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Evolution patterns and family relations in G–S reactors

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Abstract

Reactor selection strategies for gas–solid (G–S) heterogeneously catalysed processes can be based on the requirements of the desired process and the properties of the reactions and catalysts involved. Ultimately a reactor selection will nearly always be grounded on existing or emerging reactor types slightly modified for adaptation to the specific chemical process. This procedure results in radiation of different reactor modifications from the archetypes towards niche applications. It is shown that this process has a lot of resemblance with the evolution process of animal species. The G–S heterogeneous catalytic reactors can be classified into three or four families. They are presented as adaptations from only three archetypes: packed bed, fluid bed and barrier wall.

The properties of these reactors and their family members are discussed. Examples are given of a few relatively new variants and of competition of very different reactors for the same application niche. The classification system can be used as a means for the creation of new reactors and if extended with a database or knowledge system it can facilitate reactor selection. Similar classifications can be set-up for other types of chemical reactors like G–L and G–L–S reactors.

Keywords: Gas–solid reactors; Reactor selection; Catalytic reactions

1. Introduction

The selection of an optimal reactor for a particular process duty may be a difficult task. If a new process is concerned often the requested information, e.g. on chemical kinetics is not yet available with sufficient accuracy as many process development items like catalyst modification and shaping are studied simultaneously to reduce the time to the market of the new product.

Once a reactor has been provisionally chosen and process development is started based on a particular reactor design it is often difficult to change to a radically different type of reactor in a later stage. There are at least two reasons for this. First in view of the high (financial) risks involved in process development it should be demonstrated beyond reasonable doubt that results obtained in one particular reactor can be translated to another type. Another reason is that a basic reactor type can be modified or "stretched up" to adapt to the new demands derived from new insights.

Also for well-known processes and their reactor technology taking into account all the experiences built up over years, it may be quite difficult to change the reactor type. If it becomes evident that another design will give "killing" advantages it is often considered preferable to obtain a licence for the other technology and get access to the experience gained elsewhere.

Especially for a new process it requires a lot of effort in the initial stage to avoid the trap of getting caught in a sub-optimal reactor type. Several strategies have been developed to this end. Villermaux [1] defined the "royal" way to get to an optimal process and reactor selection. This would involve several sequential steps (study of the reaction kinetics and transport limitations in a laboratory reactor, preliminary reactor choice, reactor modelling, etc.) and a few iterations. Krishna and Sie [2] proposed a systematic approach of finding an ideal reactor configuration for a particular process by considering three strategy levels:

(1) "catalyst" design;
(2) injection and dispersion strategy;
(3) choice of hydrodynamic flow regime.

On top of these considerations practical reactor solutions should be confronted with the process "musts" (operability in desired region of temperature (T), pressure (P), residence time (τ), safety, environment and scale up) and "wants" (conversion, selectivity, easy operability, lowest capital and operation costs) [2]. This procedure is close to what most experienced process developers would consider the ideal case but just as for the "royal" way it needs a lot of information

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often not available at the critical stage where management would request a preliminary proof of the process principle.

It has been argued, e.g. by Froment and Bischoff [3] that a reactor choice would have to be made as early as possible in the process development. While this is highly desirable it is also unlikely that this can be done. It would, therefore, be preferable that the first proof of the principle of the reactor is carried out in a laboratory device that still can reflect large-scale behaviour of a broad class of reactors. For multiphase catalytic reactors this seems possible as most reactors for a given phase combination can be considered as being modifications of only two to six basic types. With two or three modifications of a bench-scale unit the options for a wide selection of reactors remain open. The purpose of the present contribution is to facilitate selection of the most suitable reactor type for a given process. Due to a great variety of the entire chemical reactor family the different family relations and evolutionary pattern of reactors for only gas–solid (G–S) heterogeneously catalysed reactions will be discussed here. In the future, we will expand this approach to other types of reactors and to the design of bench-scale test reactors.

Human ingenuity produced a wide range of chemical reactors and this even holds for the restricted class discussed here: reactors for G–S heterogeneous catalytic reactions. Generally the process of invention starts with an existing reactor (concept) and realising that the system is not optimal with respect to one of the technical features like conversion, selectivity, control of temperature, primary energy consumption, safety, construction details, maintenance, etc. often leading to economical disadvantages. Then by careful analysis or by an intuitive jump a creative spark may lead to a new solution. In patent literature or publications, the advantages of the new system will be broadly discussed, especially in relation to the failure of the existing solutions. The often-restricted niche for the new solution is generally not described in so much detail and the same holds for the disadvantages of the new concept. A designer of a new reactor is, however, equally interested to know the disadvantages of the system in his selection process. In fact the disadvantages of the new system may reflect a hidden and not well-realised advantage of the current technology.

The whole process of reactor development shows a pattern quite similar to that of the evolution of animal species.

Apparently after a wild period in the history of life on earth in the pre-Cambrian and early Cambrian period only a few basic construction plans for animals survived of which the vertebrates is one. If we take the mammals as an example the archetype may be an insect eating small mammal which remained present in its essential form but also gave rise to a wide radiation of species which were able to occupy niches of life in the environment, often in competition with species with a completely different root.

Fig. 1 shows a simplified scheme of the evolution of mammals. To stress the analogy with the invention of new reactors the direction of evolution is translated as a desire

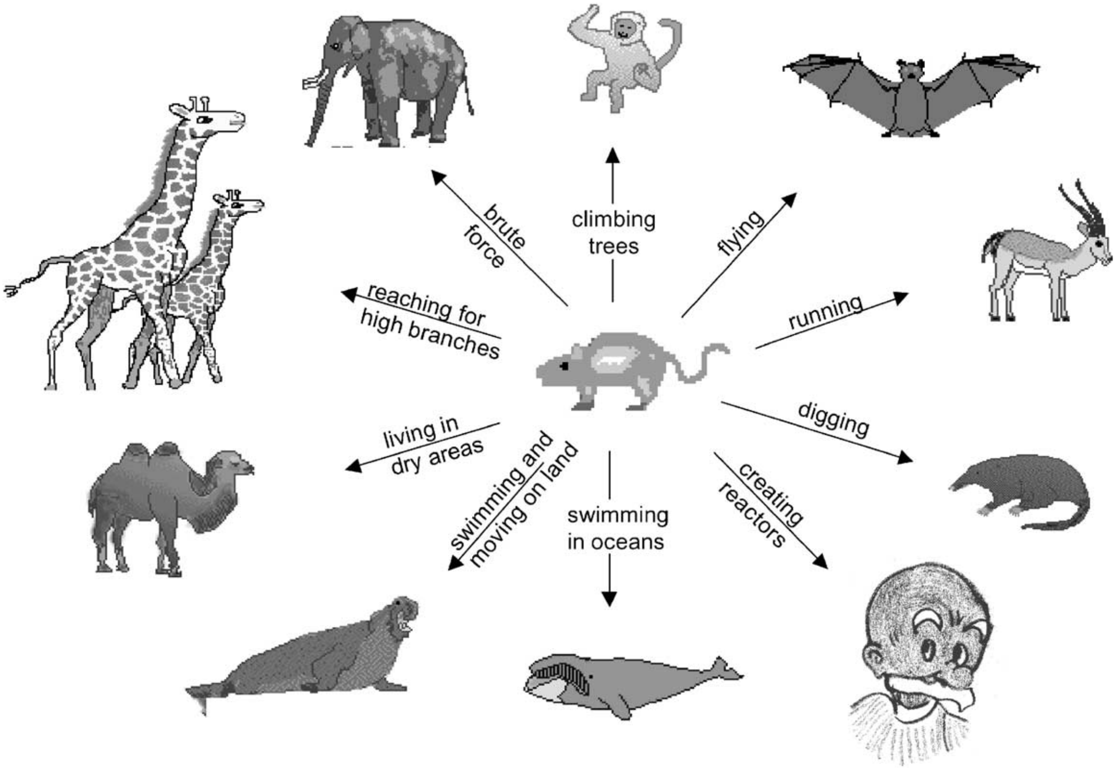

Fig. 1. Radiation of mammal species from the archetype. Different mammal types evolved to fit into the various niches for life (all animals pictures were copied with permission from the http://www.enchnatedlearning.com).

to create certain functions. This should not be taken literally of course. Competition in all areas is fierce. For example, a bat has to compete with birds and flying insects, whales with fishes, etc. It is also clear that the evolutionary change does not constitute a general improvement of the mammal. The change has a price and some of the desired general properties of a mammal are reduced or even lost. The unmodified or hardly modified archetype mammal remained in number and other measures of success a clear winner This will also be shown to be the case for the archetypes of the G–S reactors.

2. Gas–solid reactors for heterogeneously catalysed reactions

In the G–S reactor gas phase reactants are brought into contact with a catalyst at the desired conditions of pressure, temperature, etc. Normally the catalyst should also be separated again from the products and in most cases this is considered to be an integrated function of the reactor. As for gas phase reactions nearly always continuous operation is aimed for we will only consider this type of operation but including periodic operation, flow reversal, etc.

The catalyst is usually designed to be convenient for the selected reactor. It should be realised, however, that the reactor selection in its turn is strongly influenced by the nature of the chemical system involved and the available catalyst, e.g. via the system of selection strategies on the three levels of Krishna and Sie [2]. Active catalytic material can often be deposited on an inert supporting, usually porous, carrier allowing for a wide variety in internal surface area, size and shape of the catalyst thus creating freedom for the designer. In some reactors, catalyst and reactor form a single entity like the monolith reactors.

Another important function of a reactor is to maintain a desired environment (P, T, etc.) for the reaction in a controlled fashion. This involves heating or cooling by means of conventional heat exchange and intermediate injection of cold/hot feed or inert streams or in rare cases other types of energy exchange like ultraviolet or other radiation, ultra sound, etc.

If these aspects are considered to be supplemental properties the G–S catalytic reactors can be described by only four basic types (Fig. 2) or, if the moving bed is not considered to be different from a packed bed, only three types: the "packed bed", the "fluid bed", and the type we call the "barrier wall".

In the "packed bed", the catalyst is fixed in space and the reacting gases are passing via bulk flow through a macrostructure of the catalyst, which may be random packing or a special geometry. In some cases, the catalyst requires regeneration or removal from the reactor. A moving bed, often in gravity or bunker flow conditions, may then be an option depending on the time scale (Fig. 3).

