

A SYSTEMS APPROACH TO MULTIPHASE REACTOR SELECTION

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I. 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. There is therefore 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 technologically feasible reaction coordinates of temperature, pressure, and residence time;

- intrinsically safe operation, freedom from instabilities, runaways, etc.;
- environmental acceptability; and
- feasibility of scale-up to economically justified size.
- maximum possible conversion of the feedstocks;
- maximum selectivity of reaction to desired products; and
- lowest capital and operating costs, stemming from, e.g., the desire to maintain low pressure drop.

Figure 1 pictures the central question addressed in this article.

Typically, in the petroleum and petrochemical industry, even small percentage improvements, say of the order of 0.5%, with respect to selectivity can be extremely significant. For example, improvement of gasoline selectivity in fluid catalytic cracking (FCC) operations by 0.5% would mean an increased revenue of \$2.5 million per day on a global basis. Improved yield and selectivity can be crucial for process licensors. A 1% selectivity advantage in the manufacture of ethene oxide (obtained by air oxidation of ethene) could be significant enough for a process licensor to gain a marketing edge over a competitor. While the major process improvements will no doubt stem from improved reaction “chemistry” and catalyst design, there is a 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 we are able to develop a packed bed reactor

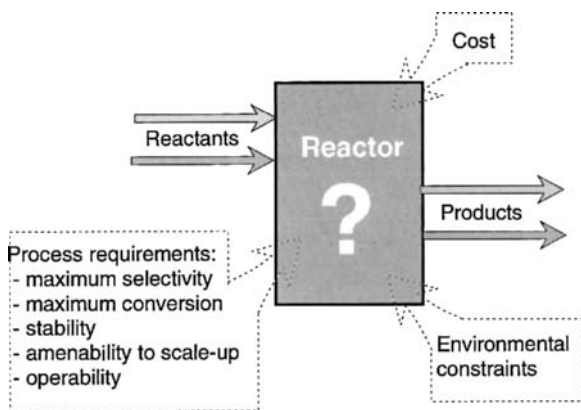


FIG. 1. The problem of reactor selection to meet the desired process requirements and constraints.

that operates under substantially isothermal conditions, this will result in significant selectivity advantages due to suppression of the combustion reaction.

During the development of new processes involving first-of-a-kind technology, the choice of the reactor assumes added importance because of the lack of prior art. This is exemplified by the relatively recent development of the hydrodemetalization (HDM) process; in this case, major companies have adopted widely different configurations, e.g., three-phase fluidized beds slurry reactors, (fixed) trickle beds, co-current down flow moving bed, and countercurrent upflow moving bed. The Shell HYCON process employing the co-current downflow moving bed concept is an example of a novel first-of-a-kind technology.

In the Shell Middle Distillates Synthesis (SMDS) process, which converts natural gas to synthetic liquid hydrocarbons via advanced Fischer-Tropsch synthesis, the synthesis reactor configuration chosen for the first commercial unit in Malaysia, started up in 1993, is the multi-tubular downflow trickle bed with catalyst inside the tubes (Sie *et al.*, 1991). 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 multi-tubular bubble column slurry 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 operation were of overriding concern for Shell, who decided to adopt the fixed-bed technology due mainly to a quicker development scenario which allowed the time plans of the business to be met. 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.

The preceding discussions serve to underline not only the importance of choosing the reactor with the promise of best performance, but also the need to anticipate scale-up difficulties. The approach we advocate in this article is to attack the problem of reactor selection in a systematic, structured manner, using some concepts borrowed from management

sciences. We develop the arguments leading to our general systems approach by first considering a case study involving recovery of oil from oil shale.

II. Case Study: Recovery of Oil from Oil Shale

Oil shale contains an aromatic component called kerogen, which on heating, in the temperature range 400–500°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 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. 2. The choice of the ideal reactor configuration is the topic addressed here. There are numerous processes and reactor configurations that have been suggested for carrying out the thermal pyrolysis reaction (Synthetic Fuels Data Handbook, 1978); these are sketched in Fig. 3. The various technologies have apparently little in common. For example, on the basis of particle size used in the process, we have: (a) large-sized ($\cong 50$ mm) particles, (b) medium-sized ($\cong 5$ –10 mm) particles, and (c) small-sized (< 3 mm) particles. Further, both packed beds [groups (a) and (b)] and fluidized operations [group (c)] are encountered. The contacting pattern between the oil vapor (+ stripping gas) and

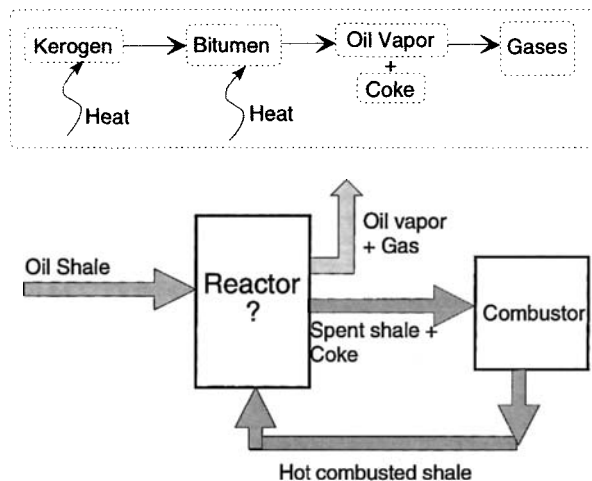


FIG. 2. Schematic process flow diagram for the recovery of oil from oil shale.

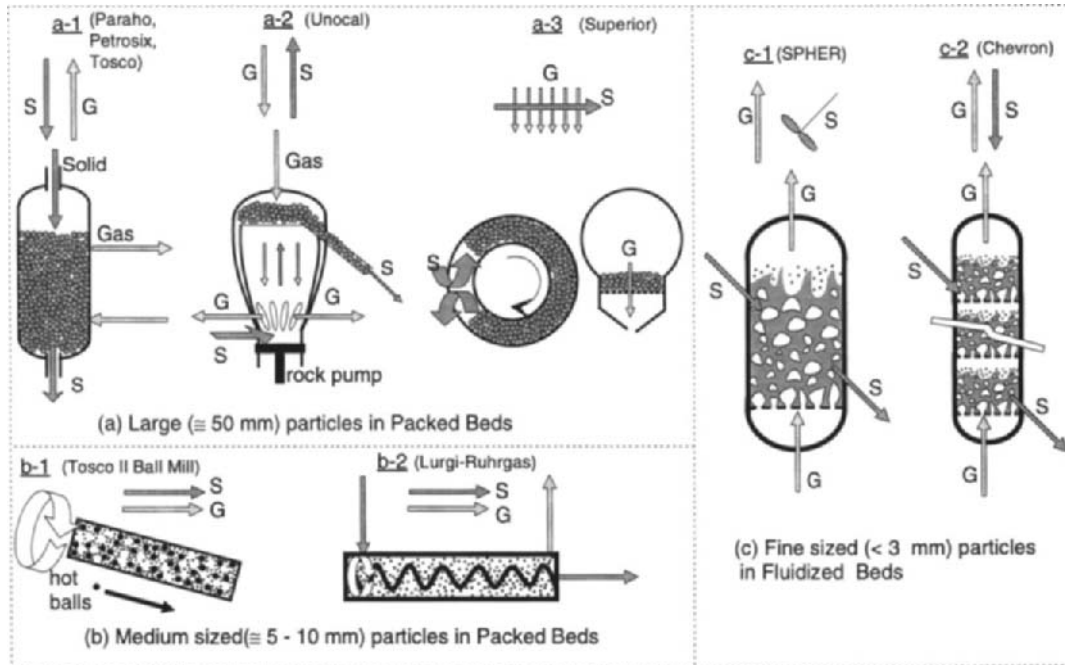


FIG. 3. Various reactor configurations used in oil shale processing technologies. Adapted from Levenspiel (1988).

the solid phase used in these technologies also varies widely: (i) counter-current in a-1, a-2, and c-2; (ii) co-current in technologies b-1 and b-2; and (iii) 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 of the solids phase. The Unocal process involves another unique technology in which the shale particles are moved upwards, countercurrent to the vapors, by means of a rock pump. For a reactor engineer involved in developing a shale oil recovery process, the diversity of the reactor configurations shown in Fig. 3 is more than a little disconcerting. How is one to make a choice among the various options? We shall demonstrate our suggested systems approach by attempting to derive the ideal oil-shale reactor configuration.

A. THE PROCESS WISH LIST

Any systematic approach to reactor selection must begin with a “wish” list of features:

Wish 1: The reactor must be capable of maximum recovery of oil. Oil recovery can be maximized by making sure that high (say, 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 tons 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, there is need to restrict the reactor volumes in order to reduce the investment costs.

Wish 4: During 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.

B. GAS-SOLID REACTOR SELECTION SUBSETS

We split up the problem of reactor selection into three sub-problems. By making decisions regarding these three separate attributes of the reactor, we obtain the final reactor choice. These three subsets of the reactor are discussed next.

1. *Subset I: Particle Size*

The “ideal” particle size to use in the reactor should meet the requirements in the wish list; concretely put, should we use small particles, medium-sized particles, or coarse particles? (See Fig. 4.)

2. *Subset II: Gas–Solid Contacting Flow Pattern*

Here we have to decide among the following three contacting patterns between the gas (= oil vapor + liberated light gases + stripping gas) and the (hot) shale particles (see Fig. 4).

- (a) *Countercurrent contacting*,
- (b) *Co-current contacting*, and
- (c) *Cross-current contacting*.

Each of the two contacting phases (gas and solid) can be either in plug flow (perfectly staged) or backmixed (perfectly mixed) condition. At this stage of reactor selection it is only necessary to specify what the ideal contacting pattern ought to be; the technical limits of feasibility are taken into account in a subsequent analysis.

3. *Subset III: Gas–Solid Fluidization Regime*

Even when the above two subsets I and II have been decided, the definition of the reactor configuration is not complete; there remains the choice of the appropriate gas–solid fluidization regime. Basically we have to choose between the following six modes of operation; see Fig. 4.

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.

