Paquet and Ray, 1994). Debling *et al.* (1994) demonstrated the influence of the residence time distribution within different olefin polymerization reactor configurations on the grade transition performance of a process. A choice of a reactor configuration that appproximates plug flow is shown to achieve efficient transitions between grades.

II(c) Separation of product(s) in situ *from the reactor zone, supply of reactants* in situ, *supply or removal of energy in the reactor* in situ

The main reasons for considering *in situ* removal of product(s) from the reaction zone are (1) to enhance conversion in equilibrium-limited reactions by shifting the equilibrium towards the right, (2) to prevent further, undesirable, reaction of products and consequently improved selectivity, and (3) as a remedy for product-inhibited reactions. The various techniques that can be considered for selective product removal are discussed below.

Extraction in situ. By deliberate addition of a second liquid phase containing a selective solvent, the desired product may be extracted from the reaction zone and further side reactions prevented (Brändström, 1983; Sharma, 1988). For example, in the bromination of dialcohols in aqueous phase, the problem is to prevent the second OH group from reacting with HBr to form the dibromide. This can be solved by adding a hydrocarbon to the reaction mixture. The hydrocarbon extracts the monobromide, but not the dihydroxy compound or the HBr, from the reaction mixture. The monobromide is thus removed from the reaction mixture as soon as it is formed and thereby the action of HBr on it is prevented by phase separation (Brändström, 1983).

In the Hofmann reaction of an amide with hypochlorite, the intermediate *iso*cyanate can be extracted out to make *iso*cyanates with high yields. In photochemical sulfoxidation of paraffins, water is used to extract sulfonic acid to prevent formation of polysulfonic acids.

The epoxide product derived from 6-methylhept-5-en-2-one is known to undergo very facile rearrangement to 1,3,3-trimethyl-2,7-dioxabicyclo[2,2,1]heptane. Under normal epoxidation conditions these two products, desired and undesired, are produced in about equal proportions. If the reaction is carried out in the presence of dichloromethane, the desired product is extracted to the hydrocarbon phase and a high yield (83–85%) of the epoxide is obtained with no detectable amounts of the rearranged product. The two-phase expoxidation strategy can be applied to a variety of olefins: cyclohexene, 1-hexene and limonene (Anderson and Veysoglu, 1973).

In the Ruhrchemie–Rhône Poulenc process for the production of butanal by hydroformylation of olefin, the *in situ* extraction of the desired product from the aqueous reaction phase prevents the formation of heavy ends; see Fig. 39 (Kuntz, 1987).

Sharma (1988) considered several examples of reactions which would profit from introduction of an additional extractant phase.

Reaction rate and selectivity in heterogeneously catalyzed liquid-phase hydrogenation can be influenced by the composition of the reaction medium in the vicinity of the liquid metal. This strategy can also be used for the selective hydrogenation of benzene to cyclohexene with powdered Pt or Ru catalyst. Introduction of an aqueous layer surrounding the catalyst particle is found to increase the selectivity towards cyclohexene (Wismeijer *et al.*, 1986; Struijk, 1992); see Fig. 40. The desired product cyclohexene distributes preferentially into the organic phase and is thus prevented from further hydrogenation to cyclohexane. Asahi chemicals are believed to utilize such a concept in their commercial process.

Supercritical extraction in situ. In equilibrium-limited biocatalyzed reactions the removal of the desired products, which are often thermally labile, by *in situ* supercritical extraction with carbon dioxide

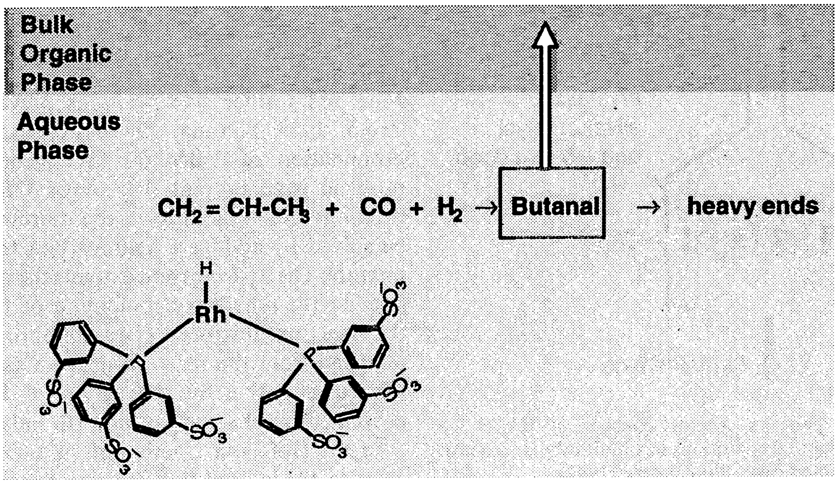


Fig. 39. *In situ* extraction of desired butanal in hydroformylation of olefins.

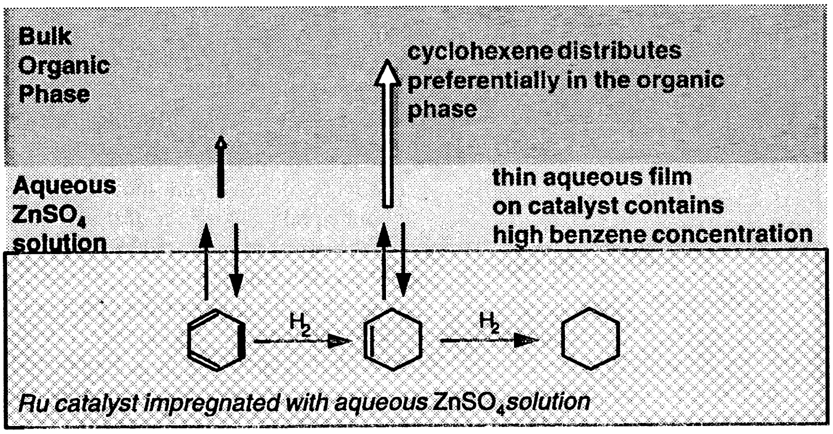


Fig. 40. Use of aqueous layer on catalyst particles to enhance the selectivity towards cyclohexene during hydrogenation of benzene. Adapted from Wismeijer *et al.* (1986) and Struijk (1992).

can lead to substantial benefits. In the lipase-catalyzed interesterification of triglycerides, for example: tricaprylin + methyl oleate ↔ 1-oleodicaprylin + 1,3-dioleocaprylin + methyl caprylate, a high degree of incorporation of required fatty acids into triglyceride cannot be obtained because of its reverse reaction. Adschiri *et al.* (1992) applied supercritical carbon dioxide extraction to the removal of products from a liquid-phase reaction system as a means of solving the problem. Supercritical CO_2 is non-toxic, and its critical temperature (304.2 K) is both sufficiently low for dealing with thermally labile materials and close to the optimal temperature for the enzymatic reaction. Significant improvement in the degree of incorporation of oleic acid into the triglyceride, above equilibrium values, was achieved in a batch reactor; see Fig. 41 (Adschiri *et al.*, 1992); Aaltonen and Rantakylä (1991) listed the various advantages of using supercritical CO_2 as a solvent in enzymatically catalyzed reactions, compared to aqueous media.

Distillation in situ. *In situ* product separation by distillation (Fig. 42) offers applications in esterification (e.g. for ethyl acetate), *trans*-esterification (e.g. for butyl acetate), hydrolysis (e.g. for ethylene glycol, *iso*propyl alcohol), metathesis (e.g. for methyl oleate), etherification (e.g. for MTBE, ETBE, TAME) and alkylation reactions (e.g. for cumene). The most dramatic example of the benefits of *in situ* separation within the reactor is afforded by the Eastman Kodak process for methyl acetate where the conventionally used reactor followed by several distillation columns was replaced by one integral reactive distillation column with considerable economic advantages (Doherty and Buzad, 1992). The *in situ* distillation concept has gained considerable attention recently for carrying out catalyzed liquid-phase reactions such as etherification; the catalyst in this case is usually incorporated in the form of a structured packing (DeGarmo *et al.*, 1992).