If the catalyst is moving freely inside the reactor under influence of the fluid stream, the system is called a "fluid bed". In a strict sense, fluidisation normally refers to the situation that the catalyst is supported by the flowing gas phase and the entire bed behaves like a liquid but we will also include other actions of (self) fluidisation like vibration, stirring, etc. to make the solids move.

The third family, the "barrier wall reactor" is relatively new. It includes a few types of the membrane reactor but not all types. The barrier that incorporates a catalyst keeps two gas spaces separated from each other by a reactive layer or zone. A membrane tube with a packed bed of catalyst inside is not a barrier reactor in this classification system but a packed bed with mass exchange, just like a wall-cooled or -heated tubular packed bed reactor is still a packed bed reactor. Up to now, the barrier reactor family is still in its infancy but in the process of intensification, miniaturisation and structuring with their related fabrication methods, it may become important in the future.

All G–S catalytic reactors found in the literature so far can be related to these three families. Combination of the families is in principle also possible as shown in Fig. 4. A fluid bed selected for its heat managing properties is put in series with a packed bed selected for its plug flow and

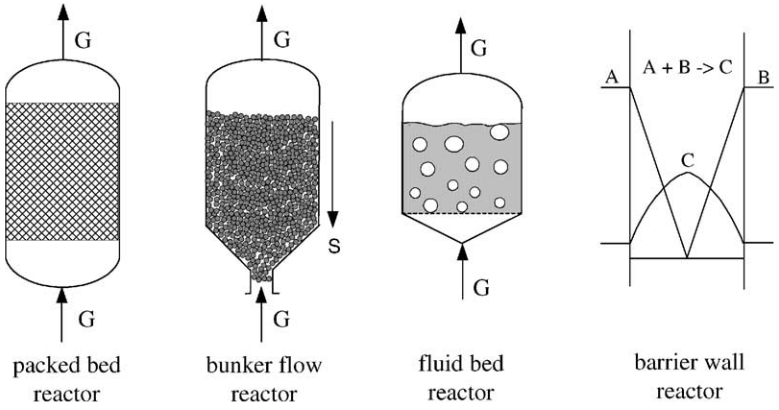

Fig. 2. The four basic types of heterogeneously catalysed G–S reactors. If bunker flow is considered to be a packed bed variation only three archetypes remain of which all G–S catalytic reactors can be derived.

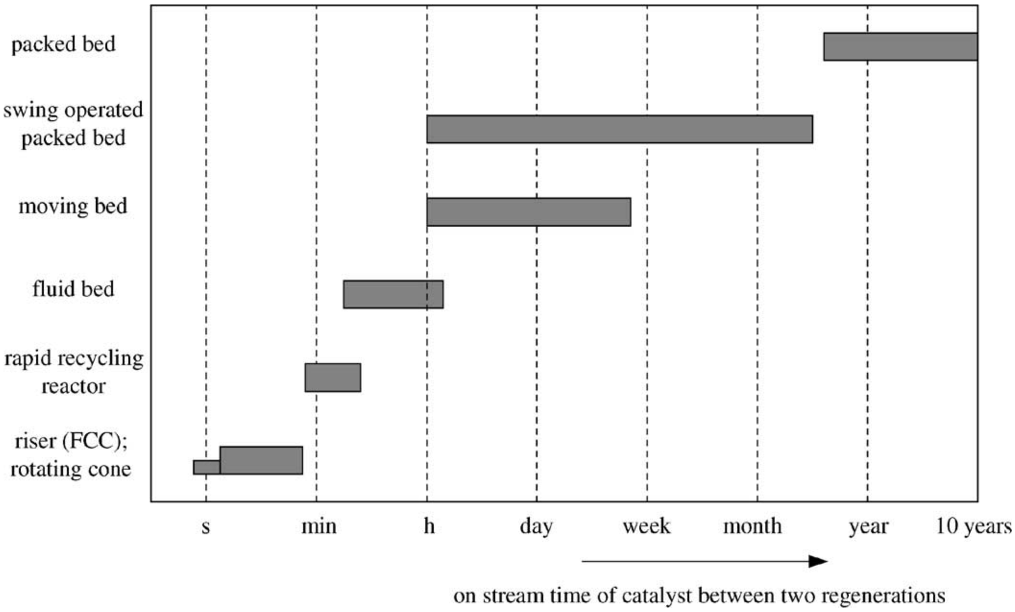

Fig. 3. Reactor type preferred as a function of on stream time of the catalyst between two regenerations.

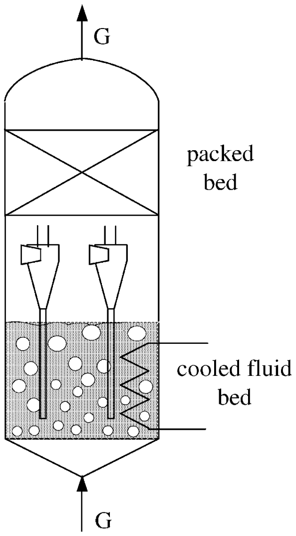

Fig. 4. Example of a combination of reactor types within one set-up. In the cooled fluid bed most of the heat is generated while the packed bed ensures high conversion.

excellent contacting allowing to achieve high conversions. Possible practical problems like plugging of the packed bed remain to be solved.

3. Packed bed family

The packed bed is probably the oldest type and related to the genesis of heterogeneous catalysis itself in the early 1800s. The packed bed family is displayed in Fig. 5. In the centre, the archetype is given. It is an assembly of catalyst particles, randomly arranged, which are held firmly in position within a reactor tube. The catalyst varies in size from approximately 1–10 mm. A contact is achieved between the catalyst and the reactant fluid as the later flows along the tube (axially) through the voids between the catalyst particles. In Table 1, several properties of this basic type are given both those that are generally positive and those mostly negative. A more detailed and complete list like given in Table 1, would be of great importance to a designer and for the future a database should be made available, preferably with easily accessible typical data or data generation programs.

A number of configurations have evolved from the basic type to fit the requirements of specific chemical reactions. The different directions within the family are identified by specific desires, dissatisfaction with normal parameter values or extreme conditions.

For very fast reactions, like oxidative dehydrogenation of methanol to formaldehyde over silver catalyst a short bed or pancake adiabatic reactor is used. The thickness of the catalyst layer in the formaldehyde synthesis process is about 20–30 mm and the residence times are very short (<10 ms) [4]. This process was developed by BASF about 100 years ago. An extreme case of very fast reactions is ammonia oxidation in nitric acid production. The packed bed in the reactors (they are usually called in practice: the burners) takes the shape of a few gauze layers (Fig. 5, number 2) [5].

3.1. Reaction control via heat and/or mass exchange

The requirements to handle heat addition/removal for an optimal reaction pathway may influence strongly the ultimate choice of the catalytic reactor. This may also be

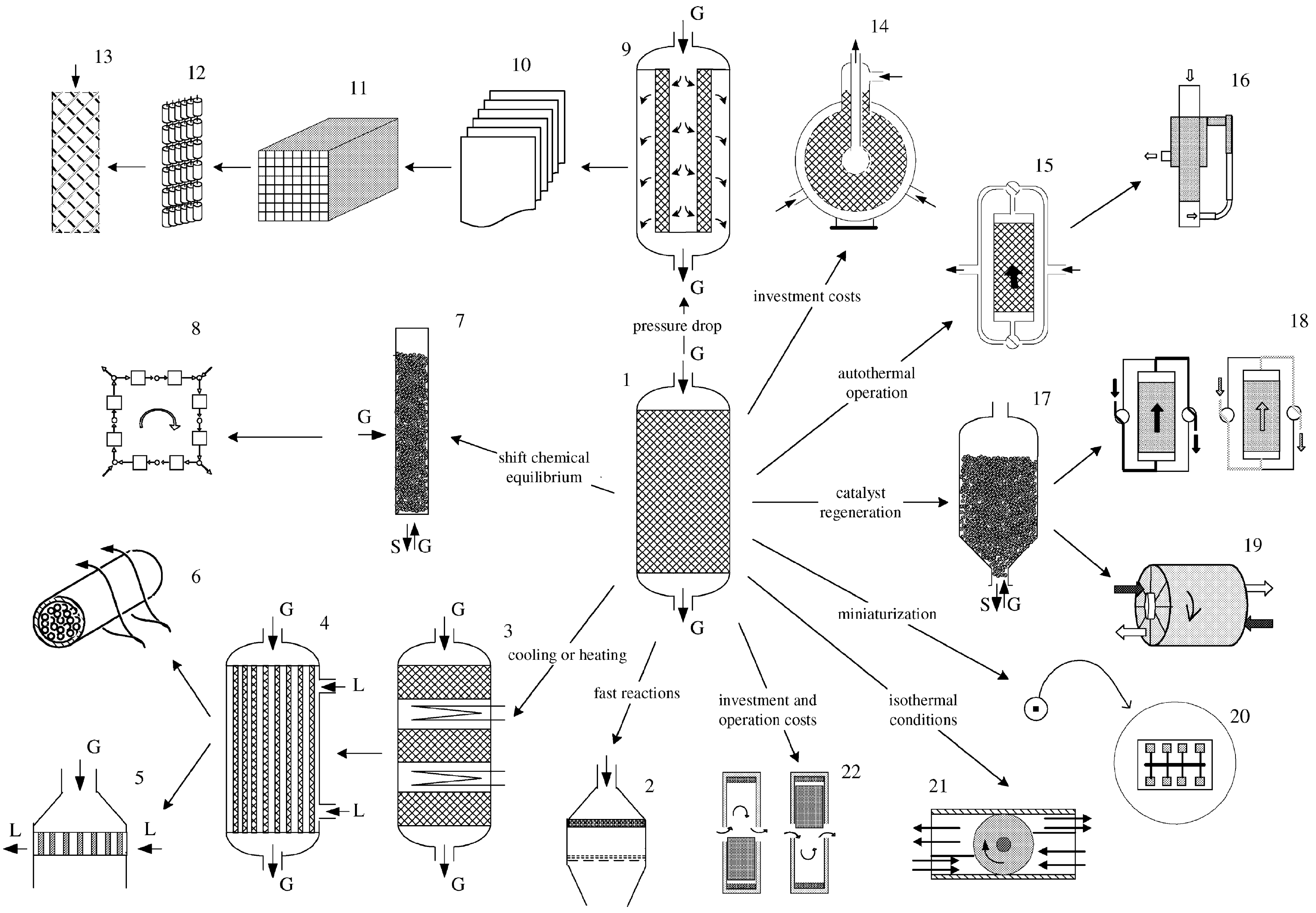

Fig. 5. The packed bed family: (1) adiabatic bed; (2) gauze layers; (3) adiabatic with intermediate cooling; (4) multitubular; (5) short bed with cooling; (6) annular bed; (7) continuous chromathographic; (8) simulated moving bed; (9) radial flow; (10) parallel passage; (11) monolith; (12) bead string; (13) polylith; (14) spherical; (15) reverse flow; (16) circulation loop; (17) moving bed; (18) coupling of endo- and exothermic reactions; (17) simulated moving bed; (19) rotating fixed bed; (20) microreactor; (21) rotating disks; (22) pulsed compression.