2. *Fluidized bed* operating under *homogeneous fluidization* conditions (i.e., just above the minimum fluidization velocity). This regime of operation is only prevalent for fine particles, and the operating window is extremely limited. It is not possible to design a gas–solid fluidized bed commercial-scale reactor to operate under this regime in a stable manner because it is difficult to prevent the onset of bubbles due *inter alia* to flow instabilities resulting from, say, improper gas distribution at the inlet.

3. *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.

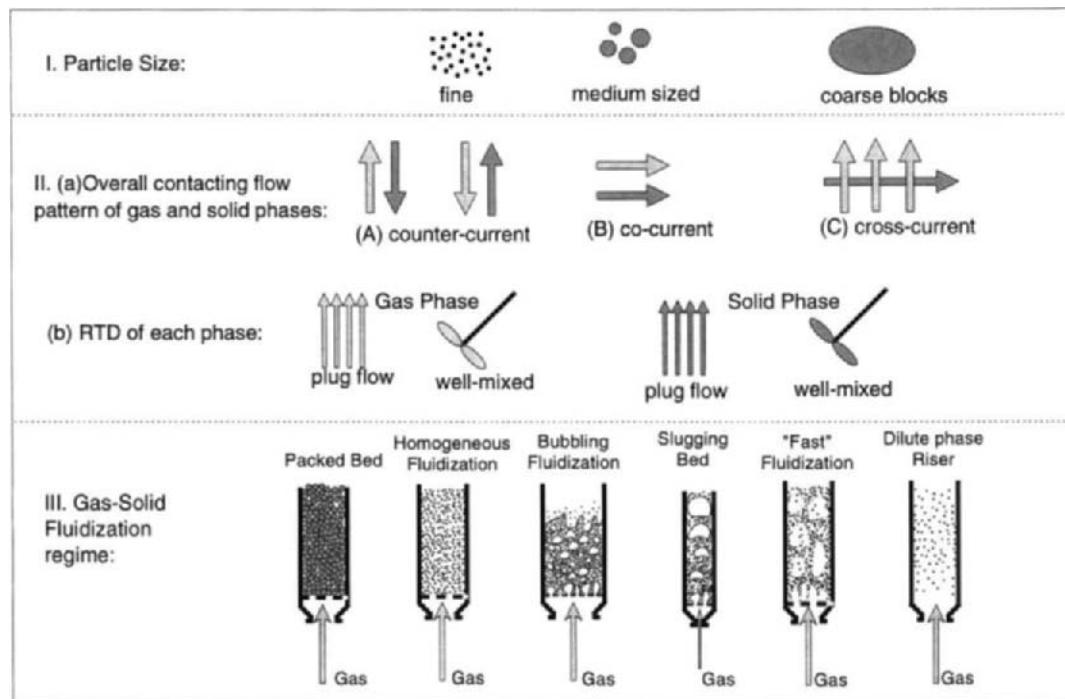


FIG. 4. The three subsets, or attributes, of a gas-solids reactor.

4. *Slugging bed*. For relatively small-diameter columns, e.g., typically of the order of 0.1 m, the size of the bubbles attains the dimensions of the vessel and slugging conditions prevail. This regime of gas–solids flow is quite common in pilot plants operating at high velocity. For commercial-scale units with diameters larger than 0.5 m, it is usually not possible to attain slug flow conditions.

5. *Turbulent regime* and “*fast*” *fluidization*. 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 particle hold-up is typically in the range 0.3–0.45. There is heavy entrainment of the solids, and bed inventory is 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*. The particle hold-ups in this regime are typically 0.1–0.2.

6. *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.

Besides significant differences in the particle hold-ups in the foregoing modes of fluidization, there are other differences, e.g., in gas–solids contacting efficiency, solids mixing, gas-phase mixing, and heat and mass transfer characteristics.

We now analyze each of the three subsets above in turn.

C. PARTICLE SIZE SELECTION

As already seen in Fig. 3, existing oil shale processes display a wide range of particle size specifications. In order to arrive at the decision regarding the ideal particle size, we need to analyze the transport and chemical reaction processes inside the particle. The kinetic scheme for the thermal pyrolysis reaction is depicted in Fig. 5, following Wallman *et al.* (1980). For a temperature of 482°C, the residence time requirements for 99% conversion of kerogen can be calculated using the kinetic data of Wallman *et al.* (1980). The residence time requirements for the limiting cases of plug flow of solids (perfectly staged) and backmixed solids (perfect mixing) are shown in Fig. 6; for plug flow of solids $\tau = 8$ min, whereas for a backmixed reactor $\tau = 174$ min. Also shown in Fig. 6 is the time required to heat up the particle of shale to within 95% of the surrounding temperature. We can distinguish three distinct ranges of particle sizes in Fig. 6. For particles smaller than 20 mm (Range I), the heating-up times

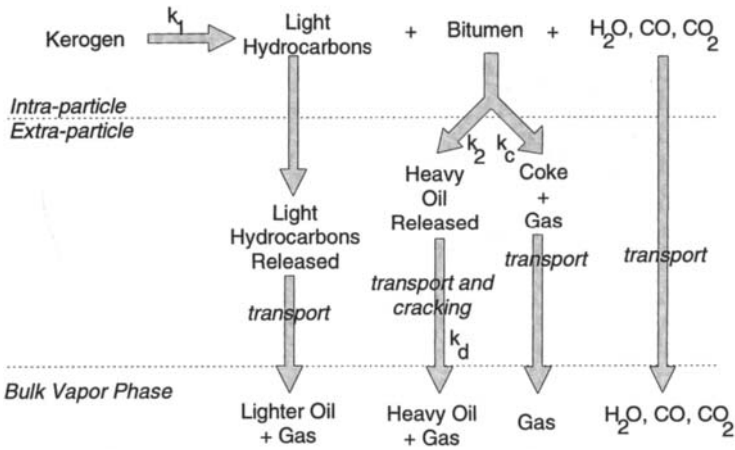


FIG. 5. Oil shale pyrolysis kinetic scheme according to Wallman *et al.* (1980). The first-order reaction rate constant for kerogen decomposition is $k_1 = 9.633 \times 10^{10} \exp(-21943/T) [\text{s}^{-1}]$. The first-order reaction rate constant for heavy oil production is $k_2 = 3 \times 10^3 \exp(-11370/T) [\text{s}^{-1}]$. The first-order reaction rate constant for coking is $k_c = A_c \times 10^3 \exp(-11370/T) [\text{s}^{-1}]$, where $A_c = 30$ for $d_p = 3$ mm; $A_c = 15$ for $d_p = 2$ mm; $A_c = 6.667$ for $d_p = 1$ mm; $A_c = 5$ for $d_p = 0.4$ mm.

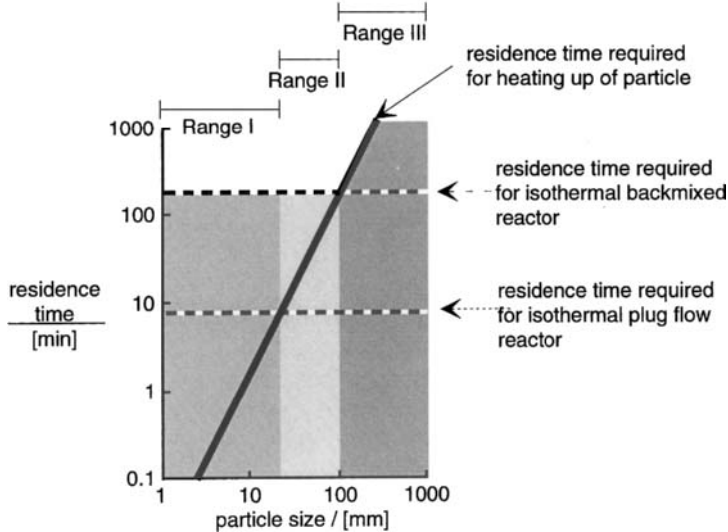


FIG. 6. Particle residence time requirements for isothermal oil shale reactor operating at 482°C. The residence time requirements for achieving the desired degree of conversion were obtained from the kerogen decomposition kinetics of Wallman *et al.* (1980); see Fig. 5. The heating-up requirements of the shale particles were calculated assuming an effective thermal diffusivity inside the particle of $2.7 \times 10^{-7} [\text{m}^2 \text{s}^{-1}]$.

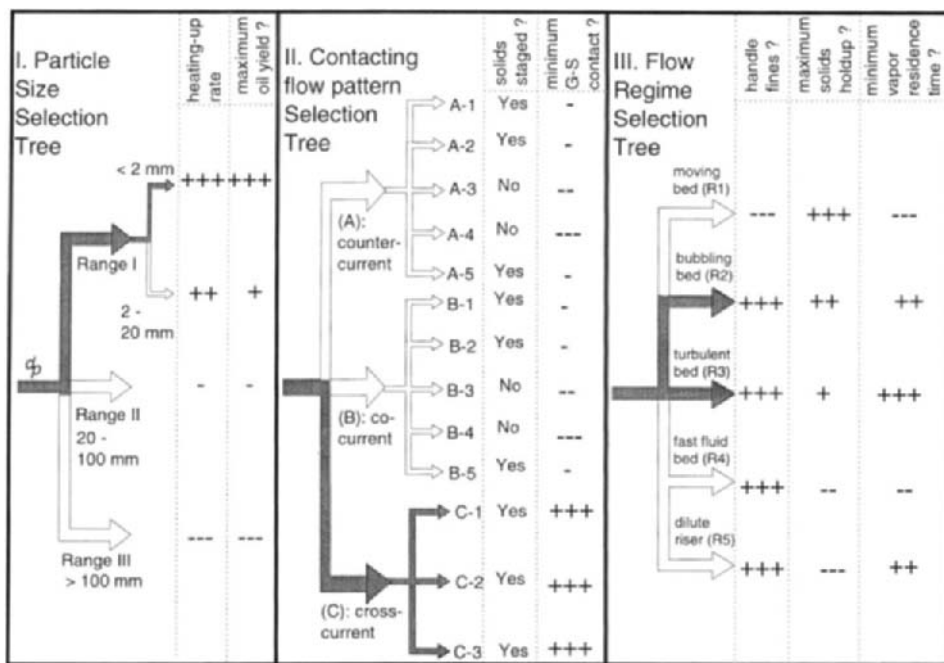


FIG. 7. Decision tree analysis for oil shale reactor selection.

are insignificant compared to the time required for converting the kero-gen. The residence time requirement of particles is therefore governed purely by backmixing characteristics of the solids. For particles larger than 100 mm in size (Range III), the heating up time becomes dominant and it does not matter whether the solids are backmixed or not. For particles of size between 20 and 100 mm (Range II), both heating-up and backmixing characteristics play important roles.