Membrane reactor for selective removal of product. Falconer *et al.* (1993) and Saracco and Specchia (1994) give several examples of *in situ* separations using membrane for the purpose of improving yield and selectivity. The basic concepts involved are shown schematically in Fig. 43. The majority of reactions

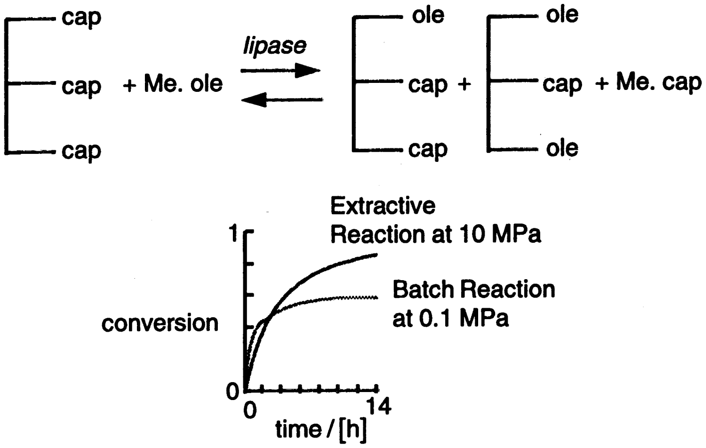


Fig. 41. Supercritical extraction of product *in situ*. Adapted from Adschiri *et al.* (1992).

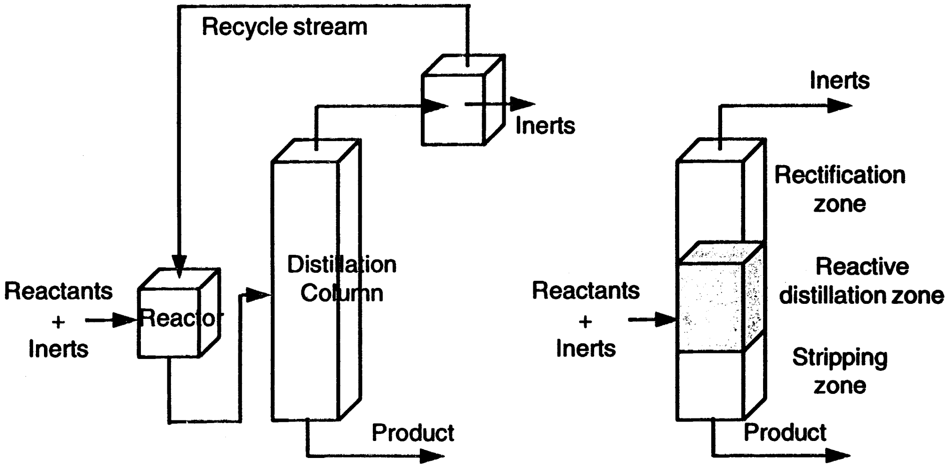


Fig. 42. Comparison of (reactor-followed-by-distillation) concept with (reactor-with-*in situ*-distillation) concept. Adapted from DeGarmo *et al.* (1992).

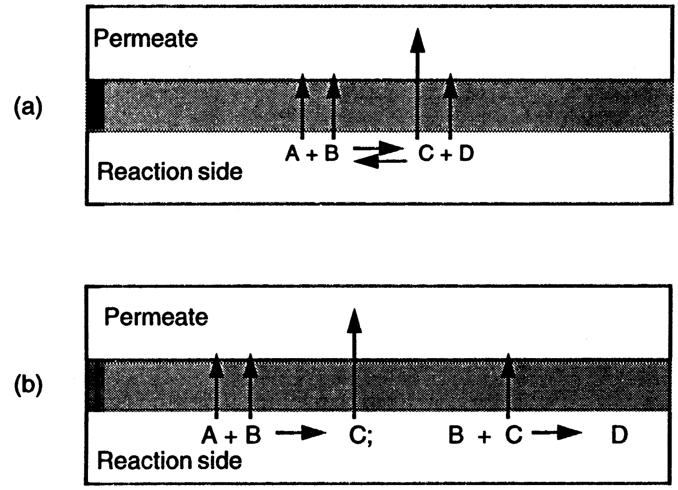


Fig. 43. Membrane concept for *in situ* product removal to (a) shift equilibrium or (b) prevent side reactions. Adapted from Falconer *et al.* (1993).

studied in catalytic membrane reactors have taken advantage of the ability of membranes to selectively remove a product, usually hydrogen, through Pd alloys or by Knudsen diffusion through microporous glass or ceramic membranes. For example, for propane dehydrogenation, significant improvements over conventional packed bed reactors have been realized (Ziaka *et al.*, 1993). Selectivity can also be enhanced when only the desired product of a set of equilibrium reactions is selectively removed through the membrane, or when the permeating component is an intermediate product of a set of consecutive reactions. Matsuda *et al.* (1993), during *iso*butane dehydrogenation in a Pd membrane reactor, noticed that the selectivity to *iso*butene was enhanced by *in situ* hydrogen removal through the membrane due to suppression of undesirable side reactions such as hydroisomerization and hydrogenolysis.

Other reactions where the use of permselective membranes in catalytic reactors can be expected to lead to significant improvements include dehydrogenation of ethane, cyclohexane and ethylbenzene. For example, an experimental study by Becker *et al.* (1993) showed that use of this concept for dehydrogenation of ethyl benzene results in a 20% increase of conversion over the conventional fixed bed operation. A survey of potential applications of inorganic membrane reactors is given by Falconer *et al.* (1993), Hsieh (1991) and Saracco and Specchia (1994).

The Knudsen selectivity achieved in glass or ceramic membranes is limited; much higher selectivities can be obtained by making use of the principle of shape selectivity, possible with membranes made of microporous materials such as zeolites or carbon molecular sieves. For equilibrium-limited isomerization of paraffins, it is advantageous to remove the normal paraffins *in situ* in the reactor. Two membrane reactor concepts are sketched in Fig. 44; these concepts have the potential of achieving near to complete conversion to either *iso*paraffins or *n*-paraffins from a mixed paraffin feed (Sie, 1994).

Membrane reactors may well be the future for many equilibrium reactions requiring effective removal of water—a small molecule that usually boils at higher temperatures than reactants, making it tough to remove by continuous distillation. Polymeric membrane reactors have been used for esterification of oleic acid and acetic acid with ethanol in the presence of an asymmetric polyether imide membrane; in this case, selective permeation of water allows 100% conversion levels to be achieved (Kita *et al.*, 1987).

Du Pont's fluorinated sulfonic acid polymers have been found useful in the separation of carboxylic acids. Valeric, propionic and butyric acids all diffuse through Nafion 125 in protonated forms with essentially identical rates whereas functional acids (levulinic, succinic, lactic) flow at a significantly lower rate (a half to one-fifth). In a process involving the reduction of levulinic to valeric acid the product can be removed selectively (Chum *et al.*, 1983).

An increasing number of bioreactor studies have focused on immobilized cell systems because their high cell density leads to improved volumetric productivity. But sometimes cells reduce their activity in the presence of the product. Concurrent production and recovery help in such situations. One well-known system of feedback inhibition is the fermentation of glucose to ethanol by *Saccharomyces cerevisiae*. For this process Steinmeyer *et al.* (1988) report on the operation of a multimembrane bioreactor system with an extraction solvent (see Fig. 45). Membranes in the reactor separate gas, cell, nutrient and solvent layers. The hydrophobic membrane that separates the gas phase from the cells allows for the removal of carbon

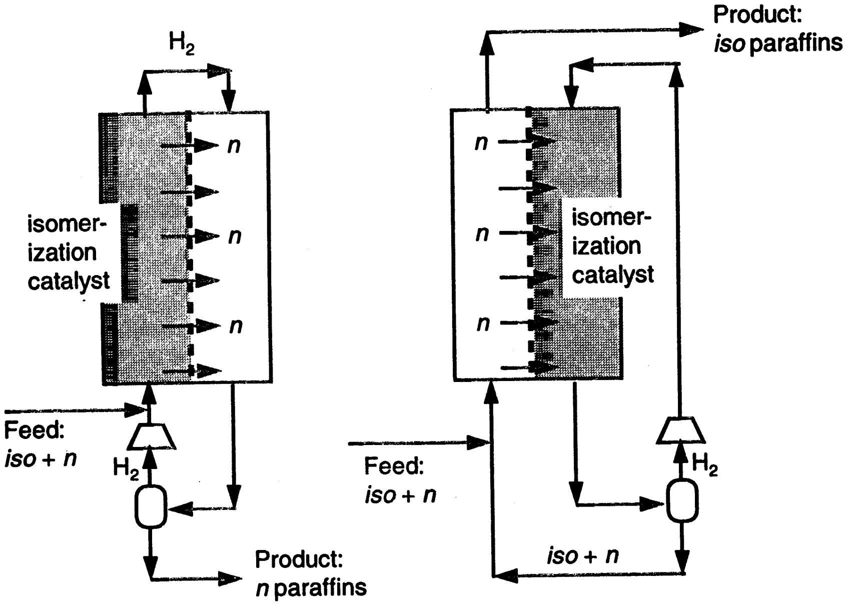


Fig. 44. Membrane reactor concepts for paraffin isomerization. Adapted from Sie (1994).