Table 1
Properties of the archetype packed bed

Properties generally positive	Properties generally negative
1. Very simple design, robust and cheap	1. Pressure drop is considerable
2. Ease of operation	2. Poor lateral heat transfer inside the bed: no temperature control, not suitable for reactions with large heat effects and high temperature sensitivity
3. Large capacity	3. Easily plugged by fine particles or by-product disposal
4. Relatively good heat and mass transfer between gas and particles	4. Mechanically sufficiently strong catalyst is needed
5. Mass and heat transfer relations are well established	5. Homogeneous filling of reactor can be a problem
6. Gaseous reactants in almost plug flow	6. Thermal stress of reactor and catalyst
7. Catalyst replacement relatively easy	7. Start up/shut down procedure can be complex (for instance, mechanical stress due to high temperature gradients)
8. Mild catalyst attrition if any	8. High rate of reprocessing of the catalyst is difficult
9. No need for separating and recycling the catalyst	
10. Catalyst zones (layers) are possible	
11. Relatively large particle size, which is relatively easy to make	
12. Easy to scale up from lab experiments	
13. High heat capacity per unit volume stabilising the operation	
14. High concentration of catalyst and large catalytic surface area per unit reactor volume	
15. Easy to make a pilot plant	

valid for mass exchange. A packed bed membrane reactor (mass exchange) is thus equivalent to a cooled tubular reactor (heat exchange) and storage of heat is equivalent to absorption/adsorption of components from the gas phase. A simple but effective method for temperature control is intermediate cooling or heating between adiabatic beds by means of heat exchangers (Fig. 5, number 3). The mass transfer equivalent is the intermediate supply or removal of (one of) the components by membranes [6], solvents [7,8] or other means aiming for improved selectivity or equilibrium shift. Addition of gas phase components is relatively easy. Sometimes a cool reactant is injected between the beds for cooling (so called cold shot cooling). An example is the ICI process for methanol [9]. All these methods are supplements to the systems of the adiabatic packed bed reactor.

With very exothermic or endothermic reactions, the number of beds would become too large to limit the temperature change per bed. In this case, the wall of the bed is used as a heat exchanging area and the cooled (or heated) tubular reactor is created which usually takes the shape of a multitubular reactor (the mass equivalent is packed beds enclosed within membrane tubes). In this wall cooled reactor, relatively narrow tubes of 20–100 mm are used and the main heat flow is perpendicular to the gas flow. This is a well-established technology both for exothermal reactions like ethylene oxide production or endothermic reactions like methane steam reforming. The total number of tubes in the reactor can reach as many as 20,000–30,000. In a well-designed reactor all the tubes are in identical conditions. This means that the reactor can be studied in process development by creating a single tube set-up. Apart from the multitubular reactors shown in Fig. 5 (number 4) other multitubular reactors are sometimes used in which the catalyst bed is arranged around the tubes and the heat transfer medium flows through the tubes [10,11].

Special variants are the short bed or pancake cooled multitubular reactors for rapid reactions with the product selectivity highly sensitive towards the temperature (Fig. 5, number 5). BASF tested a version of a pancake reactor for production of aldehydes via oxidative dehydrogenation of unsaturated alcohols over silver catalyst and using molten salt as a coolant [4]. An aldehyde selectivity of 90% has been demonstrated, compared to 60% obtained using the short bed without cooling. Currently the short bed multitubular reactor is in BASF service [4].

An extreme case of a wall-cooled reactor is the cooled catalytic wall reactor, where the catalyst is deposed or directly connected to the wall (Fig. 6) [12,13]. The latter set-up is meant to increase the cooling intensity. It could be considered as a combination of 10 or 11 and 4. However, pressure drop reduction is usually not the drive towards catalytic wall heat exchange tube reactors. In order to improve the transport characteristics of such reactors the annular bed reactor has been proposed [14]. This reactor has the form of a bundle heat exchanger. The tubes of the reactor are packed with small size catalyst in the annular space between the wall and the central core of inert spheres (Fig. 5, number 6). Reactant gas flows axially through the inert core and is radially dispersed to the catalytic bed where the reaction

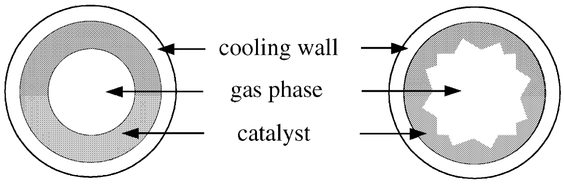

Fig. 6. Cooled catalytic wall reactor. The catalyst layer may have a more complex geometry to improve G–S contact or may be deposited on the outside of the tube.

occurs. The reactor showed excellent thermal behaviour in the hydrogenation of benzene [15].

A special mass transfer equivalent of the continuous cooling or heating is the G–S–S trickle flow reactor (GSSTFR) elaborated by Westerterp and co-workers [16–18] for equilibrium limited reactions. In this reactor, the reaction product is removed from reaction zone by means of counter-current stream of a selective adsorbent. An enhanced conversion for equilibrium limited reactions can also be achieved by combining a chemical reaction together with chromatographic separation [19]. The easiest way to realise a continuous process is a counter-current flow of solid and fluid phase with the feed supply in the middle of a column (Fig. 5, number 7) [20]. Abrasion of the solid adsorbent catalyst and axial mixing are disadvantages. The troublesome movement of the solid phase is avoided in simulated moving bed reactors (Fig. 5, number 8) where the solid does not move. The counter-current flow of the solid phase is simulated by periodically switching the in- and outlets [21,22]. As a result the axial mixing is also partially reduced.

3.2. Pressure drop

Pressure drop (ΔP) with the related energy consumption (W) is an important cost item ($W = \Phi_v \Delta P$) especially when a large fraction of the effluent gases is recycled. At a given catalyst and required space velocity (Φ_v), minimisation of ΔP would lead to a fixed bed of large diameter and low height (pancake reactor). It is then more practical to fold the packed bed into a radial flow shape and use an annular catalyst bed with radial flow (Fig. 5, number 9). This reactor type is particularly suitable if large amounts of catalyst are involved and where change in moles is large. For the radial flow reactor, gas distribution and providing a homogeneous packed catalyst are more difficult than for the basic type. Nevertheless these type reactors have operated very successfully in many applications [23–25]. Shell has developed a reactor with lateral flow for selective catalytic reduction of NO_x from flue gas—the DeNOx process [26].

A further step to lower pressure drop is the use of structured catalysts, such as the parallel passage reactor (Fig. 5, number 10). Here, the catalyst is put into plates or gauze envelopes and gas is passing between the plates. Gas contacting with the catalyst relies on transversal mass transfer to and into the catalyst “plates”. In the late 1960s, early 1970s, Shell developed a combined desulphurisation and DeNOx process that operated in this version [27]. Later the first commercial reactor was used for DeNOxing only, which simplified the operation, as the SO_2 removal was an acceptor process requiring regenerative cycles.

The next logical evolution step is toward the monolith reactor with parallel channels (Fig. 5, number 11). In addition to low pressure drop, monoliths have very high specific surface area and the external mass and heat transfer in the monolith channels is much more uniform than in random packings. This was a big success in selective catalytic reduction of NO_x in DeNOx reactors in power stations, three-way catalyst in cars, ozone destruction in aeroplanes, etc. [28]. In terms of numbers, this may be the most successful variation of the packed bed as it has been installed in millions of motorcars exhaust lines. Many more applications also for multiphase reactors can be expected in the future [29]. Channel dimension and shape, porosity of the walls, wall materials and different channels can have different functions (cooling, walls as membranes, etc.) and many more options become available. Entire symposia are devoted to this subject [30].

The low flow resistances, small tendency for dust collection, almost no attrition are prominent advantages. The initial flow distribution guidance, thermal cracks in the monolith as a whole, incomplete sealing between monolith and reactor tubes are problems, which can, however, be solved in practice.

Although the flow is normally laminar in monoliths because of the small channel sizes this does not necessarily lead to low mass transfer rates or high axial (Taylor) dispersion due to the small channel size. Already, Le Goff showed that the laminar regime can be an interesting regime for G–S contacting in the optimisation of momentum transport for mass transport (the Le Goff number, see [31]).

The interconnectivity of the flow channels is lost in the parallel channel monolith in comparison to the original packed bed and new evolution lines were opened to restore this highly desired property. Both the problem of initial distribution, mass and heat transport and mixing profit from interconnectivity. Bead string (in fact an expanded stacked catalyst bed) [32] and polylith reactors (Fig. 5, numbers 12 and 13, respectively) [33] and reactors with foam type monoliths, crossed, corrugated plate packets [10] and geometrical mixing elements covered with catalyst and similar in design to those used in distillation and adsorption columns and/or static mixers, etc. are developed to this end. The more complex fabrication techniques required are a disadvantage in comparison with the basic packed bed type while also the easy replacement of the catalyst remains a tough competition element.

3.3. High pressure, high capacity reactors: investment

The packed bed may have different shapes and be placed in different positions. Normally it is cylindrical due to manufacturing reasons, but especially for structured packings other vessel geometries may be chosen. Even for random packing particularly for very high pressures a spherical shape could have advantages related to the weight of the structure and the related investment costs (Fig. 5, number 14) [34].

Hartig and Keil [34] argued that the required wall thickness of the spherical high-pressure vessel could be half of that of a cylindrical vessel leading to reduced costs of material, erection and bottom structures. Moreover, the radial type of flow with associated lower pressure drop gives considerable savings in the recycle costs.

The M.W. Kellogg Company produced recently spherical reactors in a methanol production plant of 2500 t per day in Chile (Punta Arenas) [35]. As in the radial flow cylindrical reactor care should be taken to allow for the catalyst bed shrinking in these more complex geometries during start-up as otherwise easily shortcut paths devoid of catalyst could be created. In fact the "simple" accommodation of bed volume change in a regular bed is a hidden advantage of the simple packed bed.