A typical large oil shale complex will have a solids flow rate of 500 kg/s, and there is a great incentive to keep the required residence time of shale particles to the minimum possible level (Wishes 1, 2, and 3). This desire will be met if we choose a particle size below 20 mm (Range I) with no heating-up limitations and, further, ensure plug flow of the solids phase. This conclusion is summarized in the form of a decision tree in Fig. 7.

The oil vapor produced within the particle will have to be transported to the bulk vapor phase, and during this transport process it will suffer further degradation and cracking; this can be seen in the kinetic scheme in Fig. 5. The yield of heavy oil, which is the desired product, has been found to be dependent on the particle size, as evident from calculations on the

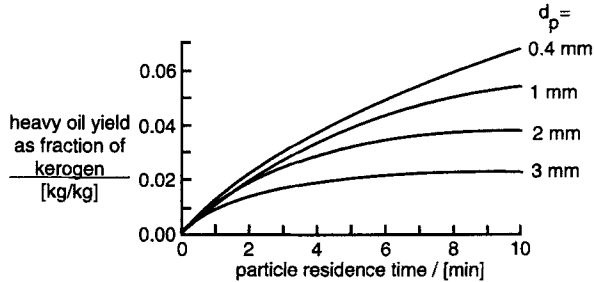


FIG. 8. Heavy oil yield as a function of particle residence time for a range of particle sizes. Data for oil shale reactor operating isothermally at 482°C. The yields are calculated using the Wallman *et al.* (1980) kinetic data in Fig. 5.

basis of Wallman kinetics; see Fig. 8. There is a significant yield improvement in using particles below 2 mm. Now in any grinding operation, if we specify 2 mm as the top size, there will be a significant proportion of particles smaller than this top size. To fulfill Wish 1, we further branch up the particle size decision tree by choosing a size smaller than 2 mm; see Fig. 7.

D. CONTACTING FLOW PATTERN

Several contacting flow patterns are possible; the important ones are pictured in Fig. 9. Scheme A-1 is used by Paraho, Petrosix, Tosco and Chevron. Scheme A-2 is used in the Unocal rock pump contactor with upwards flow of solids. Scheme A-3 corresponds to the SPHER process with a backmixed solids phase. The horizontal co-current contacting scheme B-5 is used in Lurgi-Ruhrgas and Tosco-II. The cross-current contacting schemes C-1 and C-2 are used in the Superior Oil traveling grate process, where the gaseous heating medium traverses up or down a packed bed of solids placed on a grate. The cross-current contacting scheme C-3 is used in the moving bed concept of Kiviter with radial outflow of gas.

In the contacting flow pattern selection tree (Fig. 7), we choose only those branches where the solids phase is in plug flow because of our desire to reduce the reactor volume requirements (Wish 3). There is a further factor that needs to be taken into account. The oil vapor that is formed during the process is in contact with other hot shale particles within the reactor, and the chance of further degradation of this oil increases with the gas phase residence time (*cf.* Fig. 5). Wilkins *et al.* (1981) have studied the oil vapor degradation kinetics, and calculations based on their kinetics

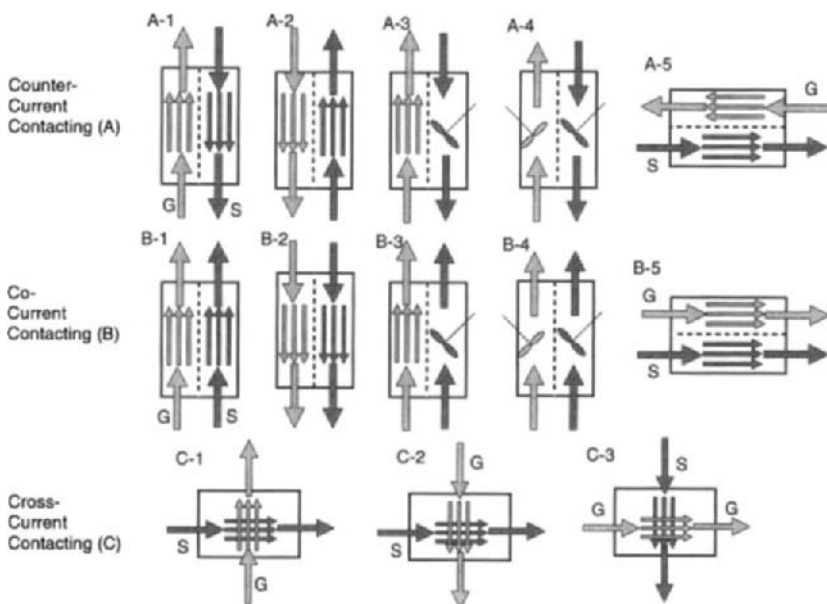


FIG. 9. The various possible gas–solid contacting flow patterns.

are shown in Fig. 10. It is noteworthy that 5% of the oil suffers further degradation for a vapor residence time of 2 s. Clearly, to reduce the chance of oil degradation (*cf.* Wish 1), it is necessary to remove the oil vapor from the reaction zone as soon as it is formed. The important conclusion to emerge from this analysis is that neither counter- nor co-current contacting is desired. What we require is cross-current contact-

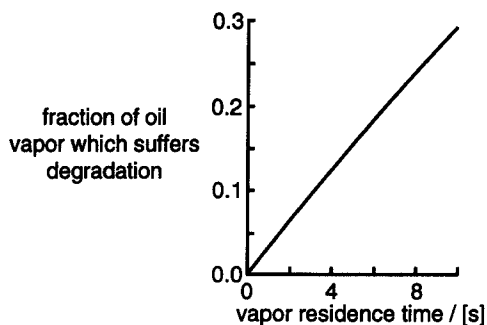


FIG. 10. The fraction of oil vapor formed which is degraded due to overcracking as function of oil vapor residence time. Data for isothermal operation at 482°C (Wilkins *et al.*, 1981). The calculations were carried out with a first-order reaction rate constant for oil degradation, $k_1 = 3 \times 10^3 \exp(-8700/T) \text{ [s}^{-1}\text{]}$.

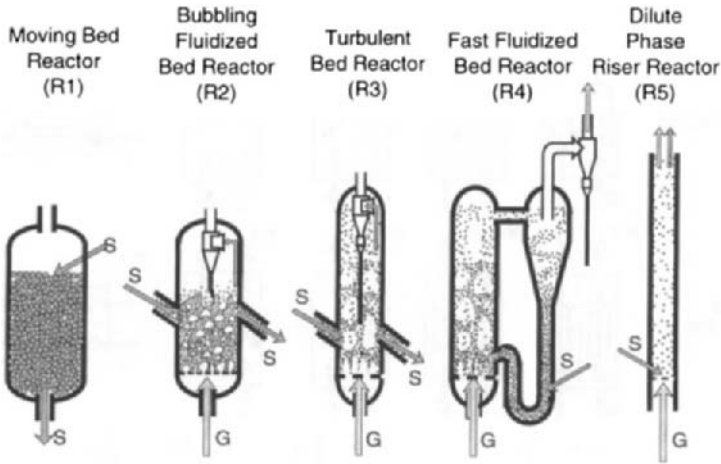


FIG. 11. Gas-solid reactor configurations involving operation with various regimes.

ing of oil vapor and hot solids, wherein the chance of contact between the phases is minimized. The favored contacting flow patterns are, therefore C-1, C-2, and C-3; this is incorporated into the contacting pattern selection tree in Fig. 7.

E. GAS-SOLIDS FLUIDIZATION REGIME

For commercial operations, the regimes of homogeneous fluidization and slug flow (see Fig. 4) are not feasible, and the practical implementation of the various fluidization regimes is shown in Fig. 11. A moving bed of packed shale particles (R-1), moving downwards, upwards, or horizontally, is the most commonly used flow regime in the existing processes. This packed bed flow regime has one serious disadvantage that fine particles (smaller, than, say, 0.5 mm), inevitably formed in the crushing operation, will block moving-bed operation or will be blown away by the gases. Existing moving-bed processes such as Paraho, Unocal, Petrosix, Superior, and Kiviter operate with lumps of particles of average size 50 mm and are not capable of handling fine powders (see Wish 4). Note that we have already discarded operation with large lumps of particles from oil yield and reactor volume considerations (Wish 1, 2, and 3).

Respecting the requirements of Wish 3, we aim to maximize the solids hold-up in the system. Using this criterion we have the hierarchy of choices, indicated by pulses and minuses, in Fig. 7. Dense- and dilute-phase

riser transport operation, operating at solids hold-ups below 0.2, cannot therefore be serious contenders as oil-shale reactors.

There is another factor that needs to be taken into consideration: the need to reduce oil vapor degradation (Wish 1), requiring us to reduce the oil vapor residence time in the reactor. In bubbling fluidized beds (R-2) and turbulent fluid beds (R-3), the bubble rise velocities are of the order of 1.5 m/s, and in a shallow bed of, say, 2 m the oil vapor residence time may be restricted to below 2 s.

The flow regime selection tree has been summarized in Fig. 7. On the basis of the qualitative reasoning, we may conclude that the best operating regime for the oil shale retort is a bubbling or turbulent bed operation.