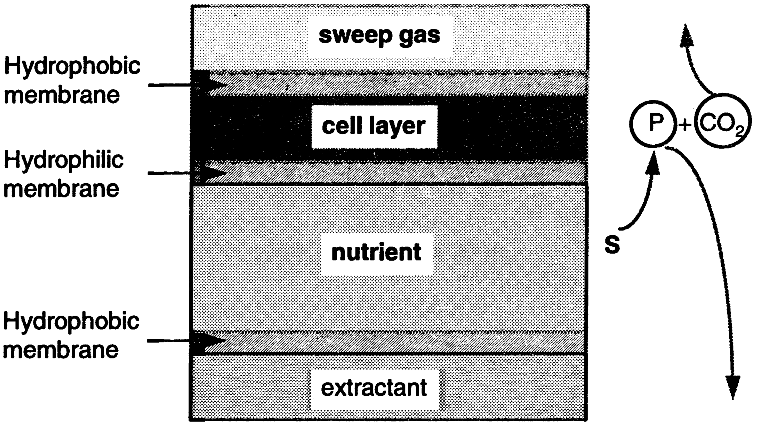


Fig. 45. Multilayer membrane reactor for biochemical application. Adapted from Steinmeyer *et al.* (1988).

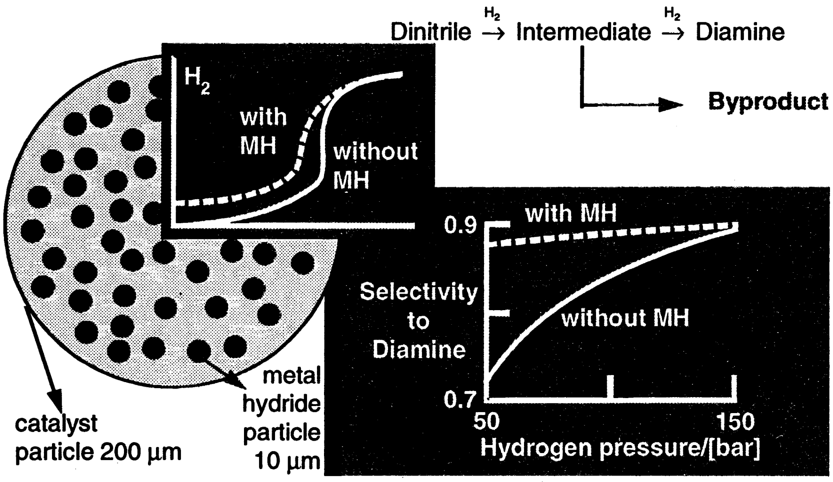


Fig. 46. *In situ* supply of hydrogen by incorporation of metal hydrides within catalyst. Adapted from Snijder *et al.* (1992).

dioxide from the cell layer and allows for the entry of oxygen, which is needed for lipid synthesis in yeast. A hydrophilic membrane separates the cell layer from the nutrient layer and allows the medium to readily pass through it. Nutrient supply and ethanol removal are achieved by a combination of diffusive and convective flows across this membrane. A hydrophobic membrane separates the nutrient and solvent layers. The solvent wets the membrane but does not pass through it to the nutrient side if a critical pressure differential is maintained. Successful compartmentalization of the solvent prevents emulsification and subsequent toxic effects on the cells. Solvent selectivity removes ethanol from the nutrient, thereby lowering ethanol inhibition of fermentation and increasing reaction rate and extent.

In the fermentation process for acetic acid, the use of electrodialysis for separation of product overcomes product inhibition and improves the space time yield considerably (Von Eysmondt and Wandrey, 1990). Another example is presented by Tichy *et al.* (1990) where not only the product inhibition by amino acid methionine is resolved by electrodialysis but where the losses of the substrate (in this case hydroxymethylthiobutyric acid) for the fermentation are reduced as well.

The hydrogenation of dinitriles to diamines is of practical importance since the diamines are used as the monomer for the production of nylons. The hydrogenation of succinonitrile is usually thought to proceed via reactive intermediate imines (Mares *et al.*, 1988). Deficit of hydrogen within the catalyst particle can cause excessive by-product formation. Van Swaaij and co-workers (Snijder *et al.*, 1992) developed a novel method for carrying out catalytic hydrogenation reactions. They incorporated metal hydride particles within the catalyst particles which served as *in situ* suppliers of hydrogen; see Fig. 46. For succinonitrile hydrogenation the selectivity of the diamines can be expected to increase markedly in comparison with conventional catalyst systems without metal hydride incorporation. This selectivity improvement is particularly significant at lower operating pressures. Incorporation of metal hydrides can therefore provide a means for reducing the severity (pressure) of hydrogenation reactions in the fine chemicals industry.

Removal of energy in situ. Removal of the heat of reaction *in situ* is often effected by use of an evaporating component of the reaction medium. This can be a product (as in reactive distillation) or a solvent. For example, in the sulfuric acid alkylation process sketched in Fig. 29, the concept of auto-refrigeration is used. Vaporization of a portion of the *iso*butane and propane in the feed mixture is used to control the temperature of each stage.

II(d) Counter-, co-, or cross-current contacting

The decision whether to adopt counter-, co-, or cross-current contacting of two phases is dictated by factors such as equilibrium limitations, flooding, pressure drop and degree of conversion required. For gas treatment applications such as absorption of CO_2, H_2S and COS using amines where high conversion levels are usually desired, it is common to adopt counter-current operation from considerations of phase and reaction equilibrium. For the equilibrium-limited hydration of butenes to produce *tert*-butyl alcohol, Fig. 47 illustrates the significant advantage of counter-current operation over the conventionally used co-current trickle flow reactor (Jansen *et al.*, 1995).

For the equilibrium-limited reaction of gaseous ammonia with phthalic anhydride to yield phthalimide, a continuously operated multistage counter-current reactor offers significant advantages over batch operation (Bartholomé *et al.*, 1978) and a high purity product containing a negligible amount of unreacted anhydride is obtained; see Fig. 48.

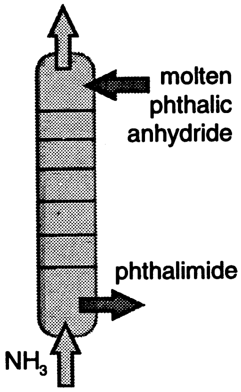


Fig. 48. Continuous counter-current multistage contacting for production of phthalimide. Adapted from Bartholomé *et al.* (1978).

Co-current gas–liquid downflow trickle bed reactors are widely applied for hydroprocessing of heavy oils. This co-current mode of operation is disadvantageous in most hydroprocesses, and counter-current flow of gas and liquid would be much more desirable. This is because reactions such as hydrosulfurization and hydrogenation are inhibited by the hydrogen sulfide formed, even when using so-called sulfur-tolerant catalysts of the mixed sulfide type. The removal of sulfur from heavy oil generally follows second-order kinetics in sulfur concentration, which is a reflection of the presence of a variety of sulfur-containing compounds with different reactivities. The second-order kinetics imply that a relatively large proportion of sulfur is removed in an early stage of the process (due to conversion of the bulk of reactive molecules) while removal of the remaining sulfur takes place

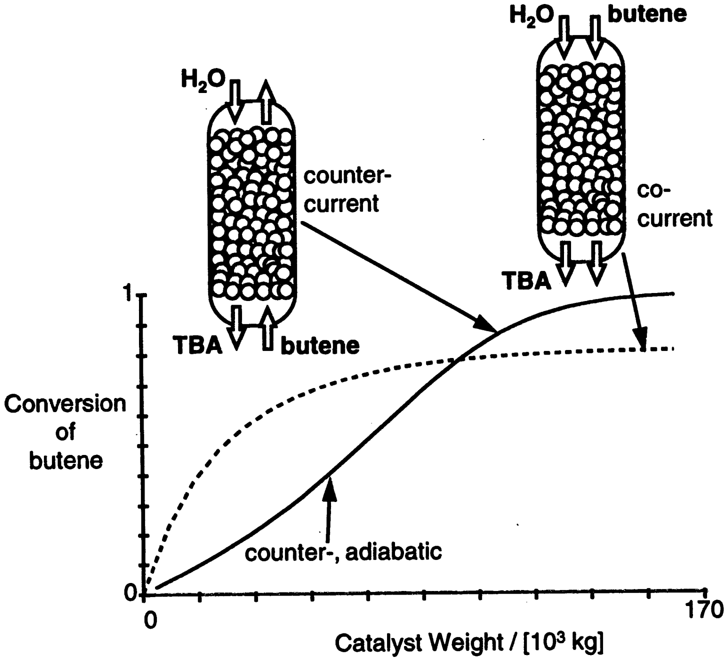


Fig. 47. Advantages of counter-current contacting over co-current contacting for hydration of butenes to *tert*-butyl alcohol. Adapted from Jansen *et al.* (1995).