3.4. Autothermal operation

If the heat of reaction is utilised to heat the reactor feed and neither addition nor removal of heat occurs during the reactor operation, this is referred to as autothermal operation. Autothermal operations can of course be realised by external heat exchange between reactants and products. If these heat exchangers are of a regenerative type, periodic switching of the heat exchangers changing their role from coolers to heaters can be practised. If the flow direction through the heat exchangers is at the same time reversed a very popular set-up is obtained which only requires switching valves at the low temperature ends simplifying the set-up (Fig. 7). These types of reactors are used for removal of traces of organics in air, operating at relatively high temperature with only low values of the adiabatic temperature rise.

The next step in evolution is to use the fore and aft parts of the catalytic bed itself for regenerative heat exchange. In this way, the reverse flow reactor is obtained (Fig. 5, number 15) [36]. Full-scale commercial plants like sulphuric acid plants have been based on this principle [37] and theoretical analysis of this operation is available [38–40].

Applications are slowly expanding. The flow reversal principle can also be used for storage of mass. BASF considered the catalytic reduction of NO_x with NH_3. The emission of NH_3 should be avoided at high conversions of NO_x; this can be realised by temporary storage of the excess of NH_3 by adsorption and flow reversal [41].

In a fixed bed reactor with periodic flow reversal an exothermic reaction zone moves forward and backward due to switching of the flow direction. In contrast to that periodically forced process, Gilles and co-workers presented a novel reactor concept, the so-called circulating loop reactor (Fig. 5, number 16) [42], which is operated in an autonomous periodic mode and does not need any periodic forcing for proper operation. Heat exchange in the reactor is arranged so that the reaction zone moves slowly downstream and, when leaving the reactor, ignites a new reaction zone in the cold feed stream entering the reactor.

3.5. Catalyst regeneration

In many cases regeneration of catalyst is required, such as coke burn off. This may lead to moving beds or to periodic operation (Fig. 5, numbers 17 and 18, respectively). An example is the production of olefins by dehydrogenation of alkanes [43]. As the catalyst regeneration is exothermic and the main reaction is strongly endothermic it is interesting to couple the heat released by the regeneration of the catalyst to the heat consumption by the main reaction. If necessary,

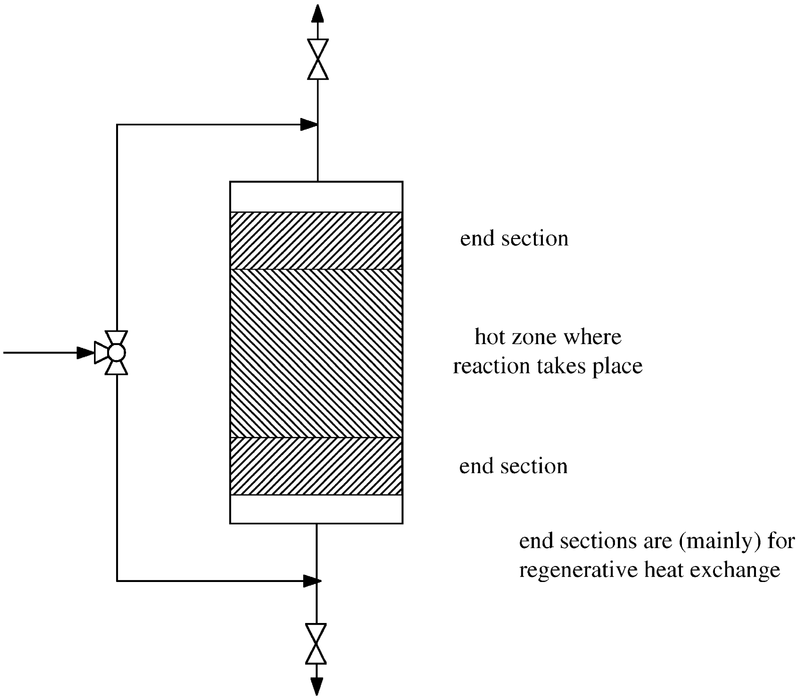

Fig. 7. Reverse flow reactor. During down flow the reactants are heated up by heat stored in the upper section produced by the previous up flow cycle. The heat released by the reaction is stored also in the lower section. After some time the flow is reversed again to up flow.

the heat requirement can be balanced by co-combustion of another reactant like methane. This can be done in the simple adiabatic packed bed in successive cycles if necessary with intermediate purging (Fig. 5, number 18). Combinations with flow reversal schemes are possible. Kolios et al. [44] have given a good overview of these possibilities. van Sint Annaland et al. [45] investigated a rapid cycling system to intensify this operation. Other systems for coupling endo- and exothermic reaction via direct heat exchange through inner walls have been proposed [44]. Problem areas are complexity and control of the cycles.

Simulated moving beds where feed ports are switching (Fig. 5, number 8) and the catalyst remains in place could also be used as reactors with catalyst regeneration.

A particular form of the reactors with catalyst regeneration is a slowly rotating packed bed, moving sections along feed points (Fig. 5, number 19) [10,46]. The connection of the streams to the rotating bed sections is a difficult mechanical problem. Moulijn and co-workers [47] tried momentum of the inlet jets to provide separation between streams. In the so-called heat wheel used for heat exchange between air and flue gas in a power station, some leakage can be tolerated and slowly revolving exchangers are applied on a large scale. Also chemical reactions can be used in these structures, such as DeNOxing [48,49]. The packed bed reactor concept is really stretched in these examples and tends to solutions typical for fluid beds as solids are moved.

3.6. Miniaturisation

Fig. 5 also contains the development to micro-reactors (number 20). The term “microreactor” means now not a small laboratory reactor but designates chemical systems fabricated with techniques originally developed for electronic circuits [50]. In fact many microreactors keep their catalyst fixed in space and can be classified as belonging to the fixed bed family or the catalytic barrier reactors. The microreactors form a rapidly expanding area using techniques from micro electronic chips production but for our reactor family approach an important feature of microreactors is the possibility to bring the cooling closer to the active site and the ability to control reaction temperature and contact time. A nice example of this effect on selectivity of a dehydrogenation reaction of an alcohol has been given by Wörz et al. [51].

3.7. Exotic reactors

Fig. 5 contains two more exotic reactors. One has a thin fixed bed or catalyst layer on both ends of a cylinder (Fig. 5, number 22) in which a free piston driven, e.g. by the reaction itself reciprocates with very high frequency (up to 400 Hz) and creates the favourable reaction conditions of high temperature and pressure [52].

In contrast to the engine reactor [53] no piston rod, sealing rings and lubricants are used. As a result, the application area could significantly be expanded. The free piston reactor is optimal in terms of energy efficiency—only compensation of the energy losses due to friction and gas leakage is required to maintain the piston oscillations. The reactor comprises the entire (or almost entire) processing train and has very high space velocities (millions/h).

The other one (number 21) is based on an existing heat exchanger [54] with several disks on an axis. The disks rotate with a high speed of 2000–4000 rpm and pump two feed streams. Heat exchange between the two streams occurs via the disks. Attractive features of this device are high G–S heat and mass transfer rates due to the flow components transverse to surface of the disks and almost no mixing between counter-current streams. If coated with a catalyst the spinning disks can also catalyse G–S reactions. A modification could be used for, e.g. catalytic partial oxidation of methane where highly exothermic combustion reactions are followed by an endothermic reforming reaction. In a packed bed or monolith, there is a danger of too high peak temperatures at the inlet and the pre-mixing of methane with oxygen could potentially create an unsafe situation. In the catalytically active rotating disk, temperature peaks could be smoothed out due to high rotation speed and pre-mixing could possibly be done between the fast rotating disks by careful positioning of inlet ports. This reactor has never been tried out before not even on a lab scale and is only an idea.

4. Fluid bed family

An overview of the fluid bed family is given in Fig. 8. The first time a fluid bed was introduced on an industrial scale was the Winkler coal gasifier in 1926 [55]. This is not yet a catalytic reactor, but during the Second World War, Exxon developed the fluid catalytic cracker at Baton Rouge in a courageous process development induced by the urgent need for gasoline. In fact a set of reactors had to be invented with the complete catalyst circulation system between the reactors [56]. After the war a lot of chemical processes were developed in which a fluidised catalyst bed was used as a reactor, many were successful (such as for acrylonitrile, vinyl chloride, phthalic anhydride and polyethylene), others were clear disasters (early Fischer–Tropsch) due to the fact that the nature of the G–S contacting pattern was not well understood. Especially the bubble formation, growth and mass transfer with dense phase has subsequently been a focal area for research of many decades and a rich source of Ph.D. projects. Even today, these phenomena are not yet completely understood. This situation has been well documented [55,57–59] and there is no need to repeat this here. No need to repeat here also different flow regimes which are well described in several handbooks [55]. The classical fluid bed (Fig. 8, number 1), a dense bubbling fluid bed of relatively fine