F. SUMMARY OF OIL SHALE REACTOR CONFIGURATION DECISIONS

The various decisions on the reactor subsets, outlined in Fig. 7, can be summarized in words as follows. The ideal oil shale reactor, respecting all items in the wish list, is one in which fine particles, say smaller than 2 mm, are used in a reactor configuration wherein the overall gas solids contacting pattern corresponds to cross-flow of gas and solid. The solids phase in the reactor should be staged, and the oil vapor residence time is limited to a few seconds by use of the bubbling/turbulent fluidization regime. The resulting cross-flow fluid bed reactor configuration is shown in Fig. 12. This is the configuration of the Shell Shale Retorting Process that is under development by Shell Research. This process was developed using the decision analysis sketched earlier (see also Poll *et al.*, 1987). Raw shale

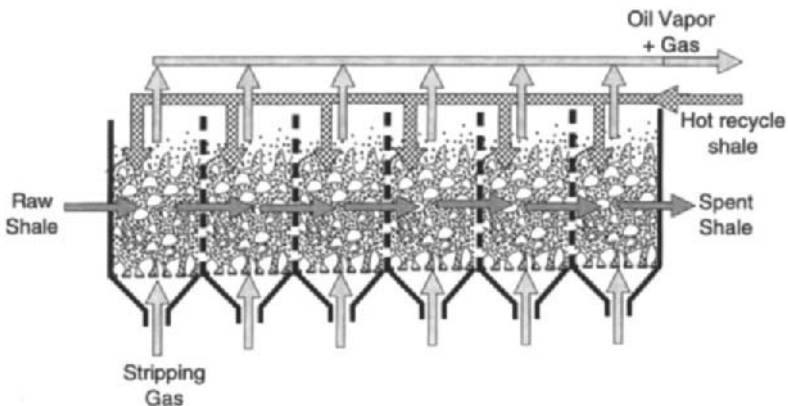


FIG. 12. The cross-flow multi-staged fluidized bed reactor concept used in the Shell Shale Retorting Process (Poll *et al.*, 1987).

enters the multi-compartment bed at the left. Baffles with large free area separate adjacent compartments, each of which may be considered to be well mixed. The flow of fluidized solids from one compartment to the next is by means of "hydrostatic" head, similar to the flow of water in a bathtub. If the number of horizontally disposed compartments exceeds about 10, we approach plug flow conditions of the solids. The overall contacting flow pattern for the reactor train as a whole is cross-flow. Within individual compartments, however, the gas (containing oil vapor) traverses up the bed in the form of bubbles virtually in plug flow, while the solids phase is almost completely backmixed.

A careful comparison of the Shell process with the existing technologies (Fig. 3) shows that none of the "ideal" subsets chosen is unique. Fine particles smaller than 3 mm are used in the SPHER and Chevron processes. Cross-current contacting is employed by Superior Oil and Kiviter technologies. The Chevron process uses a fluidized bed. However, the *combination* of these ideal subsets is apparently unique, and the promise of improved yield was sufficient to justify a substantial development effort (Poll *et al.*, 1987). There are also no scale-up problems envisaged in the multi-compartment 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. A vertically disposed multi-compartment configuration (Chevron; see Fig. 3) poses scale-up problems in addition to the undesirable long gas-solid contact time implicit in counter-current operation.

The benefits of employing a systems approach to the oil shale reactor selection example can be gleaned from the fact that the number of possible combinations of

- three particle size ranges (*cf.* Fig. 6),
- thirteen gas-solids contacting flow patterns (Fig. 9), and
- five gas-solids fluidization regimes (Fig. 11)

is $3 \times 13 \times 5 = 195$ reactor types! By adopting a *sequential* decision-making strategy, we have been able to arrive at the ideal reactor choice without brute-force evaluation of all the options.

III. General Selection Methodology for Multiphase Reactors

The oil shale reactor selection can now be generalized to the general case of multiphase reactors (gas-liquid, gas-solid, gas-liquid-solid,

liquid-liquid, liquid-liquid-solid), retaining the essential structure of the methodology. The discussions of the various ingredients of the general methodology are illustrated next, using several practical examples of commercial reactor selection.

A. THE WISH LIST

One of the most important aspects of the reactor selection example is the setting up of the wish list. This list may be crucial in arriving at the final decision. Omission of one item may in some cases lead to a completely different reactor choice. To take the example of the oil shale reactor, it was the "wish" to maximize yield of oil and prevent degradation of the oil vapor which culminated in the cross-flow configuration choice. On the other hand, in the interest of reducing process development costs, if we had wished for a simple, proven reactor configuration, the choice would perhaps have fallen on moving (packed) bed operation. For many organizations involved in process development, one common item in the wish list is that the reactor hardware choice should not constitute a major "step-out" in technology; such step-outs require huge development efforts. The cross-current multi-compartment fluid bed shale process does not constitute a major step out for Shell, which has considerable in-house expertise in fluid bed reactor design and scale-up (see, e.g., Van Swaaij and Zuiderweg, 1972, and Krishna, 1981).

Often the desire to maximize yield and selectivity of the reaction may lead to a reactor configuration that may pose operability problems; it is then the task of the experienced process developer to carefully weigh the alternatives and assign a hierarchy to the wish list. Operability, stability, and environmental constraints usually gain precedence. To give one example, the wish to maximize yield and selectivity may lead to the choice of 1-5 μm sized catalyst particles in a slurry reactor. This choice, though "ideal" from a transport phenomena-chemical kinetics analysis, will pose problems of separation from the product stream (operability problems). If the benefits of the use of 1-5 μm particles can provide a substantial competitive edge it may be worthwhile to examine the possibility of magnetizing the fine catalyst particles and employing an electromagnetic separation device. The net result of the systems approach could be a novel technology.

B. REACTOR SUBSET I—(VOLUME/SURFACE AREA) SELECTION

For multiphase reactors, the first important decision to be made concerns the choice of the (volume/surface area) ratio for each of the phases

in the reactor. We discuss some general guidelines for arriving at this choice for specific reactor types.

1. Gas-Solid Systems

The solid phase could be a reactant, product, or catalyst. In general the decision on the choice of the particle size rests on an analysis of the extra- and intra-particle transport processes and chemical reaction. For solid-catalyzed reactions, an important consideration in the choice of the particle size is the desire to utilize the catalyst particle most effectively. This would require choosing a particle size such that the generalized Thiele modulus ϕ_{gen} , representing the ratio of characteristic intraparticle diffusion and reaction times, has a value smaller than 0.4; see Fig. 13. Such an effectiveness factor-Thiele modulus analysis may suggest particle sizes too small for use in packed bed operation. The choice is then either to consider fluidized bed operation, or to use shaped catalysts (e.g., spoked wheels, grooved cylinders, star-shaped extrudates, four-leafed clover, etc.). Another commonly used procedure for overcoming the problem of diffusional limitations is to have nonuniform distribution of active components (e.g., precious metals) within the catalyst particle.

Often an important reason to avoid intraparticle diffusion resistances is from selectivity considerations. To maximize the intermediate product in a consecutive reaction scheme, we should avoid intraparticle diffusional resistances. For butene dehydrogenation it can be seen in Fig. 14 that

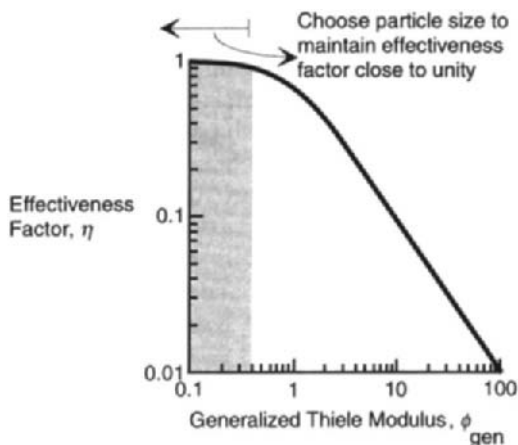


FIG. 13. Isothermal effectiveness factor, η , inside catalyst particles as function of the generalized Thiele modulus ϕ_{gen} .

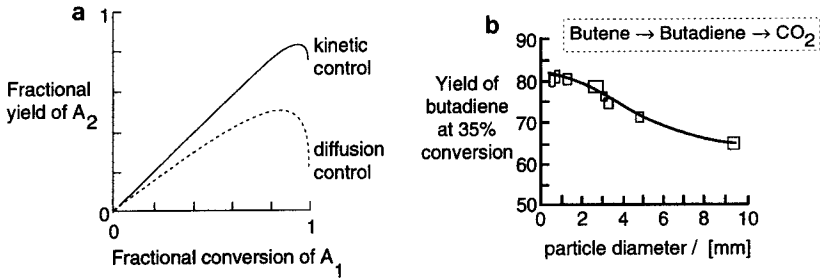


FIG. 14. Yield of intermediate product A_2 for the consecutive reaction scheme $A_1 \rightarrow A_2 \rightarrow A_3$. (a) Calculated fractional yield of A_2 as a function of conversion of A_1 . (b) Dependence of the yield of butadiene on iron oxide catalyst particle size at 620°C (Adapted from Voge and Morgan, 1972).

increased particle size has a significant deleterious effect on the yield of the intermediate product butadiene (Voge and Morgan, 1972).

For highly exothermic reactions, under certain operation conditions the effectiveness factor may exhibit multiple steady-state values; see Fig. 15. The “hot” branch has a high effectiveness, while the “cold” branch exhibits relatively low effectiveness-factor values. From an operation viewpoint, it may be prudent to avoid the region exhibiting multiplicity altogether (see shaded region in Fig. 15). Steady-state multiplicity within a single catalyst pellet has been experimentally confirmed for the oxidation of ethene. Such multiplicity of steady states within a single catalyst pellet can lead to multiplicity of steady states for the reactor considered as a whole (Adaje and Sheintuch, 1990), leading to problems in operation and control.

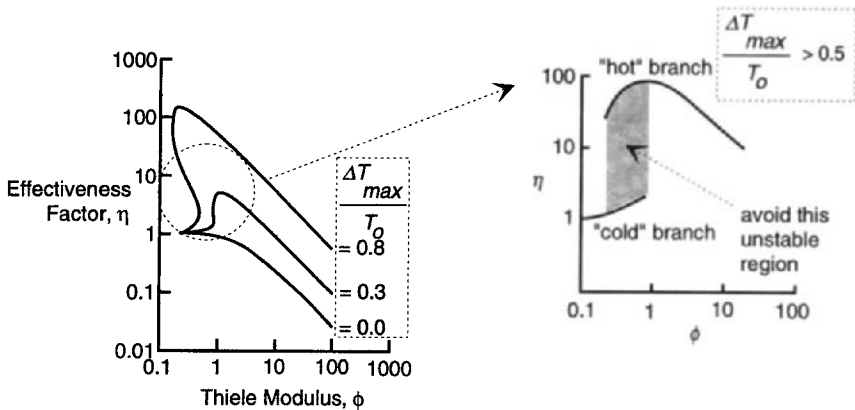


FIG. 15. Non-isothermal effectiveness factor for spherical particle as function of the Thiele modulus, ϕ . Adapted from Weisz and Hicks (1962) and Trambouze *et al.* (1988).