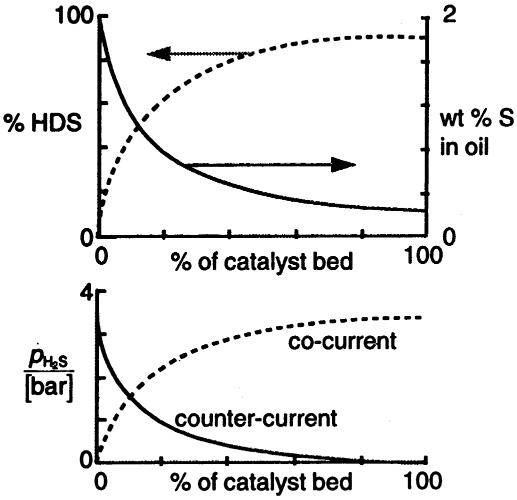


Fig. 49. Partial pressure profile of hydrogen sulfide in counter-current and co-current operation during hydrodesulfurization of gas oil.

much more slowly in later stages. This means that the bulk of the H_2S is generated in a small inlet part of the bed and that this H_2S exerts its inhibiting influence in the remaining part of the bed. Figure 49 shows the profiles of sulfur in liquid and H_2S in the gas phase for hydrodesulfurization. It can be seen that in co-current operation the larger part of the bed operates under a H_2S-rich regime; see Fig. 49. The situation is clearly more favorable in the counter-current mode of operation since in this case the major part of the bed operates in the H_2S lean regime. The co-current mode of operation is particularly unfavorable since the inhibiting effect is strongest in the region where the refractory compounds have to be converted, which calls for the highest activity.

A similar situation exists in hydrocracking. The by-product of conversion of nitrogen-containing organic compounds, namely ammonia, is a very strong inhibitor for hydrogenation and particularly for hydrocracking reactions. For the hydrogenation of aromatics, too, the co-current operation is unfavorable. This is not only so from a kinetic point of view (inhibition by H_2S and NH_3), but also because of thermodynamics (Trambouze, 1990). Deep removal of aromatics from an oil is generally limited by thermodynamic equilibria. In the co-current mode of operation the partial pressure of H_2 at the exit end of the reactor is lowest because of the combined effects of pressure drop, hydrogen consumption and build up of gaseous components other than H_2 (H_2S, NH_3, H_2O, and light hydrocarbons).

Problems with counter-current operation, however, are excessive pressure drop and flooding limitations. To overcome these problems larger sized (say 5 mm) "shaped" catalysts could be considered, in the form of Raschig rings (Trambouze, 1990). Note that in order to fulfill the requirements of Strategy level II the Strategy level I decision needs reconsideration. Alternative conceptual catalyst configurations for counter-current G–L contacting are shown in Fig. 50. The philosophy behind these configurations is that typically in hydroprocessing of heavy oils the gas–liquid mass transfer is not a limiting factor. By allowing gas and liquid to flow through separate channels, with the possibility of contacting each other at regular intervals, the momentum losses are reduced by sacrificing gas–liquid contacting efficiency. Figure 50(a) shows a possible construction in which a granular catalyst with a particle size around 1 mm is enclosed between horizontal screens. The screens are made from wire mesh or perforated plate. The upper screen is a flat one, while the lower screen has folds which serve as the vertical passages for gas. In the "tea bag" concept of Fig. 50(b), the filling consists of catalyst containers which have permeable walls that can be made from wire mesh or perforated sheet. These containers can have a spherical shape with diameters of the order of a few centimeters. The screens containing loose particles can be dispensed with if these particles are bonded together to form aggregates which can be considered as porous macroparticles. The techniques to form such agglomerates may involve sintering, cementing, superficial peptization of the particles, etc. The technique should not affect catalytic performance in a negative way and should also produce macroparticles of sufficient strength.

Cross-current contacting of phases is the strategy to be adopted when the contact between the phases needs to be limited rather than maximized. Some processes such as the dehydrogenation of propane to propene and *iso*butane to *iso*butene require a short (typically less than 3 s) contact time between the gaseous reactants and a solid catalyst. Moreover, the residence time distribution of the gas phase should be narrow, i.e. the aim should be for plug flow in order to achieve high selectivity and yield. This requirement is due to consecutive reactions where the desired product is the intermediate in the reaction sequence. Furthermore, for such processes, continuous catalyst regeneration is necessary to remove coke deposited during the reaction. Wolff *et al.* (1995) describe a novel circulating cross-flow moving bed reactor system for such applications; see Fig. 51. In this concept the variable gas residence time is independent of the longer, solids residence time. The latter can be adjusted by the superficial gas velocity and reactor inclination angle.

STRATEGY LEVEL III—CHOICE OF HYDRODYNAMIC FLOW REGIMES

The choice of the "fluidization" regime of operation is to a large extent a logical consequence of the various decisions already reached at Strategy levels I and II with respect to particle sizes, phase hold-ups, desired backmixing characteristics of each of the phases, etc.

Gas–solid systems

Basically, a choice has to be made between the following five modes of operation (see Fig. 52).

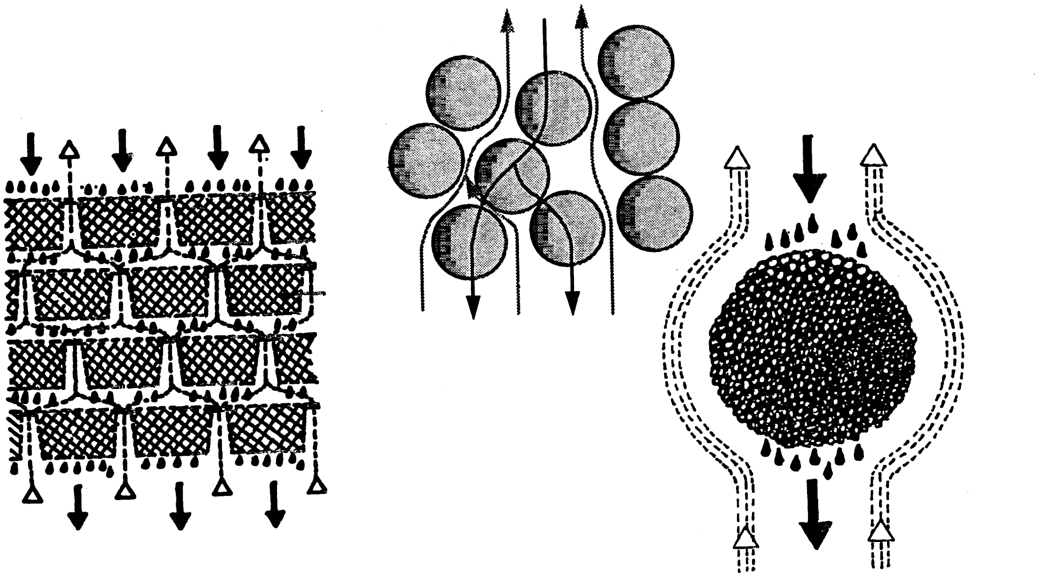


Fig. 50. Three-levels-of-porosity concept for counter-current contacting of gas and liquid phases. (a) Catalyst enclosed in wire-screen structure, (b) the "tea bag" concept, (c) agglomerated catalyst.