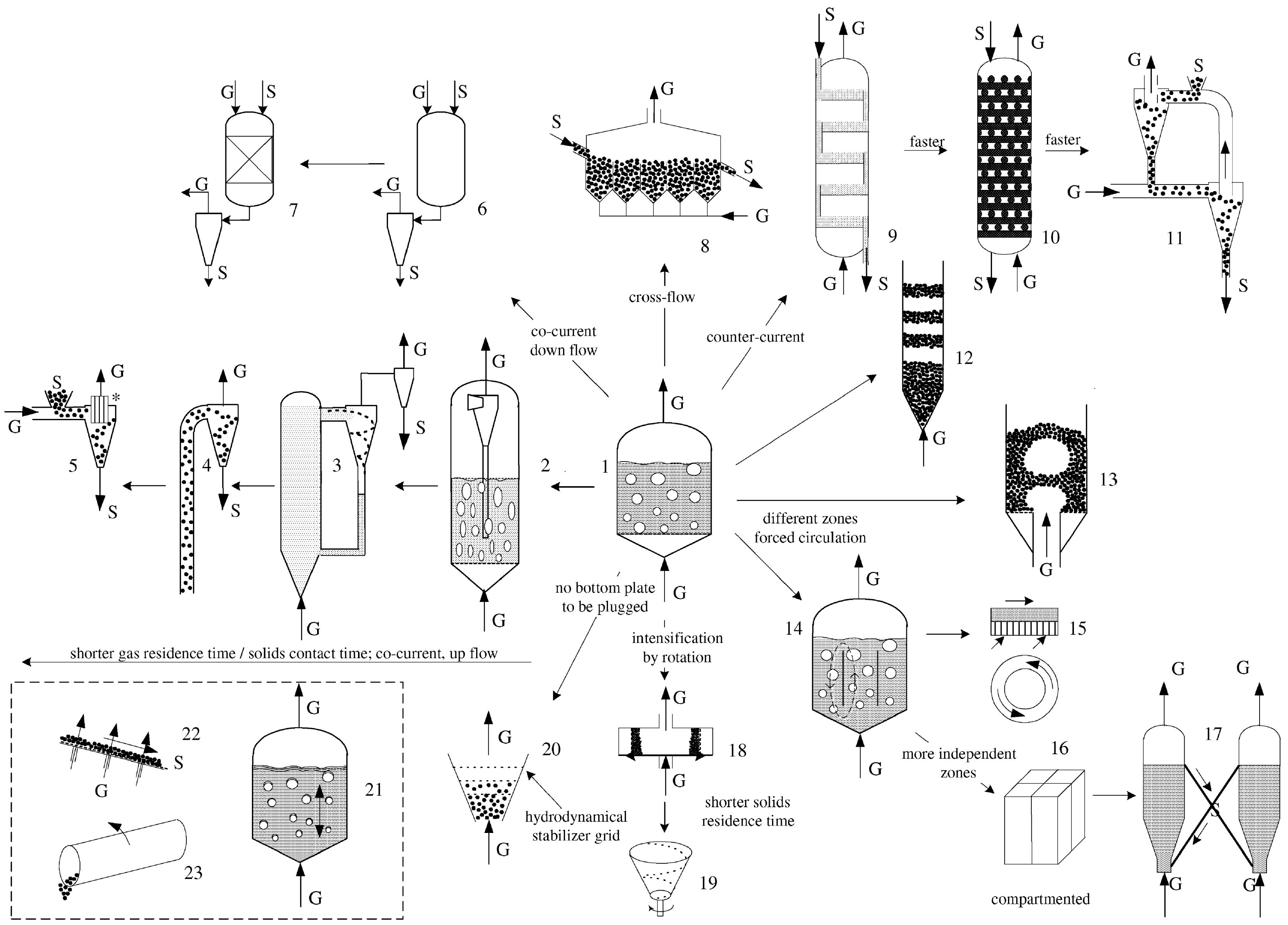

Fig. 8. The fluid bed family: (1) (bubbling) fluid bed; (2) turbulent fluid bed; (3) fast fluidised bed; (4) pneumatic conveying; (5) cyclone (*: with rotating particle separation); (6) co-current down flow; (7) co-current trickle down flow; (8) cross-current fluid bed; (9) counter-current multistage fluid bed; (10) counter-current trickle flow; (11) counter-current cyclones; (12) slugging fluidised bed; (13) spouted bed; (14) draft tube; (15) Torbed; (16) compartment bed; (17) external circulating fluid bed; (18) rotating fluid bed; (19) rotating cone; (20) conical floating G–S fluidised bed; (21) vibrating fluid bed; (22) inclined fluid bed; (23) rotary kiln.

Table 2
Properties of the archetype fluid bed

Properties generally positive	Properties generally negative
1. Excellent heat transfer (e.g. no temperature gradients)	1. Gaseous reactants show back-mixing
2. Solids are intensively mixed	2. G–S contacting questionable
3. Heat transfer rate to submerged heat exchanger or wall is high	3. Pressure drop equals hydrostatic head and is relatively high. Bottom plate is 10–50% of ΔP_{bed}
4. Catalyst easily removed, continuous removal and external solid circulation is also possible.	4. Not easy to scale up from lab-experiments in packed or fluid beds
5. Resistant for bed plugging	5. Attrition
6. Relatively small particle size, wide range of sizes possible	6. Erosion
7. High heat capacity per m^3 volume (advantage for steady state, not for start up)	7. Elutriation
8. High catalyst density, important for slow reactions	8. Gas from solid separation needed (cyclones and filters)
9. Robust dynamics (isothermal heat fly wheel)	9. Mechanical and abrasive strong catalyst needed
	10. Plugging of bottom plate/gas distributor (back flow of solids during start up/shut down)
	11. Controllability

particles (say 50–500 μm) has a number of very positive points which are summarised in Table 2 together with some disadvantages. The most prominent property is the intense mixing due to the stirring action of the bubbles, providing for a uniform temperature at nearly all practical conditions. The same action strongly promotes the heat transfer through the wall or to submerged surfaces. Heat transfer to the catalyst particles is also good offering very rapid elimination of differences in temperature between gas and solid already near the bottom plate. The difference with mass transfer is due to the extreme ratio of heat capacity per unit volume of solid phase over gas phase. However, for extremely fast exothermic reaction the heat removal rate may not be sufficient. For example, in coal combustion and (initial) polymerisation reactions temperature runaway can occur [60,61].

Due to chaotic movement of a catalyst over a reactor volume gas composition and temperature at the surface of each catalyst chaotically changes and the state of the catalyst surface can differ from that at steady state conditions for a given gas phase composition. This presents an important difference between a packed bed and a fluid bed which should be taken into account in an early stage of the process development.

The catalyst particles can be made small enough to avoid internal diffusion limitation as a wide range of particles can be fluidised in a bubbling bed. However, attention should be paid to the possibility of attrition, erosion and elutriation. The fact that solids can be easily added or removed is a very important feature of a fluid bed reactor. The fluid bed is only moderately sensitive towards plugging although one should be alert on sticky solid surfaces under reaction conditions leading to lump formation and defluidisation while plugging of the distributor can still be a problem. Also the difficulty of the gas distributor design is often underestimated. In the design requested pressure drop for stable operation, starting up procedures and turn down ratio are to be considered. Controllability and design can be complicated by the fact that the heat transfer coefficient in a fluid bed to submerged surfaces can be almost constant or even be a decreasing function of the gas velocity, which may limit the operation range. Finally, the recovery of entrained particles by cyclones or filters can be a complicated matter.

It should be realised that most fluid bed reactors have features that already make them special. For example, a partial oxidation reactor producing products like phthalic anhydride or maleic anhydride, may contain different feed inlets for the hydrocarbons and oxidiser (oxygen or air), may have high gas velocities (may resemble a turbulent or circulating fluid bed), be packed with heat exchanger tubes which at the same time may suppress large bubble formation, etc. These reactors may, therefore, resemble more derived members of the fluid bed family and some of their advantages already become apparent in what otherwise looks like a classical fluid bed.

Scale up of classical fluid beds can be complicated. First there is the question of fast bubbles (flowing faster than the gas between the particles). Fast bubbles usually occur with fine particles like cracking catalyst powder (see also the Geldart classification of powder [62,63]). Mass transfer between bubbles and dense phase must be considered, as these bubbles are more or less closed identities [64]. By careful control of the particle size distribution large and efficient beds can be constructed with limited bubble growth [65].

For large particles bubbles may flow slower (slow bubble regime) than the gas between the particles and in principle bypassing of gas is less severe. However, bubble growth for coarse particles may be strong in deep beds leading to intense shaking of the bed and other mechanical difficulties. If such beds are required, the bed height is often limited to 1 or 2 m and bubbles are broken-up by internal heat exchangers (as in fluid bed coal combustion). If the bed has a small diameter, bubble size gets soon in the order of magnitude of the bed diameter forming slugs (slug flow, see Fig. 8, number 12). This regime is often encountered in small-scale pilot plants but is seldom preferred in the full-scale reactor. As a riser reactor it may have advantages for polyolefines production as was pointed out by van Putten et al. [66].

4.1. Higher gas velocities and/or shorter contact time

A special line of development is to higher gas velocities and/or shorter contact time (Fig. 8). The first step is the turbulent bed (Fig. 8, number 2). The regime borderlines have been discussed in literature but are not very clearly defined. Instead of clear bubbles the dilute and dense parts of the bed are of a highly irregular shape and sometimes in the centre of the bed the volume density of particles is relatively low. Many regenerators of catalytic crackers operate in this regime. At higher gas velocities a significant amount of catalyst is entrained and returned via the cyclone diplegs (cycle time in a fluid catalytic cracking (FCC) regenerator is typically 15 min for the whole bed inventory). This is more clearly so for the next regime that takes place: the "fast fluidisation reactor" (Fig. 8, number 3). The borderline of regimes is derived from the pressure drop lines at different solid circulation rates [67,68]. Typical gas velocities for FCC powder fast beds are 4–10 m/s and some catalytic cracker risers operate just within these limits. In others the pneumatic conveying (Fig. 8, number 4) regime is reached with still higher gas velocities (up to 30 m/s) and lower solid hold-ups. Ultimately the whole riser is left away and the short contact time reactor takes the shape of a single cyclone reactor (Fig. 8, number 5). With the exception of this last reactor in the same direction of the shorter residence time the intensity of back-mixing in the solid phase decreases. Coupled to this phenomenon the back-mixing of heat is also strongly reduced. While in a bubbling fluid bed the back-mixing of solids provides a strong back-mixing of heat content and creates the isothermicity of the fluid bed and the heat buffer capacity, this is not the case in circulating beds. Overall heat can be "back-mixed" by the returning solids but in the risers depending on the heat balance important axial temperature gradients can occur.

The G–S contacting is not perfect as is sometimes suggested. While bubbles disappear, nevertheless solid agglomerates remain present in turbulent beds, circulating fast fluid beds and to a smaller degree in pneumatic conveying. Moreover, one should realise that shorter contact times usually imply higher reaction rate for which smaller agglomerates still form transport barriers for G–S contacting. Venderbosch et al. [69] have studied this influence of agglomerates on G–S contacting. Fig. 9 gives a plot for comparing mass transfer and reactor for a few processes [2].