2. Gas-Liquid Systems

For a gas liquid system with reaction within the liquid phase, there are fundamentally three different modes of gas-liquid contact: (i) gas bubbles dispersed in liquid (as encountered in bubble columns), (ii) liquid droplets dispersed in gas (e.g., tray operating in the spray regime), and (iii) a thin flowing liquid film in contact with a gas (e.g., gas-liquid contacting in a packed column); see Fig. 16. 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, reactor subset I, for a gas-liquid system is the choice for this parameter β ; this choice is analogous to the particle size decision for a gas-solid reactor. The value of β takes on values in the range of 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. 17, which diagram is entirely equivalent to the effectiveness factor-Thiele modulus diagram of Fig. 13. The overall aim is to choose the value of β such that the reactor volume is effectively utilized. Thus, for slow liquid-phase reactions we should aim to increase the bulk liquid volume at the expense of interfacial area. We achieve a high value of β 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 we should choose a contactor with low value of β (e.g., spray towers and packed columns). Further, 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

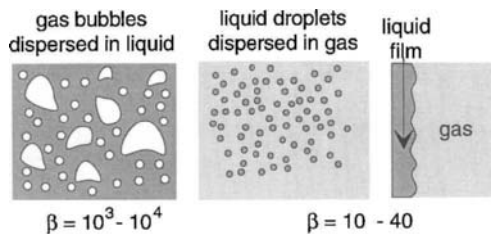


FIG. 16. Three fundamental procedures for contacting gases and liquids. β is the ratio of the liquid phase volume to the volume of the diffusion layer within the liquid phase.

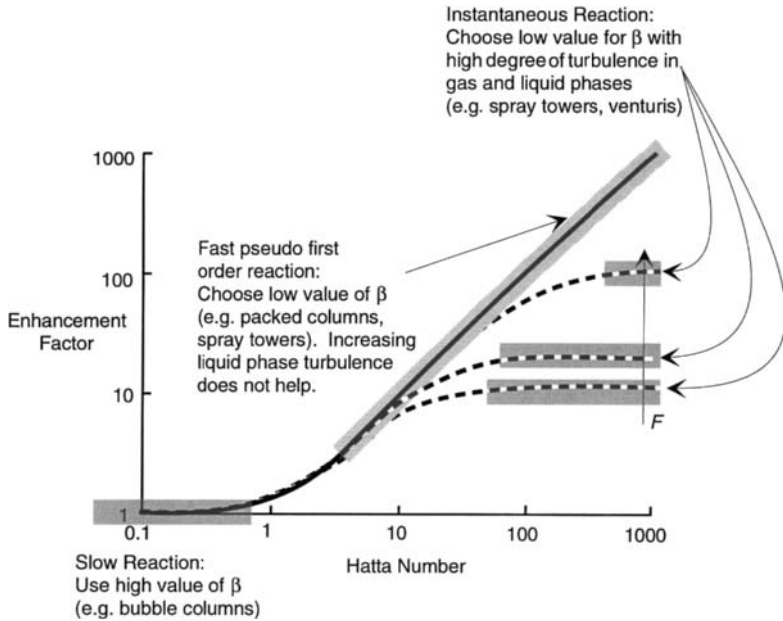


FIG. 17. Enhancement factor for gas-liquid reactions as function of the Hatta number; adapted from Trambouze *et al.* (1988).

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, our efforts, once again, should be to maximize the interfacial area at the expense of bulk liquid volume. In contrast to the fast pseudo first-order reaction 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 because of the desire to remove heat from the liquid phase; this heat is generated by the highly exothermic sulfonation reaction.

Often a more important aspect is the choice of β so as to maximize selectivity to a desired product. We shall illustrate this by considering the

example of selective absorption of hydrogen sulfide from a gaseous mixture containing carbon dioxide using amine solutions (Astarita *et al.*, 1983; Darton *et al.*, 1988; Doraiswamy and Sharma, 1984). The reaction between H₂S and amines takes place in the instantaneous regime, whereas the reaction between CO₂ and amines usually corresponds to the fast pseudo first-order reaction regime. The selectivity towards H₂S can be defined as the ratio of the number of overall gas phase mass transfer units for H₂S transfer to that for transfer of CO₂:

$$\text{Sel} = \frac{\text{NTU}_{\text{H}_2\text{S}}}{\text{NTU}_{\text{CO}_2}}$$

This ratio equals the ratio of the overall (gas-phase) mass transfer coefficients for transfer of H₂S and CO₂; see Darton *et al.* (1988). The overall gas-phase mass transfer coefficient for H₂S is the gas-phase transfer coefficient k_g . The overall gas-phase mass transfer coefficient for CO₂, is $H_{\text{CO}_2} \text{RTE} k_l$, where E is the enhancement factor for CO₂ transfer. Efficient reactor utilization and improved selectivity are obtained by (i) choosing low values of β , (ii) increasing k_g , and (iii) increasing the ratio k_g/k_l (see Bosch, 1989). Selectivity values Sel have been determined for several modes of gas-liquid contacting by Darton *et al.* (1988), some of which are pictured in Fig. 18. For tray columns, usually used for this selective absorption duty, the value of Sel has been estimated to be 72 for operation at a superficial gas velocity of 1 m/s, and this selectivity value can be increased to 138 by operating at a superficial gas velocity of 2 m/s. The probable explanation for this increase is that by increasing the gas velocity, we shift the flow regime on the tray from the froth regime to the spray regime with consequent decrease of β and increase of k_g . Use of cyclone scrubbers (thin liquid films in contact with high gas velocity stream) yields a selectivity value of 175. Use of a novel co-current upflow swirl tube promises a selectivity value of 1,250; see Darton *et al.* (1988). This exercise shows how a careful study of the factors influencing β , k_g , and k_l can lead to clues on how to achieve improved selectivities by improved contactor configurations. The swirl tube contactor has commercial potential of replacing conventionally used sieve tray absorbers.

Considerations of intrinsic process safety often dictate the choice of β ; we often desire to minimize the hold-up of hazardous materials in the reactor.

3. Gas-Liquid-Solid Systems

Here we need to choose both the solid particle size d_p and the ratio β . The considerations leading to the choices for these parameters are the

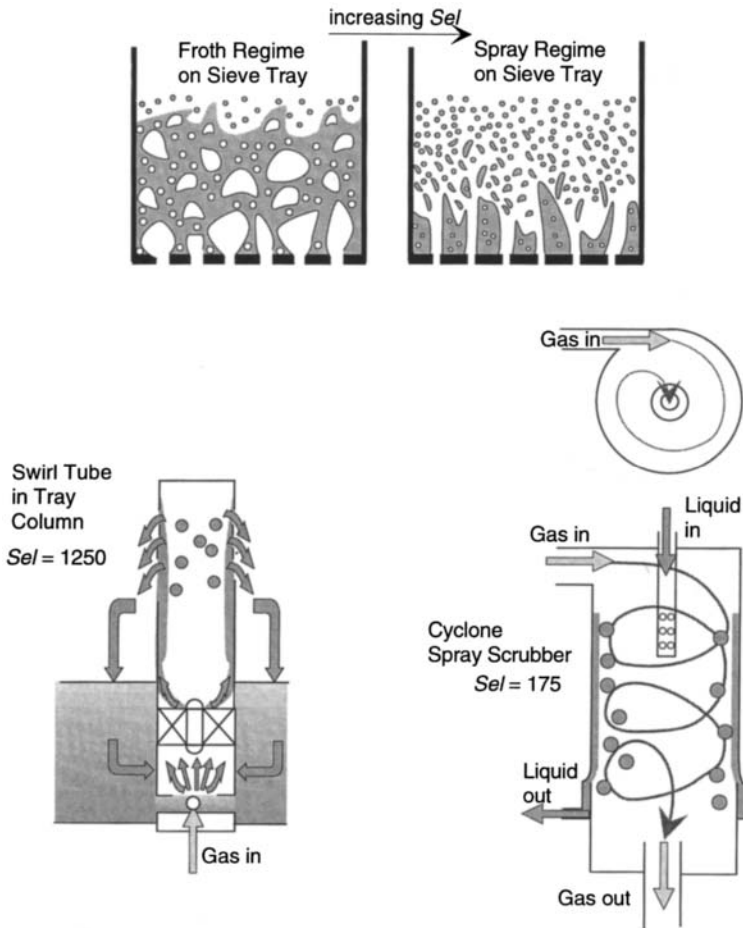


FIG. 18. Some contactors for selective absorption of hydrogen sulfide from carbon dioxide containing gaseous mixtures using amine solutions. Adapted from Darton *et al.* (1988).

same as before. If from a transport-reaction analysis we choose particle sizes smaller than 1 mm, we would need to consider slurry operations. On the other hand, if particle size larger than, say, 2 mm are allowable we have 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 further analysis in subsets II and III.

4. Liquid-Liquid Systems

Let us assume that the reaction takes place in one of the phases say L2. The ideal choice for the parameter $\beta_{L2} \equiv \epsilon_{L2}/\delta_{L2}a$ is dictated by the same considerations as for gas-liquid systems; *cf.* Fig. 17. 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. 16), 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.

C. REACTOR SUBSET II—CONTACTING FLOW PATTERN

This subset involves arriving at decisions on the following aspects of contacting of the individual phases.

- (a) The ideal residence time distribution of the individual phases.
- (b) For each reactant in the feed to the reactor, we need to evaluate whether it should be introduced at the reactor inlet or whether there is an incentive for progressive, staged addition.
- (c) We also need to evaluate the incentives for *in situ* removal of one or more products from the reactor.
- (d) The choice has to be made between the three main overall contacting methods: (i) countercurrent, (ii) co-current, and (iii) cross-current.