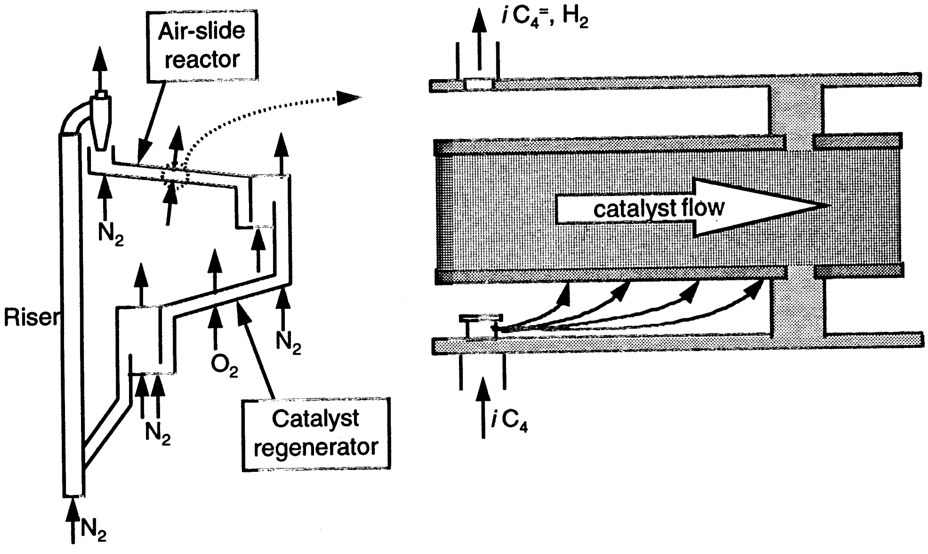


Fig. 51. Cross-current air-slide reactor concept for dehydrogenation of *iso*butane. Adapted from Wolff *et al.* (1995).

(1) *Packed bed regime (fixed or moving bed operation).* Here the particle hold-up is typically in the region 0.5–0.7. The particle size suitable in the packed bed regime is usually larger than 1 mm because smaller particle sizes result in unacceptably high pressure drops. The plug flow character of the gas phase is an important advantage of the packed bed reactor.

(2) *Bubbling bed operation.* The particle hold-up in this regime is typically 0.4–0.5 and this regime is characterized by the presence of fast-moving bubbles that tend to churn the system, resulting in an almost completely backmixed solids phase. A part of the entering gas phase serves to keep the particles in suspension and this portion of the gas is also completely backmixed; see Fig. 53. If staging of the solids is desired then a multistage fluid bed concept can be employed, either disposed horizontally or vertically, as illustrated later for the oil shale reactor configuration selection. The heat transfer coefficient to installed heat exchange surfaces in bubbling fluid beds is about a factor of five higher than in packed bed operation and this is often an advantage for reactions involving high exothermicity.

(3) *Turbulent bed* and (4) *dense-phase transport reactor.* If the gas velocity is increased further beyond the bubbling fluidization regime the *turbulent* regime of fluidization is reached. In this regime the bubbles are of indistinguishable and ever-changing shape. The

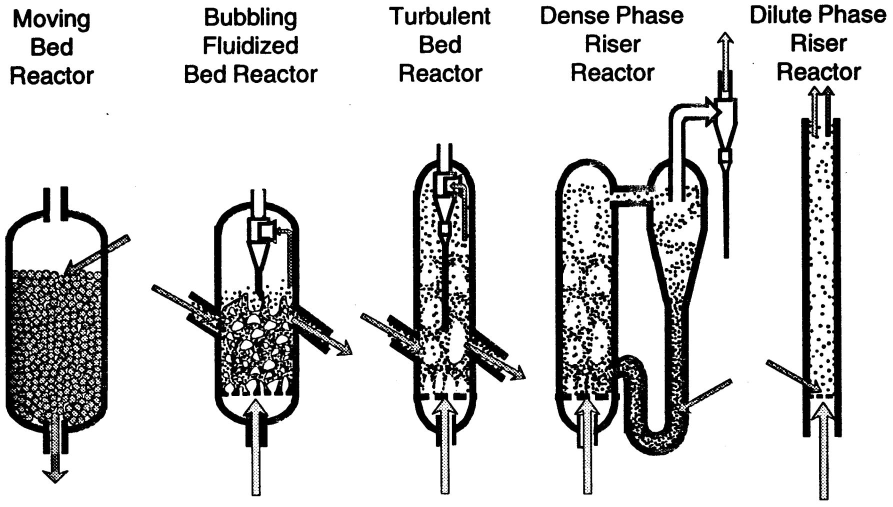


Fig. 52. Gas–solid reactors operating in various "fluidization" regimes.

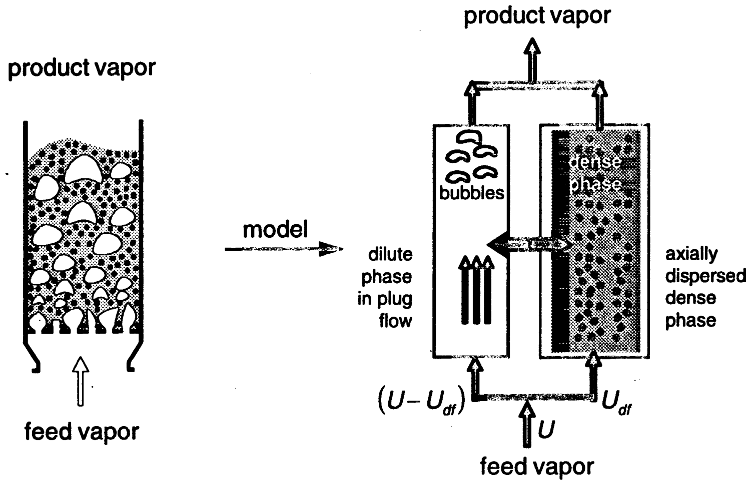


Fig. 53. Backmixing characteristics of dilute and dense phases in bubbling fluid bed.

particle hold-up is typically in the range 0.3–0.45. There is heavy entrainment of the solids and bed inventory would be lost without solids recycle by means of a cyclone. If the gas velocity is increased still further, the bed can be transported and this mode of operation is commonly termed *"fast" fluidization* or *dense-phase riser transport*. To maintain bed inventory, the contents of the reactor have to be recirculated and the reactor is also called the circulating fluid bed reactor. The particle hold-ups in this regime are typically 0.1–0.2. The backmixing characteristics of the dense-phase transport reactor are shown in Fig. 54. The exchange between the gas and solid phase is much better than in the bubbling bed operation.

(5) *Dilute-phase riser transport*. As the gas velocity is increased still further, the dilute-phase riser transport regime is reached. The particle hold-up in this regime is of the order of 0.05 or smaller. The gas and solid phases are virtually in co-current plug flow through the reactor (see Fig. 55).

The first major decision is whether to keep the solids fixed (in a packed bed) or to move the solids in a moving bed or fluidized bed. This choice is largely dictated by catalyst deactivation kinetics and the time interval between successive regenerations. If this time interval is of the order of 1 year, fixed bed operation is usually preferred. If the time interval is of the order of 1 week, swing type operation using two beds is usually opted for; swing operation is, for example, used in the regenerative naphtha reforming technology. If the time interval between successive regenerations is of the order of a day to a few hours, then moving bed operations can be considered such as in the CCR technology for naphtha reforming. If the time between successive regenerations is of the order of less than 1 h, then fluidized bed operation is called for. The decision to transport the solids to and from the reactor is a crucial one because solids motion introduces several complications such as attrition and blockage. If the catalyst is expensive (e.g. Pt based) or environmental hazardous (e.g. Cr), it is usually not

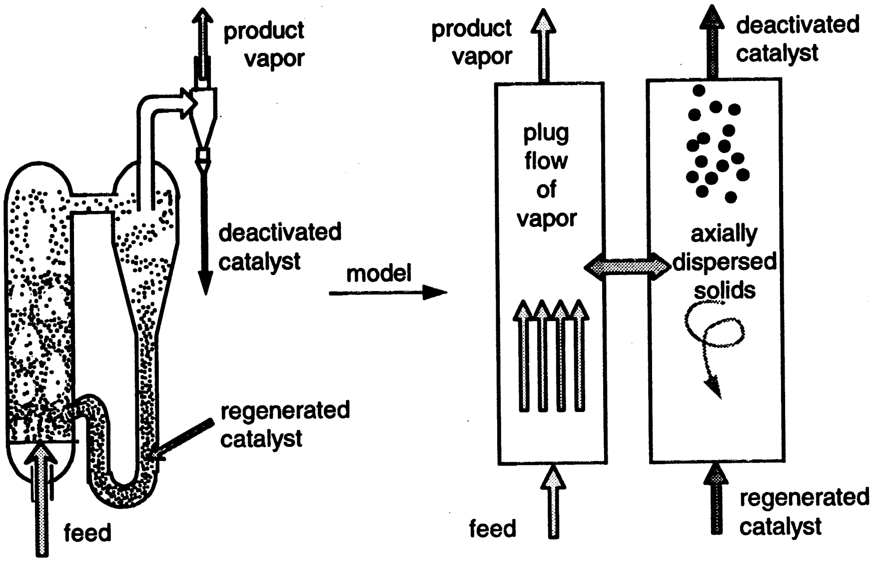


Fig. 54. Backmixing characteristics of gas and solid phases in circulating fluid beds.