4.2. Improving gas–solid contact, co-current down flow

Another manifestation of bypassing in co-current up flow is the radial segregation of solids in a kind of core annular flow [70–74]. Both effects, agglomerates and riser wall flow can be counteracted by open internal structures in such risers [75,76]. Although these internals (not displayed in Fig. 8, number 3) improve considerably the contact between gas

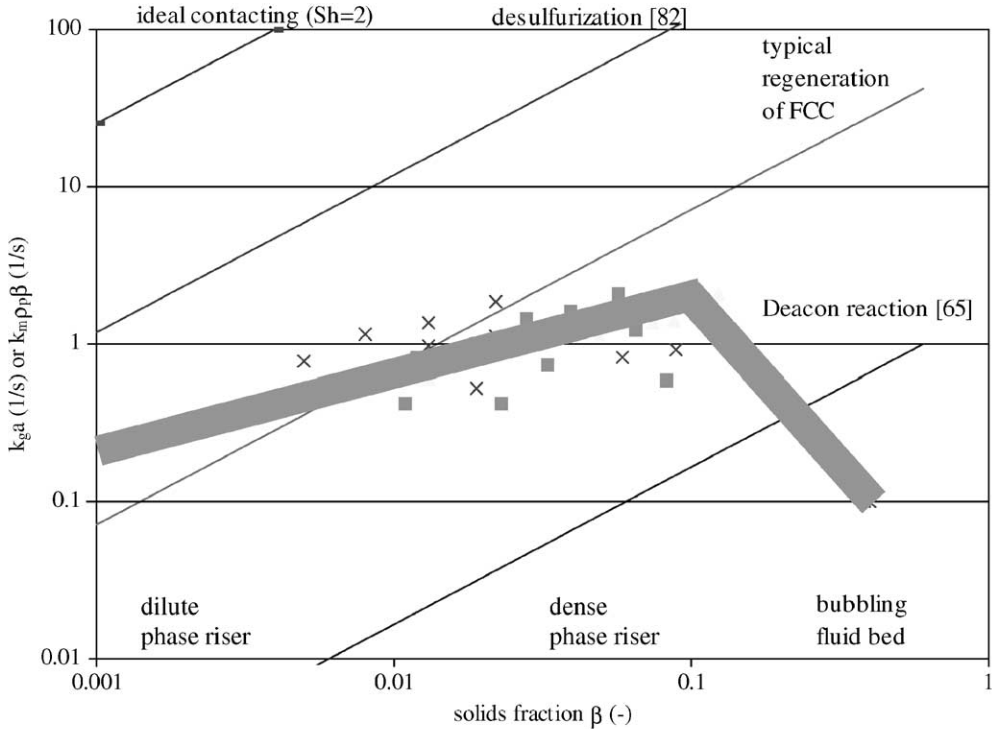

Fig. 9. G–S contacting in fluid beds and risers compared to the reaction rate of some processes, see [69,125,126]. Thick grey line and data points refer to k_ga, where k_g is the overall mass transfer coefficient from gas to particle and a the surface area of the solids per unit reactor volume. The drawn lines refer to $k_m\rho_p\beta$, which is the reaction rate constant per unit reactor volume, for different reactions [2]. See also Krishna and Sie [2].

and solid there is insufficient experience with attrition and erosion of such devices. Short contact downers (co-current down flow; Fig. 8, number 6) have also been used on full scale for catalytic cracking [77]. They show less radial segregation compared to risers, although it is not absent. The price to be paid for down flow is in the overall unit layout which maybe somewhat more complicated. Ultimately a down flow unit with packing or bars as internals (Fig. 8, number 7) would solve the problem of radial segregation. However, up flow with internals would then probably be more advantageous and the down flow version may never have been tried out so far. Cross current (Fig. 8, number 8) versions of a fluid bed can be easily derived and have been propagated for different reasons [2].

4.3. Similarity with distillation columns: counter-current operation

A whole family line has been developed on counter-current operation of fluidised G–S reactors. The simplest idea is to operate fluid beds on top of each other (Fig. 8, number 9), somewhat similar to a distillation column, with overflow weirs and down comers or, alternatively with gas and solid passing each other in holes in the bottom plates. All these constructions are not without problems like blocking of the distributors by entrained particles, limited operation range, controllability, etc. They have nevertheless been applied commercially, although not frequently, for catalytic reactions with catalyst deactivation and for high temperature desulphurisation of coal gas [78]. A crude version with relatively high solid flow uses inclined plates with fluidisation holes in oil stripping of a FCC unit.

4.4. Similarity with gas–liquid trickle flow

G–S trickle flow (Fig. 8, number 10) is another possibility. Here particles are raining or trickling through a packing, often specially designed in a way that has some analogy with G–L trickle flow. This operation has been used in industry for G–S heat exchange [79,80] but also for the recovery of H_2S on pilot plant scale [81,82]. Kiel and co-workers [83,84] used it for simultaneous recovery of SO_2 and DeNOxing of flue gases. Trickle flow can only be used for fast reactions due to the relatively low solid hold-up. The pressure drop is low, however, in most cases the particles are not completely carried by the gas phase but partially by the packing via momentum exchange during collisions [85]. Another idea is to use a cyclone cascade set-up (Fig. 8, number 11) with overall counter-current flow for ultra short contact times [55]. Finally one could use co-current contactors sections of different kinds for overall counter-current operation. Fig. 10 shows a possible set-up proposed in analogy to a G–L system by Blauwhoff et al. [86] and van Swaaij and Versteeg [87] but never tried out in practice.

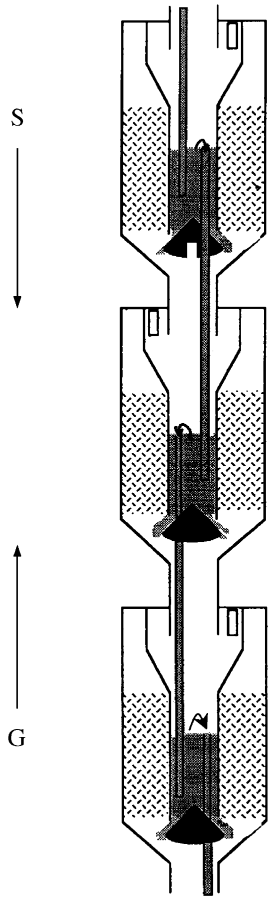

Fig. 10. Overall counter-current set-up of co-current packed riser sections.

4.5. Creating different zones

An important family line of G–S fluid bed reactors is the direction of creating different zones by forced circulation (Fig. 8). This ranges from simply non-uniform introduction of gas in the fluid bed bottom plate like a spouted bed to different fluid bed vessels connected by transfer lines. The spouted bed (Fig. 8, number 13) is often used for large particles to provoke mixing with less gas than required for complete fluidisation. It is seldom used for catalytic reactions and will not be discussed here. A fluid bed with a draft tube inside (Fig. 8, number 14) can be used to enforce circulation. DSM recently patented such a reactor [88,89] for catalytic olefin polymerisation [90,91]. Two distinct zones are created in which different processes take place. A further step is the interconnective fluid bed (Fig. 8, number 16) with more or less independent fluidisation cells [55,92–94]. Important advantages of these units are their compact construction and relatively high circulation rates that can be achieved. Controllability and gas entrainment from other compartments are complicating factors. Ultimately the fluid beds are completely separated and only connected with transfer lines and standpipes (Fig. 8, number 17). If one considers the integral unit the FCC installations as a whole also fall within this family branch. It should be realised, however, that the whole unit often includes in the different vessels in the loop several members of the family (risers, fast beds, counter-current reactors, turbulent beds, etc.). A more specialised member of the branch of fluid driven forced circulation is the Torbed reactor (Fig. 8, number 15) where an overall circular flow in the bed is created by injecting the fluidising gas under an angle in a ring shaped bed. Although interesting and successful in several applications (intensified combustion [95]) it is probably not yet applied to catalytic reactions.

4.6. Intensification by rotation

Intensification by rotation has been applied to fluid beds in the so-called rotating fluid bed (Fig. 8, number 18). An important property of the fluid bed is then lost, however, it is difficult to imagine how heat exchange can be included in such a system. Also the rotating cone reactor (Fig. 8, number 19) belongs to this branch. Here, not only the gas but also the solid residence time is very short [96,97]. The solid is introduced in the centre of the cone and transported by centrifugal force and wall collisions. It has been designed for flash pyrolysis of biomass and (waste) polymers [98–100] and not yet used for rapidly deactivating catalytic reactions. However, some catalysts have been tried in these units to modify the pyrolysis products. This last reactor cannot be considered to be a full member of the fluid family as it has some mixed properties of fluid bed and packed or rather moving beds. Similar the air slide reactor of Shell (Fig. 8, number 22) [101], where particles are moving at conditions close to incipient fluidisation along an inclined porous plate and brought in cross current contact with the gas that almost fluidises the bed, is a hybrid (or a bastard) from the two families. Also if other forces than drag forces or gravity are used to make the particles move, the reactor is somewhat difficult to classify in our framework. Examples are the vibrating fluidised bed (Fig. 8, number 21) and the rotary kiln (Fig. 8, number 23). However, these reactors are not applied for heterogeneously catalysed gas phase reactions and will not be discussed here any further.

4.7. Dusty environment

In a dusty environment, fluid bed bottom plates are easily blocked and a special modified fluid bed was invented for this application: the conical bottomless fluid bed with grid stabilisers (Fig. 8, number 20). In this conical shaped fluid bed relatively large particles are fluidised, in the presence of wide opening screens [102–104]. The only known application is for the DeNOxing of dusty flue gas. It was expected originally that the DeNOx catalyst would have a short deactivation period of only weeks or months and this reactor would allow continuous replacement of the catalyst in power stations where uninterrupted flow is essential. The system showed excellent mass transport properties, little attrition due to the low particle velocities and low pressure drop [102–104]. However, the development of catalyst with longer active life stopped the development of this reactor.

5. The catalytic barrier wall reactor family

This is a new class of chemical reactors with only a short history and their basis should be defined. The family can be characterised by a barrier that incorporates a catalyst which is positioned between two gas spaces or chambers with different gas composition. Within this barrier the chemical reaction takes place and product flows may be manipulated to go to one or both sides by selective permeability or pressure gradient. Some of the reactors called membrane reactors fall within this category but others are in fact simple packed beds surrounded by a membrane which act as a mass exchanging wall, like a heat exchanging wall in a cooled packed bed reactor.

To describe the barrier reactor we start with a simple example of Sloot et al. [105]. Fig. 11 shows the reactor principle. Reactants for a rapid chemical reaction (in this case SO_2 and H_2S) are fed separately from each side of the membrane. The reaction front is inside the membrane and products are transported to both sides of the membrane. The concentration of the reactants can be varied over a wide range,

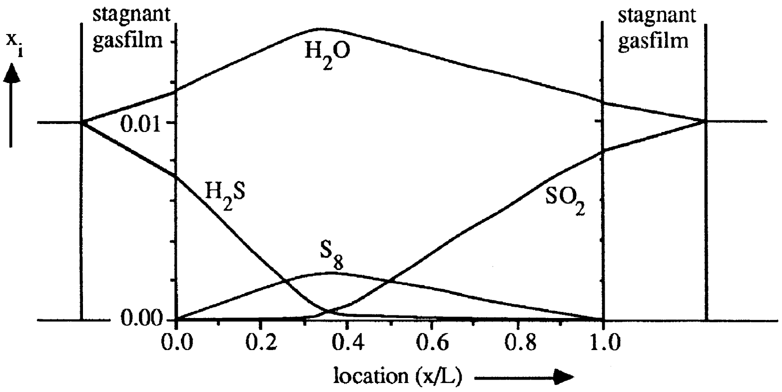

Fig. 11. The catalytic barrier reactor [105]. The reaction is very fast and changing the concentration of one of the reactants only shifts the position of the reaction plane. Inlet gas contains 1 vol.% water.