We consider each of the four items (a)–(d) in turn.

1. Subset IIa: Ideal RTD of Individual Phases

From the point of view of choosing the ideal reactor configuration, it is sufficient to decide whether we should aim for plug flow of a given phase or for a perfectly mixed state; this analysis is well covered in standard textbooks such as Levenspiel (1972). For 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; see Fig. 19. If we wish to maximize the intermediate A_2 in a consecutive

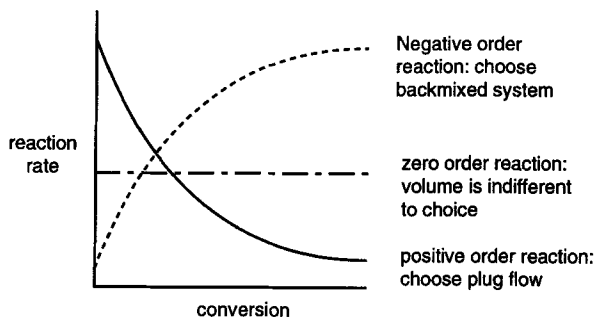


FIG. 19. Choice of residence time distribution for isothermal reactions of positive, zero, and negative order.

reaction scheme $A_1 \rightarrow A_2 \rightarrow A_3$ within a phase, we should aim for plug conditions (minimum axial dispersion); this conclusion is entirely analogous to the avoidance of intra-particle diffusion resistances (see Fig. 14).

For highly exothermic reactions, we usually have the dilemma: To mix or not to mix? From a concentration viewpoint we usually like to approach plug flow conditions, i.e., we do not wish to mix concentrations along the reactor. But from the point of view of temperatures, we would prefer a thermally well-mixed system. Let us consider the specific example of the oxidation of ethene to produce ethene oxide; see Fig. 20. This highly exothermic reaction is conventionally carried out in a cooled multi-tubular packed-bed reactor. Close to the inlet of the reactor we have a temperature peak (hot spot). At increasing temperatures there is loss of selectivity to ethene oxide because of the parallel, parasitic reaction to combustion products. The selectivity profile along the length is shown in Fig. 20; the temperature hot spot clearly leads to a loss of selectivity. Our systems approach leads to the conclusion that we ought to have a system with perfect thermal backmixing (from selectivity considerations) and no concentration backmixing (from the point of view of improved conversions). The question is: Can we achieve both? One solution to this problem is to incorporate a heat pipe on the outside of the tube wall of each packed tube that would help rapid axial thermal equilibration. Such a device has been suggested by Parent *et al.* (1983) for the oxidation of naphthalene to phthalic anhydride. Some of their key results have been summarized in Fig. 21; these show the remarkable improvement in the yield of the desired phthalic anhydride product due to near isothermal operation with heat pipes. Such systems need closer examination and further experimental study. Richardson *et al.* (1988) have incorporated a sodium heat pipe within an (endothermic) reforming reactor with the objective of approaching isothermal operation. This concept has potential application in fixed-

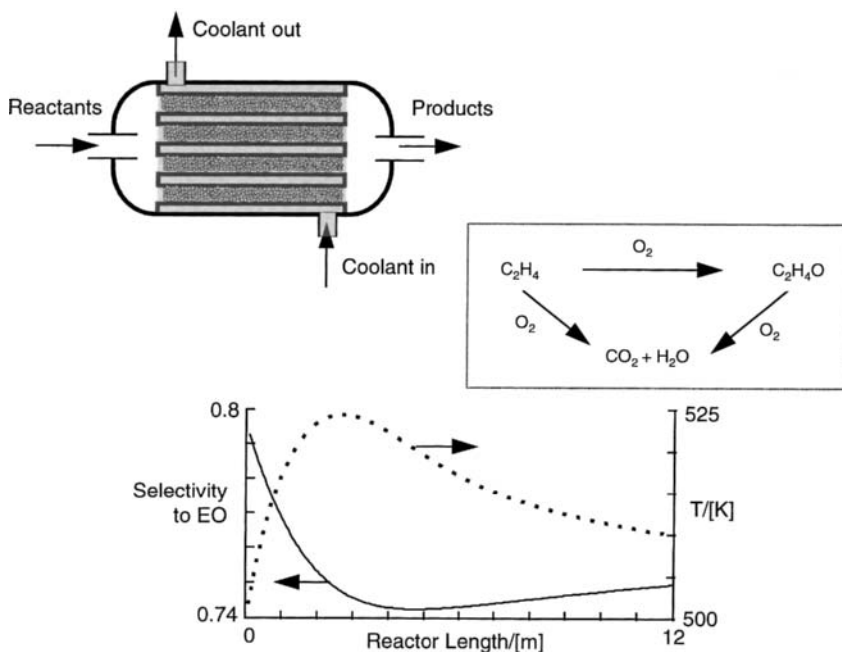


FIG. 20. Temperature and selectivity profiles for the exothermic reaction of oxidation of ethene to ethene oxide in a multi-tubular packed bed reactor. The selectivity to ethene oxide is defined as the number of moles of ethene oxide produced per mole of ethene converted. The simulations for the reactor temperature and selectivity were carried out using the kinetic data of Westerterp and Ptasincki (1984).

bed catalytic reforming where steep temperature gradients are experienced at the reactor inlet because of high endothermicity. Catalyst coking is usually a problem at the entrance to the bed. By using heat pipes to ensure temperature redistribution, we may limit this coking tendency and consequently lengthen cycle times.

Use of cold quench gases or evaporating solvents and recycle of solids are other options to obtain thermal equilibration. In the Du Pont process for production of maleic anhydride by oxidation of butane, a dense phase circulating bed riser reactor is used (Contractor and Sleight, 1988). Solids recycle allows catalyst regeneration and, further, ensures that isothermal conditions are approached. In order to avoid the attrition problems inherent with solids recycle systems, the catalyst may be coated with a thin layer of material such SiC or SiO_2 . Circulating bed reactors have tremendous potential for carrying out exothermic gas–solid reactions, especially with deactivating catalysts (see Gianetto *et al.*, 1990); this potential is as yet largely untapped.

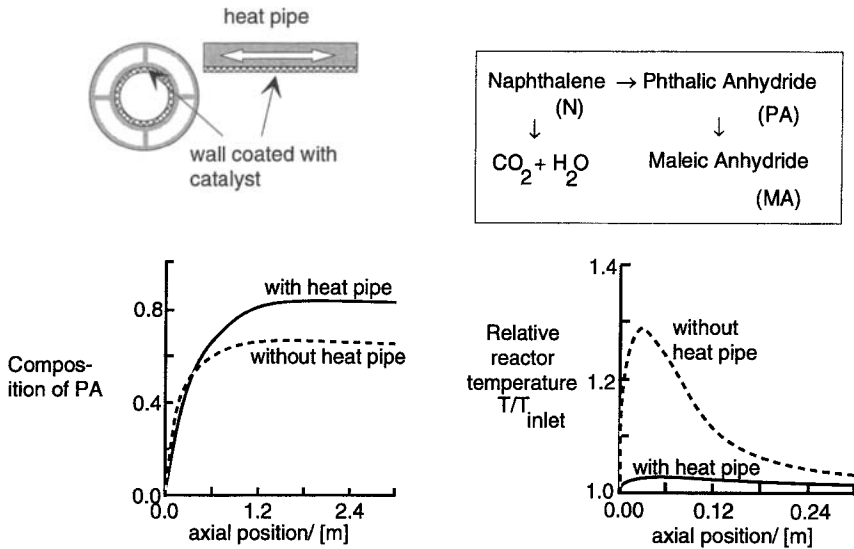


FIG. 21. Composition and temperature profiles in a tube-wall catalytic reactor, with and without heat pipe, for oxidation of naphthalene to phthalic anhydride. Adapted from Parent *et al.* (1983).

2. Subset IIb: Staged (Progressive) Injection of Reactant(s)

As our first illustration we consider the co-dimerization of propene and butene to produce heptenes (Reaction 1). This reaction is accompanied by two competing, undesirable, reactions: dimerization of propene to hexene (Reaction 2), and dimerization of butene to octene (Reaction 3). The second reaction proceeds extremely rapidly and in order to suppress the formation of hexenes we should have progressive injection of propene into the reactor with all the butenes at the beginning of the operation, as is shown in Fig. 22 (Trambouze *et al.*, 1988).

Consider the process for manufacture of detergent alcohols (ALC) by hydroformylation of liquid olefins in the C₁₁-C₁₂ range (OLF) with syngas

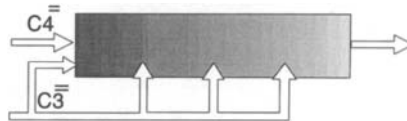
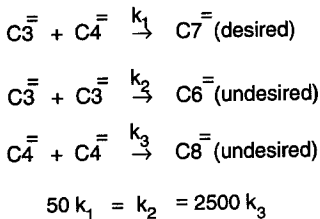
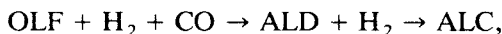
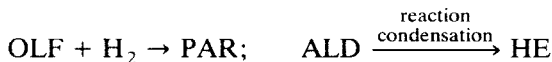


FIG. 22. Co-dimerization of propene and butene. For maximizing selectivity towards heptene we use progressive injection of propene.