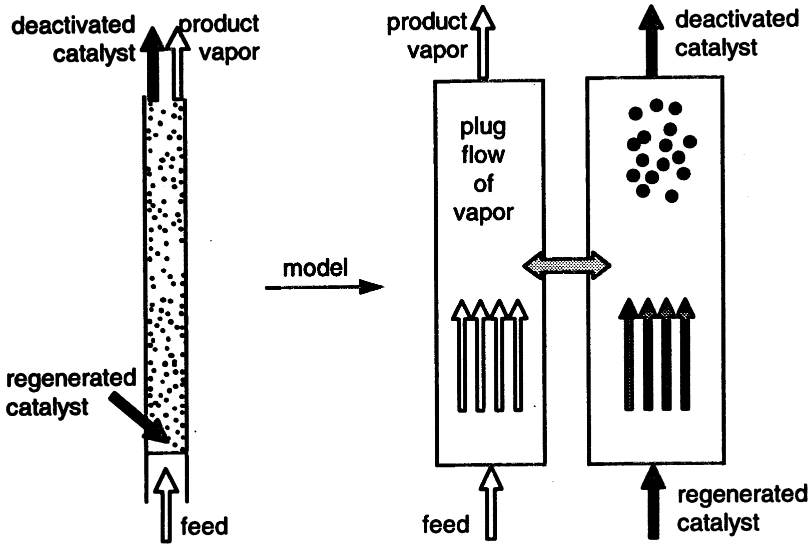


Fig. 55. Backmixing characteristics of gas and solid phases in dilute-phase risers.

advisable to fluidize it because of inevitable losses through cyclones.

Other reasons, distinct from catalyst deactivation, why fluidized bed operation is chosen could be the desire to use particles smaller than say 1 mm (such particles are usually not allowable in packed or moving bed operation due to excessive pressure drop). Another important reason to opt for fluidized beds may be the need to remove or supply large amounts of heat, taking advantage of the high heat transfer coefficients in fluid beds or the possibility to transport heat via flow of particles. Sometimes, the desire to have a completely thermally backmixed system (Strategy level II) would dictate the use of bubbling or circulating fluidized beds. This is the case for combustion of coke from deactivated FCC catalyst. Traditionally, FCC regenerator designs have adopted the bubbling fluid bed regime, because of the good backmixing of the emulsion phase. However, the major disadvantage of bubbling bed regenerator designs is oxygen slip due to poor mass transfer from bubbles; deep beds—typically 8 m in height—are required even for moderate conversion levels of about 90%. The dense-phase riser transport regime, which is the current choice for FCC regenerator operation, has vastly superior gas-to-solid mass transfer characteristics and is the regime currently favored for newer designs. In Fig. 56, the gas-to-solid mass transfer characteristics of the bubbling bed, dense- and dilute-phase transport regimes are compared with the effective chemical reaction rate. It is clear that the optimum regime of operation is the dense-phase transport regime and indeed this is the regime of choice in modern FCC designs.

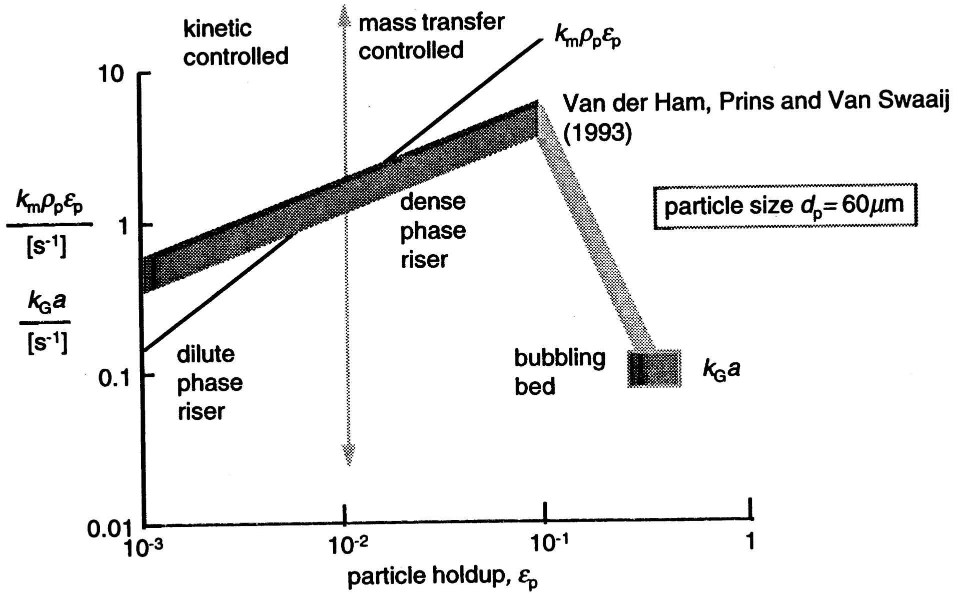


Fig. 56. Gas-to-solid mass transfer characteristics of various regimes of operation for regeneration of coked catalyst.

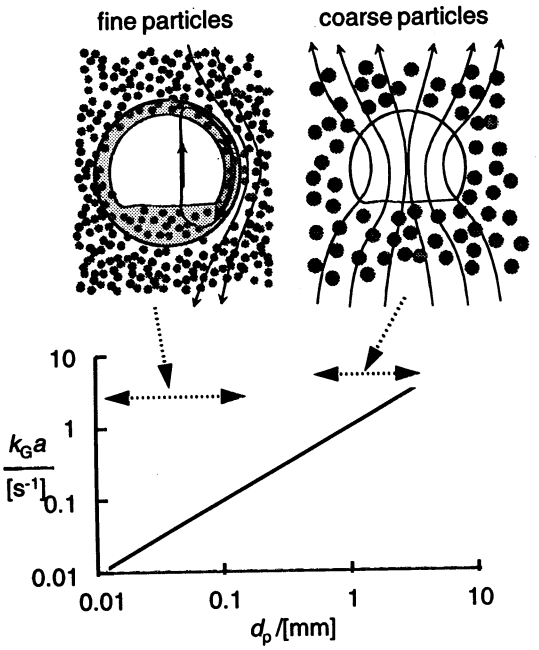


Fig. 57. Influence of particle size on bubble to dense-phase mass transfer in bubbling gas–solid fluid beds.

Another strategy to overcome the bubble to dense-phase mass transfer limitations of bubbling fluid bed operation is to resort to larger particle sizes because the interphase mass transfer coefficient is roughly proportional to the particle size; see Fig. 57. To overcome the concomitant problem of intraparticle diffusion within these larger particles it may be necessary to resort to the use of egg shell catalyst (back to Strategy level I!).

Gas–liquid systems

For upflow of gas through liquids in vertical columns, there is complete correspondence of flow regimes with gas–solid systems; see Fig. 58. The analogue of the homogeneous fluidization regime is the homogeneous bubbly flow regime. The bubbling fluid bed operation has a complete parallel in the churn-turbulent regime in gas–liquid systems (see Krishna, 1993). The choice between the various gas–liquid regimes, therefore, parallels the analysis for gas–solid systems; with increasing reaction rate the regime choice moves from left to right in Fig. 58. One possible starting point in the choice of the flow regime is consideration of the parameter β, already chosen in Strategy level I. Regimes to the left of the flow regime map of Fig. 58 correspond to high β (the choice for relatively slow liquid-phase reactions) whereas towards the right are low β values (a chöice for high rates of liquid-phase reactions). To achieve low β values it could be possible, for example, to operate in the spray regime in a tray column. The analogue of the turbulent or "fast" fluidization regime of gas–solids flow is the regime called turbulent bubbly flow in Fig. 58; this is the regime prevalent in air left fermentors, for example. In air left fermentors the aim is for good gas–liquid mass transfer to prevent oxygen depletion in the liquid phase. Both turbulent, or "fast", fluidization, and turbulent bubbly flow regimes are gaining in importance for similar reasons: they have superior mass transfer characteristics. A deeper appreciation of the analogies between gas–solid and gas–liquid systems will be helpful in reactor selection and could facilitate scale-up (Krishna, 1993).