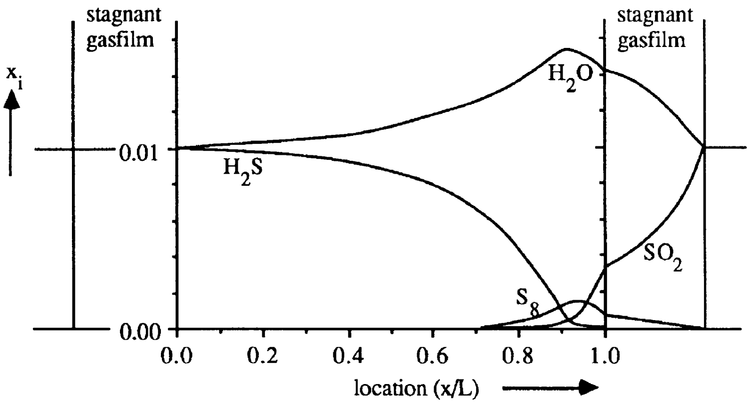

Fig. 12. The catalytic barrier section with an overpressure on one side [2]. The inlet gas contains 1 vol.% of water. The curved concentration profiles in the gas film are the result from the convective flow perpendicular to the interface.

only causing a shift in the position of the reaction front. By applying a slight overpressure on one side all products can be driven by convection to the other side, which may facilitate the separation steps (Fig. 12). This reactor has been tested successfully for combustion reactions [106], for gasification and other partial oxidation reactions [107,108] and for DeNOxing [109].

Another example of a barrier reactor is the equilibrium shift reactor of Ben Amor and Halloin [110], in which the barrier wall is cooled by a condenser placed at short distance (Fig. 13). Synthesis gas is fed to the catalytically active barrier and the withdrawal of the product methanol via the condenser (which also provides the cooling of the exothermic reaction) creates a convective and diffusive flux through the catalyst barrier. Hydrogen, which is in excess in this example, is transported by the methanol flow and diffuses back to the catalyst zone. In the ideal case only a liquid methanol product leaves the reactor. This reactor type has also been tested for hydrogenation of toluene [111].

An overview of different barrier reactors that have been created or conceived is given in Fig. 14. The concept of the partial oxidation condensing barrier reactor (Fig. 14, number 5) is a combination of the two previously given barrier reactors. Partial oxidation products are removed from the hydrocarbon side of the barrier by condensation before they can get involved in consecutive reactions. The effective conversion of the hydrocarbon at the side where oxygen meets the hydrocarbon inside the barrier is so low that the selectivity is still good. This would help in reactions like direct oxidation of methane to methanol. In a combined action of cooling and condensing the desired product can be removed. Just like in the case of the methanol barrier reactor the condensation creates a convective current through the barrier. It must be stated here that this reactor is only an idea and has not (yet) been realised. The selective barrier reactor (Fig. 14, number 3) has a much higher permeability for one of the products (e.g. in isomerisation one of the isomers) and allows withdrawal of the desired pure product on one side. Many more membrane type of reactors can be created or are under study, which can in fact be considered to be barrier reactors. Although a lot of lab scale and development work goes on at the moment, specially in the field of catalytic partial oxidation of methane full scale applications are still absent. The barrier reactors, like the structured and monolith reactors will profit a lot from new and emerging fabrication methods for creating wall structures in a cheap and reproducible fashion.

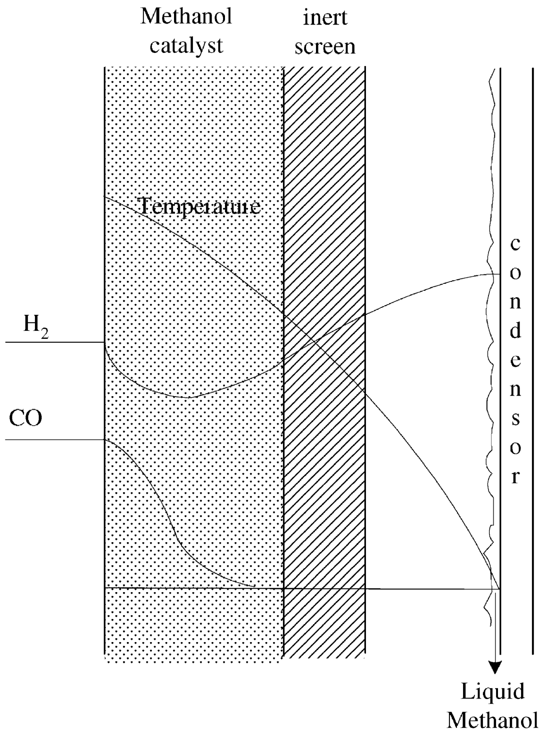

Fig. 13. A sketch of the barrier reactor with condenser of Ben Amor and co-worker [110,111]. The concentration and temperature profiles are only qualitative. In the operation shown CO is nearly completely converted. Methanol flows towards the condenser. Excess hydrogen is entrained with the methanol but not condensed and diffuses back to the catalyst.

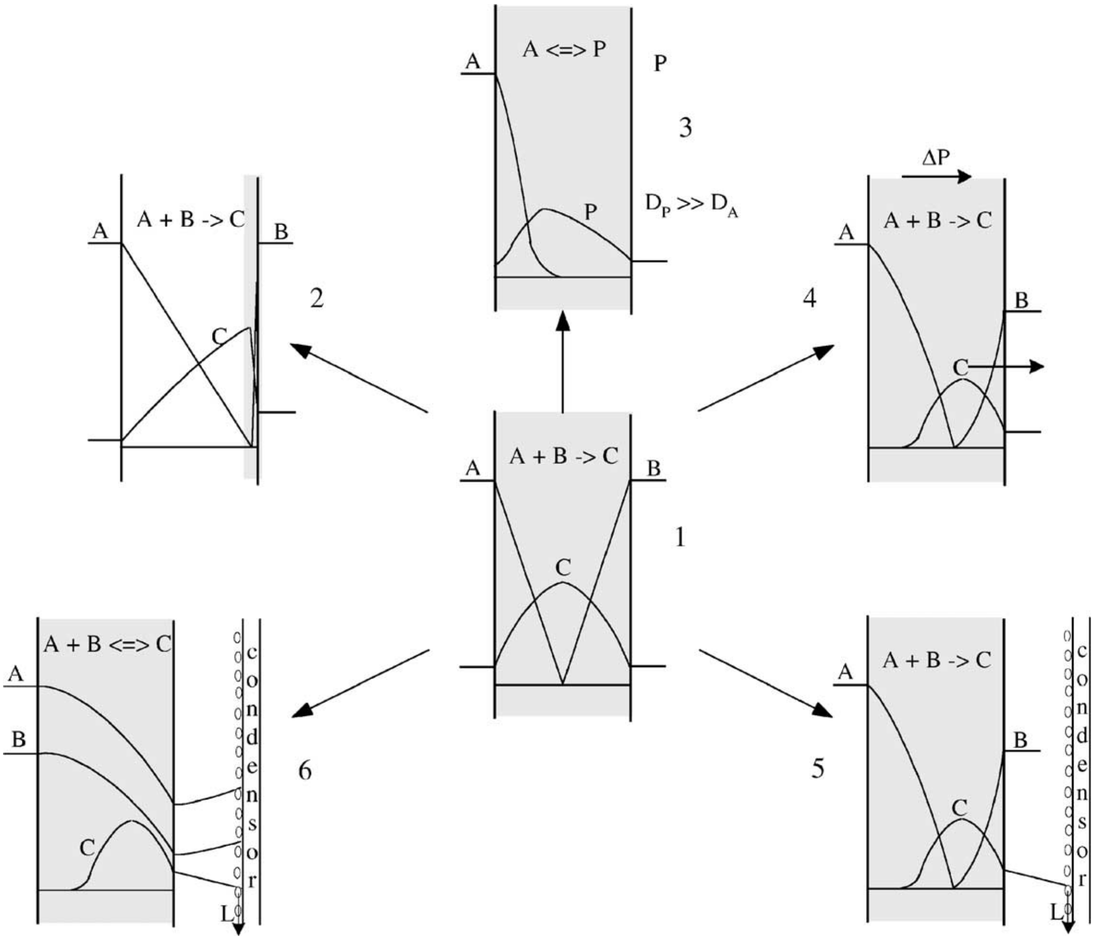

Fig. 14. The barrier reactor family: (1) standard membrane reactor; (2) membrane reactor only active at one side; (3) membrane reactor with differential diffusion; (4) membrane reactor with pressure driven convection; (5) membrane/condenser with intermediate product removal; (6) membrane/condenser equilibrium shift reactor. Shaded area represents catalyst.

6. Mimicry and competition among families

G–S trickle flow will be used here to illustrate the classification and to show how competition of reactors takes place within one family and between other family representatives. G–S trickle flow was already invented by DSM in 1948 but has been rediscovered several times afterwards [112–114].

The general idea is to create a continuous flow of particles through a packing in counter-current with a gas phase, not unlike some GLTFRs. Roes and van Swaaij [115,116] investigated the axial mixing and mass transfer with applications as a mass exchanger in mind (continuous adsorption processes, gas chromatography, etc.).

Verver and van Swaaij [81] applied this system for the first time as a chemical reactor (Fig. 15). They conceived an in-line oxidation of H_2S with oxygen to sulphur using a zeolite as both catalyst and adsorption medium for the sulphur. The H_2S could thus be removed from a combustible gas (natural gas, synthesis gas, etc.) and directly recovered separately as elemental sulphur by simply heating the solids, which can then in turn be recycled to the reactor. By removal of S_8 from the gas phase in the reactor by the solid, the conversion can be higher than calculated from equilibrium data including all the S_8 in the gas phase [81,82]. The process is strongly relying on the selectivity of the oxidation of hydrogen sulphide over other combustible gases, but fortunately this selectivity was always very high. The principle was demonstrated on a small-scale pilot plant. A competitor of this reactor is a packed bed with intermittent removal of the sulphur.