(H₂ and CO), using homogeneous liquid-phase cobalt based catalyst. The reaction can be written as



where ALD is the intermediate aldehyde. Side reactions to produce paraffins (PAR) and dimer alcohols (“heavy ends” = HE) are unavoidable in practice:



In order to suppress the undesirable side reaction to paraffins, commercial operations employ an H₂/CO ratio lower than the stoichiometric value of 2:1. A commercial hydroformylation reactor train, whose configuration is sketched in Fig. 23a, was analyzed with a view to improving the selectivity to detergent alcohols. The systems approach described in this article was used to arrive at the “ideal” reactor configuration. The complete checklist of reactor attributes and subsets was analyzed with the help of a detailed kinetic model. The clue to selectivity improvement was found to lie in the use of staged, progressive addition of hydrogen. The split syngas addition scheme is shown in Fig. 23b. The existing (a) and suggested (b) schemes have the same reactor hardware designs and total feed streams. In the split syngas scheme (b), the first reactor in the train is fed with an H₂/CO = 1.4. The balance of hydrogen (to make up for the overall ratio H₂/CO = 1.9) is supplied to the subsequent stages 2, 3, 4, and 5, in equal proportions. Figure 23c provides a comparison of the schemes (a) and (b). The higher yield of alcohols in scheme (b) is to be attributed to the suppression of paraffin formation in the first reactor by reduced supply of H₂. The reduced paraffin production is translated into a concomitant increase in alcohol production. For the commercial unit that was studied, the improvement in the product slate had a value of \$2 million per annum. The split syngas injection scheme could be realized quite simply by use of an in-line membrane separator (the Monsanto PRISM separator) for readjustment of syngas composition by selective removal of hydrogen. The payout for the capital investment in the membrane separator was on the order of 6 months.

The hydroformylation case study just discussed underlines the economic incentives for careful examination of existing processes for possible improvements by altering reactor configuration.

We may also consider staged injection of one of the reactants as a method of “quenching” exothermic reactions; cold hydrogen gas quench is used, for example, in hydrocracking of vacuum gas oils.

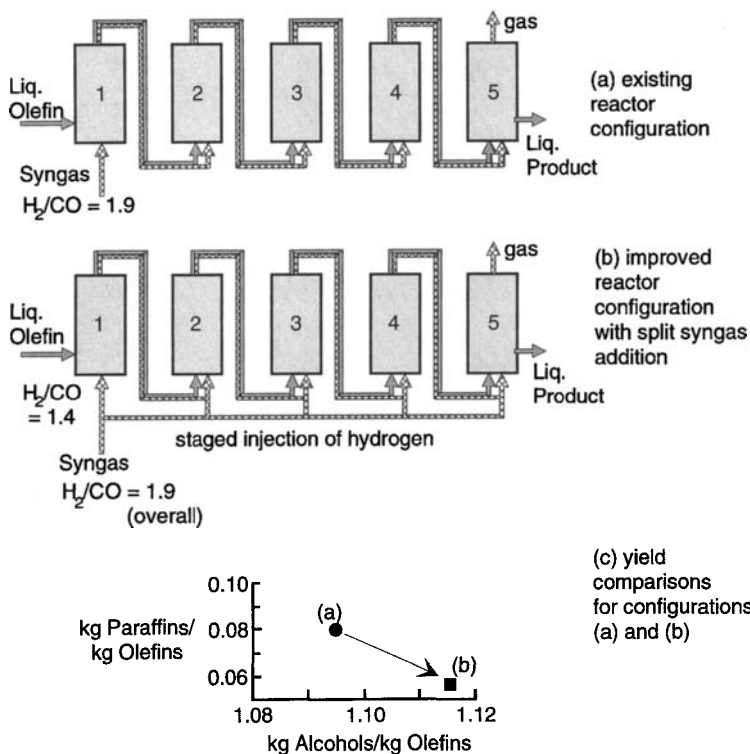


FIG. 23. Hydroformylation of liquid olefins (C_{11} – C_{12}) with syngas (H_2 and CO). (a) Configuration in existing commercial unit consisting of five bubble column reactors in series. (b) Improved configuration arrived at by systems approach, involving staged injection of hydrogen. (c) The yields of alcohols (desired product) and paraffins (undesired product) are compared for configurations (a) and (b).

In the examples just considered, one of the reactants was introduced in a progressive, staged manner. Pursuing this line of attack, we should examine the benefits in keeping the two reactants completely segregated from each other and allowing them to meet only within the pores of the catalyst. The active components of the catalyst could be incorporated within a ceramic membrane with the reactants on either side. Figure 24 shows the schematic diagram of such a catalytic membrane reactor for carrying out the Claus reaction (Sloot *et al.*, 1990):



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

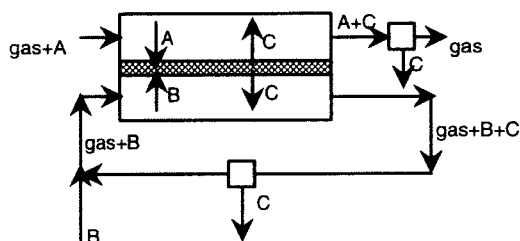


FIG. 24. Catalytic membrane reactor for carrying out the Claus reaction: $2\text{H}_2\text{S} + \text{SO}_2 \leftrightarrow \frac{3}{8}\text{S}_8 + 2\text{H}_2\text{O}$. Adapted from Sloot *et al.* (1990).

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 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, 1991) for catalytic reduction of nitric oxide with ammonia; by keeping the reactants separated and allowing reaction only within the membrane, we will be able to cope with varying ratios of concentration of nitric oxide and ammonia without incurring significant slip of reactants.

Another class of processes where it is advantageous to keep the reactants separated from each other, except within the catalyst pores, is oxidation of light gaseous hydrocarbons (e.g., ethene, propene, butene). Conventionally these processes are carried out in multi-tubular fixed-bed reactors (see, for example, Fig. 20). Flammability considerations usually restrict the feed mixture composition. By adopting the concept of a multi-tubular cooled catalytic membrane reactor (with inclusion of heat pipes?), with reactants kept separate, we should be able to avoid any flammability constraints.

3. Subset IIc: *In Situ* Separation of Product(s) from Reactor Zone

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

a. Deliberate Addition of Second Liquid Phase. By deliberate addition of a second liquid phase containing a selective solvent, we may extract the desired product from the reaction zone and prevent further side reactions.

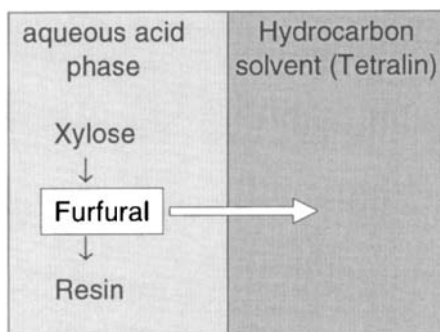


FIG. 25. *In situ* extraction of intermediate furfural (desirable product) by means of hydrocarbon solvent (tetralin).

Figure 25 shows a specific example of extraction of furfural using a hydrocarbon solvent. Sharma (1988) has considered several other examples of reactions which would profit from introduction of an additional phase. Sharma (1988) has also provided several examples of liquid-liquid reactions of industrial interest which could benefit from the addition of substances such as quaternary ammonium and phosphonium salts, crown ethers and trialkyl amines, which function as phase transfer catalysts, significantly enhancing the reaction rates and in some cases improving the reaction selectivity.

b. In Situ Distillation. The technique of reactive distillation is well known for carrying out esterification reactions (Doherty and Buzad, 1992). This concept has gained considerable attention recently for carrying out catalyzed liquid-phase reactions; the catalyst in this case is usually incorporated in the form of a structured packing. Figure 26 shows a schematic diagram of the catalytic distillation concept for the production of tertiary amyl ether (TAME). The rectifying section is packed with catalyst "bales"—a kind of rolled-up structured packing. Another alternative is to incorporate the catalyst in the form of a thin coating on conventionally used structured packing material, e.g., from Sulzer. There is considerable scope for equipment development here. For example, we may envisage suspending the catalyst in the form of "tea bags" within the froth zone of a distillation tray.

In situ product separation by distillation offers applications in esterification (e.g., for ethyl acetate), trans-esterification (e.g., for butyl acetate), hydrolysis (e.g., for ethylene glycol, isopropyl alcohol), metathesis (e.g., for methyl oleate), etherification (e.g., for MTBE, ETBE, TAME), and alkylation reactions (e.g., for cumene).

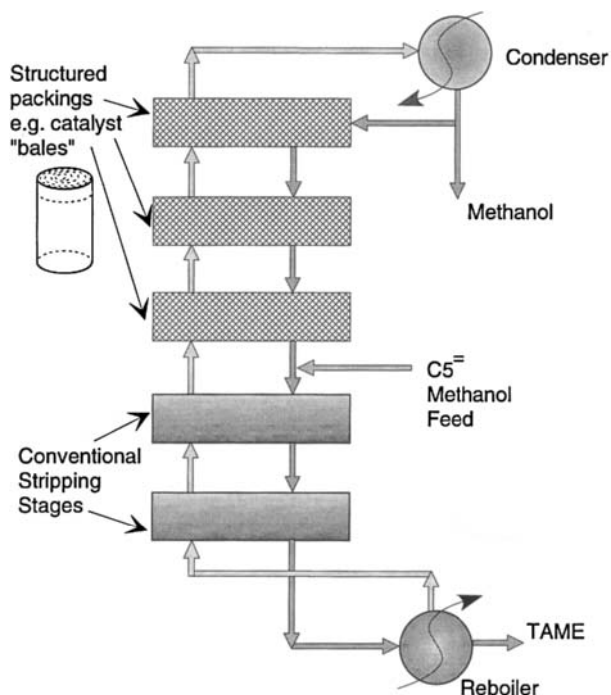


FIG. 26. Catalytic distillation scheme for tertiary amyl ether (TAME) manufacture.

c. In Situ Adsorption. A novel reactor concept suggested by Van Swaaij and Westerterp involves the use of a solid adsorbent, in trickle phase through a packed catalytic reactor, for selective removal of a product; see Fig. 27. This concept has been demonstrated experimentally by Kuczynski (1986) for synthesis of methanol, an equilibrium-limited reaction.