In the design of the Fischer–Tropsch bubble column slurry reactor, an important consideration is the choice between the homogeneous and heterogeneous

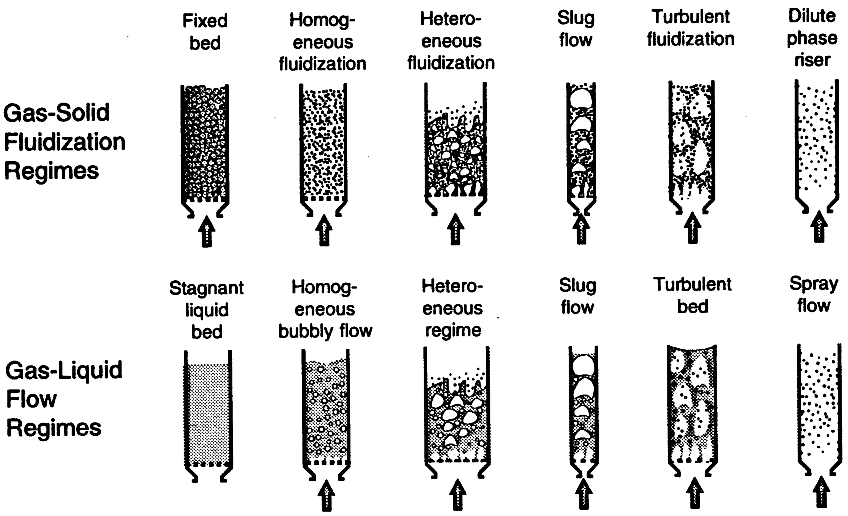


Fig. 58. Gas–solid and gas–liquid flow regimes in vertical columns with up-flow of gas.

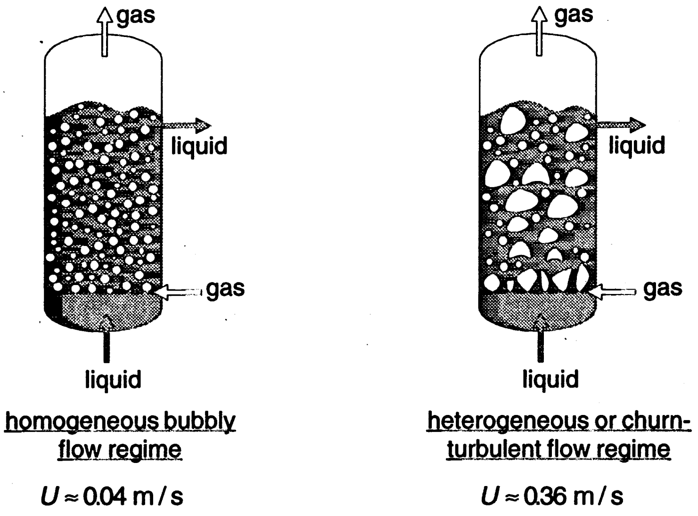


Fig. 59. Homogeneous and heterogeneous flow regimes in bubble column operation.

flow regimes; see Fig. 59. The scale-up of a bubble column slurry reactor is limited to vessels of about 6 m diameter because of mechanical considerations. Operation in the homogeneous flow regime can be realized only at a superficial gas velocity U_g below about 0.04 m s^{-1} while in the heterogeneous flow regime, U_g can be as high as say 0.36 m s^{-1}, which holds the promise of a factor of nine increase in the throughput per reactor of given diameter. The heterogeneous flow regime is therefore preferred in practice.

CASE STUDY OF OIL SHALE REACTOR SELECTION

Having discussed the various strategies for selection of a multiphase reactor, these ideas and concepts can be applied to a specific example of the oil shale reactor selection. Oil shale contains an aromatic component called kerogen, which on heating in the temperature range 400–550°C decomposes to yield oil, coke and gas. At temperatures below 400°C the reaction is extremely slow and, at temperatures exceeding about 550°C, excessive cracking of the oil vapor liberated during the reaction takes place. Burning off the coke from the spent shale in a combustor provides a source of energy for the endothermic pyrolysis reaction; see Fig. 60. There are numerous processes and reactor configurations that have been suggested for carrying out the thermal pyrolysis; these are sketched in Fig. 61, which is adapted from Levenspiel (1988). The various technologies have apparently little in common. For example, on the basis of particle size used in the processes (Strategy level I), there are: (a) large sized ($\cong$50 mm) particles, (b) medium sized ($\cong$5–10 mm) particles and (c) small sized ($<$3 mm) particles. From considerations at Strategy level II, the contacting pattern between the oil vapor (+ stripping gas) and the solid phase used in these technologies also varies widely: (1) counter-current in a-1, a-2 and c-2, (2) co-current in technologies b-1 and b-2 and

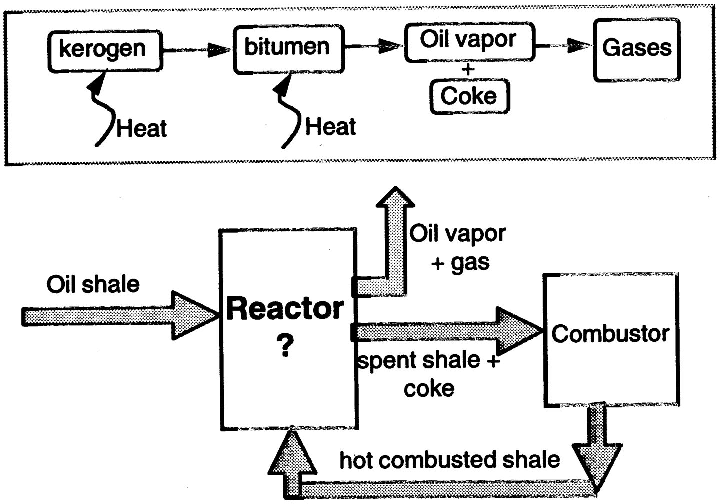


Fig. 60. The oil shale reactor selection problem. Adapted from Krishna (1994).

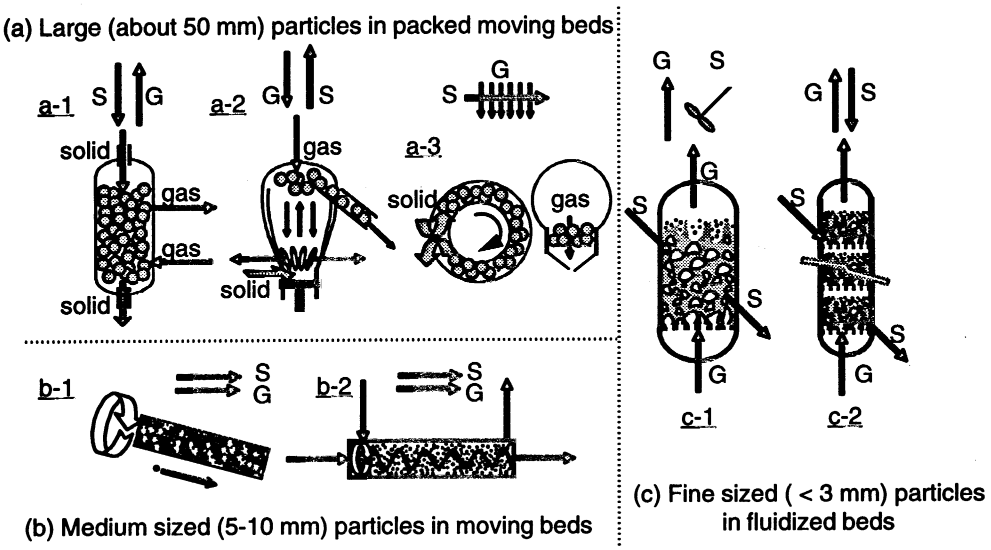


Fig. 61. The reactor choices available for the oil shale reactor. Adapted from Levenspiel (1988) and Krishna (1994).