The reactor of Verver and van Swaaij [81] should be considered as a member of the fluid bed family as the catalyst is kept in a more or less fluidised state while flowing through the reactor.

Westerterp and co-workers [16,17] were working in the same department on another TFR. In this reactor methanol was produced from synthesis gas in a packed bed reactor of methanol conversion catalyst (Fig. 15). By applying a trickle flow of solids through the packed bed that mainly absorbed methanol they were able to recover the formed methanol. While normally synthesis gas conversion to methanol is limited due to chemical equilibrium, they were able to get close to full conversion of the synthesis gas in their set-up.

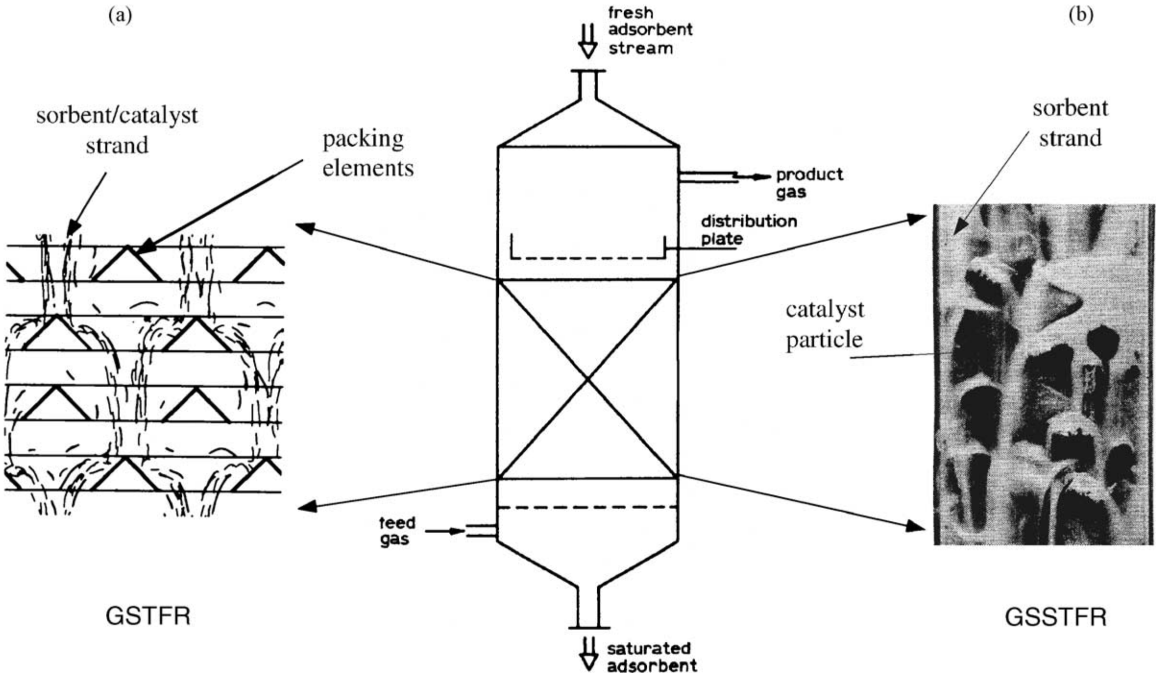

Fig. 15. (a) GSTFR for H_2S oxidation of Verver and van Swaaij [81]; (b) GSSTFR for methanol production of Westerterp and co-workers [16,17].

Although the schematic set-up of the two reactors are practically the same and both reactors carry the product out of the reactor by the solids, thereby provoking equilibrium shift, there is also a difference. The H_2S oxidation reactor belongs to the fluid bed family (catalyst is flowing) while the methanol reactor is a packed bed reactor, with an absorbent/heat carrier flowing through it.

If a membrane would have been used around the packed bed with a membrane permselective for methanol or if a liquid methanol sorbent would have been used (actually this was done later by Westerterp and Kuczynski [18]) the true family relation of the methanol reactor would have been obvious.

To demonstrate the competition of reactors of the different families we will consider the simultaneous removal of SO_x and NO_x from flue gases with copper on alumina sorbent/catalyst. The reactions are presented in Table 3. The adsorption of SO_2, the catalytic selective reduction of NO_x and the regeneration/concentrated SO_2 recovery, all take place at 400 °C. During regeneration, H_2 (or CO and/or CH_4) is consumed. Selection of catalyst, injection and dispersion strategy and choice of flow regime etc. have to be made of course but on top of that because of the large amount of flue gases to be treated, pressure drop and gas velocity are very important. Preferably also some particulates (ash) should be tolerable. Classical packed bed swing reactors cannot be used but the low pressure drop versions would do (Fig. 5, numbers 10–12). A parallel passage reactor indeed has been developed for this process by Shell [27] many years ago and commercial operation has been reported. Nowadays possibly the monoliths could also have been used. The intermittent operation is, however, somewhat cumbersome in this application as also a purge will be necessary going from oxidative to reducing conditions. Also the high temperature switching valves are complex and expensive while the changes in SO_2 concentrations during the cycles make downstream processing difficult. Replacing the catalyst is also complicated and a reactor solution with a flowing solid catalyst/sorbent should possibly be preferred. Remaining in the packed bed family a moving bed could be a solution if the pressure drop can be kept at an acceptable level and particle blocking can be avoided. The system could even work simultaneously as a continuous particle filter. Rockwell International and PETC [117] developed such a system in the USA. In fact it was a cross-current moving bed.

Also a dense fluid bed version of the process was developed by PETC [118–120] and others [121,122]. The reaction may not be sufficiently fast for fast beds or pneumatic conveying. Kiel et al. [123] used a GSTFR for this system

Table 3
SO_x sorbent, regeneration and DeNOx reactions of the flue gas treating process

Process chemistry	ΔH^0 (at 25 °C)
Absorption reactions	
$2Cu + O_2 \rightarrow 2CuO$	−155 kJ/mol Cu
$2CuO + 2SO_2 + O_2 \rightarrow 2CuSO_4$	−318 kJ/mol Cu
$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$	−407 kJ/mol NO
Regeneration reactions	
$CuO + H_2 \rightarrow Cu + H_2O$	−86.6 kJ/mol Cu
$CuSO_4 + 2H_2 \rightarrow Cu + SO_2 + 2H_2O$	−10.6 kJ/mol Cu

Table 4
Properties of the different G–S contactors used in the absorption step of the CuO–SO_2 removal process

Aspect	System			
	Parallel passage	Moving bed	Fluid bed	Trickle flow
Continuous operation	−	+/−	+	+
Counter-current contacting	+	+/−	−	+
Mass transfer fast enough for this system	+	+	+	+
Solids hold-up	+	+	+	+/−
Pressure drop (kPa)	3	1.5	4.5	1–1.5
Typical superficial gas velocity (STP) (m/s)	1.9	0.079	0.5	0.5–1

Table 5
Catalytic cracking reactors

	Fixed bed	Moving bed	Fluid bed		Riser
Catalyst	Amorphous	Amorphous	Amorphous	Crystallite zeolite	Crystallite zeolite
Reaction time (min)	15–20	15–30	1–8	0.5–1	0.05
Regeneration time (min)	40–80	80–90	60–70	40–60	30–40
Capacity (t per year)	50–100	250–450	1200	1200	2000–2500

and operated successfully an integrated bench-scale pilot plant. Later a larger pilot plant of 5 m height was erected at ECN in The Netherlands and operated with 95% recovery of SO_2 with a very favourable temperature profile in the absorber. The four different reactors tested are assembled in Table 4 and a few key parameters for operation are indicated. Continuous operation is desired and all reactors except the parallel passage reactor can realise this. For optimal loading counter-current operation is preferred, realised by trickle flow and in a way in the parallel passage reactor. A critical factor of the TFR is the sorbent/catalyst hold-up, which is only just sufficient. On the other aspects the reactors are comparable although pressure drop over the fluid bed is somewhat higher. It appears that the commercial parallel passage reactor remained on stream for a prolonged period of time operated as a DeNOx unit only and could possibly be seen as a predecessor of the present selective reduction reactors using monolith catalyst stackings. The other processes have not yet reached the commercial application as far as we know. Competition with wet, half dry and dry scrubbing process producing gypsum in combination with a modern DeNOxing unit may be too tough. The example given here is not exceptional. For quite a few processes several reactor types are simultaneously in operation, cooled packed beds, fluid beds, etc. without clear dominance of one specific type.

As explained before, the reason is often that the basic reactor types are modified/evolved in a direction to cope with the typical problems in a certain application. In other chemical processes one reactor type clearly becomes dominant. This is often steered by catalyst developments. An interesting example has been given by Slinko [124]. Due to catalyst development the required reaction time in catalytic cracking decreased by a factor 300 dramatically changing the dominant reactor type (Table 5).

7. Conclusions

G–S catalytic reactors can be classified as modifications of only two to four basic types (families). We propose three basic types: packed bed, fluid bed and barrier wall reactors. A possible fourth type, the bunker flow reactor, is considered to be a packed bed, based on the typical long cycle times with associated low solid flow rates.

It appears that the radiation of the reactors from archetypes to niche species for special applications shows a large resemblance to the evolution of animals.

The methodology of classification in families applied in this paper gives a quick overview of the different G–S catalytic reactors with their specific advantages and disadvantages and these are shortly discussed. Starting point is always a well-known and thoroughly investigated basic reactor type. The results presented in this paper are a first step and should be extended with a database containing the best available data on properties.

The barrier wall reactor family is an emerging type whose success will strongly depend on the development of new fabrication methods. However, the success of the monolith and other structured reactors show a possible high potential.

Generally it is easy to pinpoint the family where a reactor belongs. However, sometimes it is not directly clear and careful analysis is needed. It is proposed to use the location of the chemical reaction as criterion for family classification. An example has been given in the area of G–S trickle flow.

Small modifications of a basic reactor type may produce already a transition form (intermediate) towards a specific family member. In that case the properties are also intermediate. However, in the figures and tables only extremes are shown and discussed. It is shown with an example that several slightly modified reactors of different types may compete for a specific application niche for a prolonged period of time without a clear winner becoming apparent.

It would be advisable to construct a flexible bench-scale unit early in the process development period to consider the pros and the cons of different reactor families (flowing, non-flowing and “barrier layer” catalyst). Complete changes will otherwise be difficult in a later stage.

The system of classification as radiating families will be applied to other types of reactors like the G–L and G–L–S reactors in the future.

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