(3) cross-current in a-3. The solids phase is more or less well mixed in the SPHER process (c-1) whereas in the other technologies there is staging (i.e. plug flow) of the solids phase. The Unocal process involves another unique technology in which the shale particles are moved upwards, counter-current to the vapors, by means of a rock pump. Analysis at Strategy level III, shows that both packed (moving) bed [Groups (a) and (b)] and fluidized operations [Group (c)] are encountered. For a reactor engineer involved in developing a shale oil recovery process the diversity of the reactor configurations shown in Fig. 61 is more than a little disconcerting.

Poll *et al.* (1987) and Krishna (1994) have followed a systems approach to selection of the "ideal" oil reactor. First, a "wish" list is set up.

- *Wish 1.* The reactor must be capable of maximum recovery of oil. Oil recovery can be maximized by making sure that high (say $\geqslant 99\%$) conversion of kerogen is obtained and that the oil vapor once produced does not suffer further cracking and degradation to light gases.

- *Wish 2.* The reactor design should allow scale-up to large scale units capable of handling say 50,000 t per day of oil shale in one processing train; this is important for economy of scale.

- *Wish 3.* In view of the large quantities of shale rock to be handled, of the order of 500 kg s^{-1}, there is need to restrict the reactor volumes in order to reduce the investment costs.

- *Wish 4.* During the grinding operation there is inevitable production of fines and the chosen reactor should be capable of handling these fines, both from economic as well as environmental considerations.

On the basis of the wish list, one can proceed to make the choices at each strategy level.

Strategy level I

For maximizing the yield of oil from kerogen (Wish 1) the particle size has to be restricted to below 2 mm; this decision is made on the basis of a careful analysis of the kinetics of oil shale production and overcracking resulting from diffusion limitation within large sized particles.

Strategy level II

Strategy level II(b). Since large throughputs have to be handled (Wish 3), conditions of plug flow of the solids has to be strictly adhered to because otherwise unacceptably large reactor volumes will be required.

Strategy level II(c) and (d). The oil vapor, once formed, should be removed from the reaction zone and should not come into further contact with hot shale particles. Co- and counter-current contacting are undesirable and the ideal contacting pattern is cross-current contacting of gas and solid. Cross-current contacting also ensures *in situ* removal of oil vapor from the reaction zone.

Strategy level III

At Strategy level I a decision has been made to use particles smaller than 2 mm. Now, during the crushing operation, fine particles (much smaller than the specified top size of 2 mm) will also be produced. The "fluidization" regime should be capable of handling the produced fines (Wish 4) and this leads to the choice of a bubbling or turbulent fluidized bed operation.

Combination of the decisions made at the various strategy levels leads to the cross-current multistage fluidized bed concept developed by Shell (Poll *et al.*, 1987; Krishna, 1994); see Fig. 62. It is interesting to note that this "ideal" concept did not correspond to any of the "known" reactor configurations shown in Fig. 61. A careful comparison of the Shell process with the existing technologies (Fig. 61) shows that none of the "ideal ingredients" chosen at each strategy level is unique. Fine particles smaller than 3 mm are used in the SPHER [Fig. 61(c-1)] and Chevron [Fig. 61(c-2)] processes. Cross-current contacting is employed by Superior Oil [Fig. 61(a-3)]. The Chevron process uses a counter-current multistage fluidized bed. However, the *combination* of these ingredients, yielding the configuration shown in Fig. 62, was considered to hold sufficient promise of improved yield and economics to justify a substantial development effort (Poll *et al.*, 1987). There were also no scale-up problems envisaged in the multicompartment fluidized bed approach; for scaling-up purposes it is sufficient to study in detail the hydrodynamics of one of the fluid bed compartments. In theory, to obtain sufficient solids-phase residence time, the number of compartments can be increased at will without running into any scale-up difficulties.

CLOSING REMARKS

In this article the use of a systematic, structured, approach to reactor selection has been advocated. The reactor selection exercise is conveniently split into three, separate, sequential decisions on the following sub-sets, or attributes:

Strategy level I.	"Catalyst" design
Strategy level II.	Reactant injection and dispersion strategy
Strategy level III.	Multiphase hydrodynamic flow regimes.

The choice of each item at the various strategy levels discussed in the text is made on the basis of a wish list, set up right at the beginning of the reactor selection exercise. In the discussions, it has been stressed that a disciplined approach may unravel novel ways of improving reactor performance; this has been illustrated by means of several examples.

The three-level strategy approach presented here has been mainly developed for application within the petroleum and petrochemical industries and, therefore, is restricted to continuous "steady-state" processing

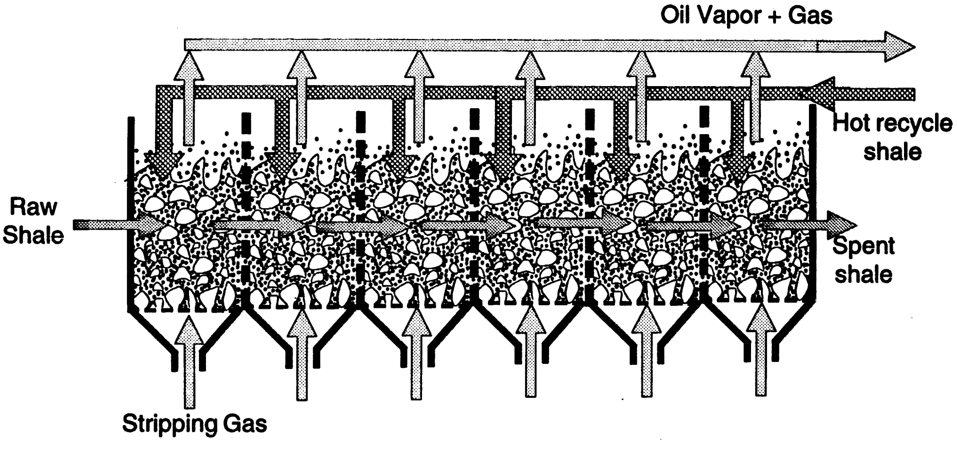


Fig. 62. The cross-current multistage fluidized bed reactor concept developed by Shell (Poll *et al.*, 1987). Adapted from Krishna (1994).

on a large scale. It is worthwhile examining the extension of these concepts to unsteady-state processing and batch operations in greater depth. Also, there may be other ways to structure the reactor selection problem to suit one's own work environment and technology culture.

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NOTATION

a	interfacial area per unit reactor volume, m^{-1}
d_p	particle diameter, m
D_{eff}	effective diffusivity within catalyst particle, $m^2 s^{-1}$
D_l	liquid-phase diffusivity, $m^2 s^{-1}$
$D_{relative}$	relative value of diffusivity inside zeolite
E	enhancement factor for gas–liquid reaction
F	effectiveness factor for storage of metals deposits in the pore volume of the catalyst
Ha	Hatta number $Ha \equiv \frac{\sqrt{k_1 D_l}}{k_l}$
k_g	gas-phase mass transfer coefficient, $m\,s^{-1}$
k_1	pseudo-first-order reaction rate constant for homogeneous liquid-phase reaction, s^{-1}
k_l	liquid-phase mass transfer coefficient, $m\,s^{-1}$
k_m	pseudo-first-order reaction rate constant for catalytic reaction, defined per kg of catalyst, $m^3\,kg^{-1}\,s^{-1}$
L	characteristic length of particle, m
PV	pore volume, ml
R	gas constant, 8.314 $J\,mol^{-1}\,K^{-1}$
SA	external surface area of particle, m^2
T	temperature, K
V	volume of particle, m^3

Greek letters

β	ratio of liquid-phase volume to diffusion-layer volume $\beta \equiv \frac{\varepsilon_l}{\delta_l a}$
δ_l	thickness of diffusion layer of liquid phase $\delta_l \equiv \frac{D_l}{k_l}$, m
ε_l	fractional hold-up of liquid phase
ε_p	particle hold-up
η	effectiveness factor of catalyst particle
ρ_p	particle density, $kg\,m^{-3}$
τ	residence time, s
$\phi^{g}{}_{en}$	generalized Thiele modulus $\delta_l \equiv \frac{V}{SA}\sqrt{\frac{k_m \rho_p}{D_{eff}}}$

Subscripts

eff	effective parameter
g	referring to gas phase
gen	generalized parameter
l	referring to liquid phase
L1, L2	referring to the two phases in liquid–liquid systems
m	referring to the main (desired) reaction
p	referring to particle; also referring to the poisoning reaction

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