Another possibility for *in situ* adsorption is to fluidize both catalyst and adsorbent phases (i.e., gas–solid–solid fluidized bed or gas–liquid–solid–solid fluidized bed). We may, for example, envisage a *four*-phase methanol synthesis process where the liquid phase, containing an inert hydrocarbon solvent, would serve as a thermal flywheel for this highly exothermic reaction.

d. In Situ Supercritical Extraction. In equilibrium-limited biocatalyzed reactions, removal of the desired products, which are often thermally labile, *in situ* by supercritical extraction with carbon dioxide can lead to substantial benefits. In the lipase-catalyzed interesterification of triglycerides, for example, a high degree of incorporation of required fatty acids into triglyceride cannot be obtained because of its reverse reaction: Tricaprylin

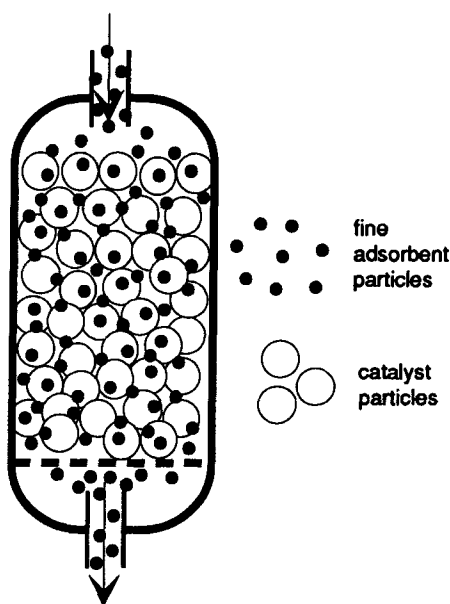


FIG. 27. Gas–solid–solid trickle flow reactor concept for *in situ* adsorption of product.

+ methyl oleate \leftrightarrow 1-oleodicaprylin + 1,3-dioleocaprylin + methyl caprylate. Adschiri *et al.* (1992) have applied supercritical carbon dioxide extraction to the removal of products from a liquid-phase reaction system as a means of solving the problem.

e. Membrane Reactor for Selective Removal of Product. A permselective ceramic membrane-walled tubular catalytic reactor can be considered for carrying out dehydrogenation reactions; the membrane serves to selectively remove the hydrogen, thus shifting the equilibrium towards the right. This concept is shown schematically in Fig. 28. An experimental study by Becker *et al.* (1993) has shown that use of this concept for dehydrogenation of ethyl benzene results in a 20% increase conversion over conventional fixed-bed operation. Other reactions where the use of permselective membranes in catalytic reactors can be expected to lead to significant improvements include dehydrogenations of propane, butane, and cyclohexane. A survey of potential applications of inorganic membrane reactors is given by Hsieh (1991).

4. Subset II*d*: Counter-, Co-, or Cross-Current Contacting

The decision whether to adopt counter-, co-, or cross-current contacting (see Fig. 9) is dictated by factors such as equilibrium limitations, flooding,

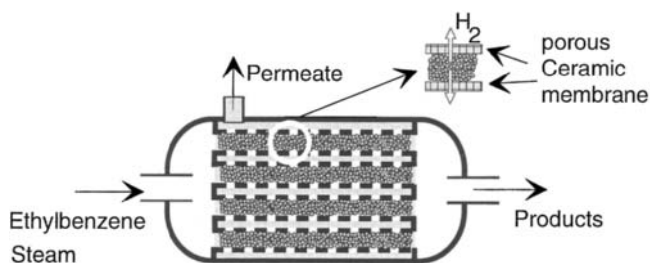


FIG. 28. Permselective membrane reactor concept for dehydrogenation of ethyl benzene to produce styrene.

and pressure drop. For gas–solid moving-bed systems the three possible modes of operation are shown in Fig. 29. Co-current downflow and cross-current moving beds are most commonly used, with the latter configuration (with radial inflow of gas) being preferred in order to reduce the pressure drop. The continuous catalyst regeneration (CCR) technology for reforming of naphtha using Pt-based catalysts uses this cross-current concept. One potential problem which may be encountered during scale-up of such reactors is the pinning of the catalyst particles to the screens; this aspect limits the allowable gas velocities. Also, catalyst attrition may cause problems such as blockage of solids flow and can cause excessive pressure drop.

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 countercurrent operation from considerations of phase and reaction equilibrium.

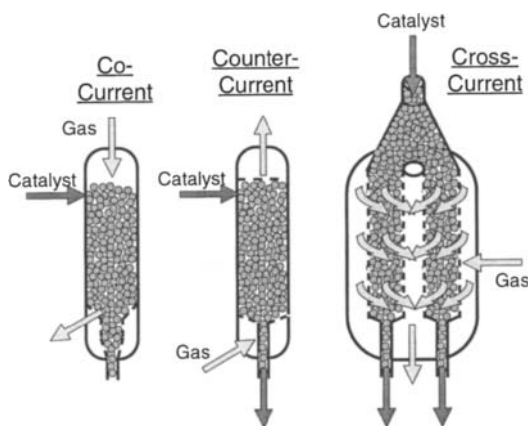


FIG. 29. Co-, counter-, and cross-current contacting for moving-bed gas–solid reactors.

For gas–liquid–solid systems, the commonly used contacting patterns are sketched in Fig. 30. Generally speaking we should anticipate several scale-up problems for three-phase reactors wherein solids are being transported (e.g., for reasons of catalyst deactivation). But the perception of these problems by different development groups could be quite different, resulting in different choices of reactor configurations. This is illustrated quite nicely by the hydrodemetalization (HDM) process. For this application the following widely different configurations are in use, or under development (Dautzenberg and De Deken, 1984):

- Fixed trickle beds with co-current down flow of gas and liquid (Fig. 30a)
- Moving beds with co-current down flow of gas and liquid (Shell HYCON process; Fig. 30c)
- Moving beds with co-current up flow of gas and liquid (IFP process; Fig. 30d)
- Three-phase fluidized beds (also called ebullating beds) with particle sizes usually larger than 1.5 mm (Fig. 30g)
- Slurry reactors with fine particles, usually smaller than 1 mm (Fig. 30f).

It is interesting to note the sharp contrast between the options in Fig. 30c and 30d used respectively by Shell and Institut Français du Pétrole (IFP), respectively. The Shell moving trickle bed technology (HYCON) for HDM was introduced for commercial operation in The Netherlands in 1989; this technology involves co-current downflow of gas, liquid, and catalyst phases. Engineers at IFP have opted for a different solution with upflow of gas and liquid phases. Any fine particles generated by attrition would be fluidized and transported out of the reactor. The two different approaches highlight the different perceptions of Shell and IFP with regard to potential scale-up problems.

In the Shell Middle Distillates Synthesis (SMDS) process starting from natural gas, the reactor configuration chosen for the first commercial unit in Malaysia, successfully commercialized in 1993, is the multi-tubular downflow trickle bed with catalyst inside the tubes (Sie *et al.*, 1991); see Fig. 30e. Because of the enormous exothermicity of the synthesis reaction and the relatively poor heat transfer an extremely large heat transfer area is required. The reactor volume is largely governed by the installable heat transfer area in a vessel of given volume. Use of the multi-tubular three-phase fluidized bed or slurry reactor (see Fig. 30k and 30l) provides much better heat transfer characteristics (an improvement of a factor of five over fixed bed units) and could lead to considerably lower reactor volumes. However, the anticipated scale-up problems with three-phase

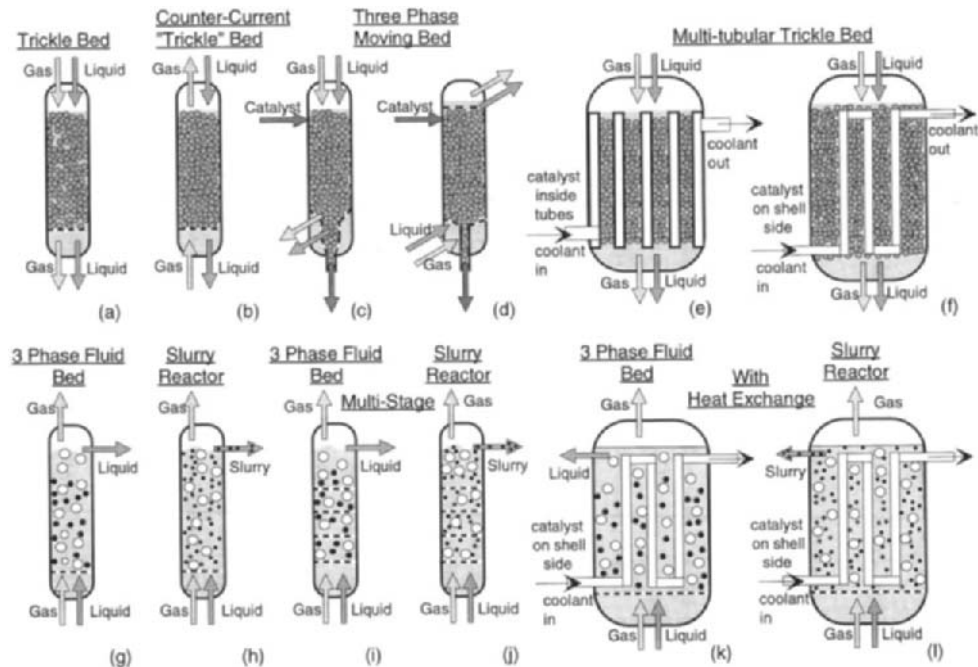


FIG. 30. Contacting patterns and contactor types for gas-liquid-solid reactors. (a) Co-current downflow trickle bed. (b) Countercurrent flow trickle bed. (c) Co-current downflow of gas, liquid, and catalyst. (d) Downflow of catalyst and co-current upflow of gas and liquid. (e) Multi-tubular trickle bed with co-current flow of gas and liquid down tubes with catalyst packed inside them; coolant on shell side. (f) Multi-tubular trickle bed with downflow of gas and liquid; coolant inside the tubes. (g) Three-phase fluidized bed of solids with solids-free freeboard. (h) Three-phase slurry reactor with no solids-free freeboard. (i) Three-phase fluidized beds with horizontally disposed internals to achieve staging. (j) Three-phase slurry reactor with horizontally disposed internals to achieve staging. (k) Three-phase fluidized bed in which cooling tubes have been inserted; coolant inside the tubes. (l) Three-phase slurry

fluidized-bed operation were of overriding concern for Shell, who decided to adopt the fixed-bed technology because of quicker development scenario. 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.

For aromatic hydrogenations, co-current downflow in fixed trickle beds is normally used, but as pointed out by Trambouze (1990), there are distinct advantages in opting for countercurrent operation because of equilibrium considerations. Hydrocracking of vacuum gas oil is another process traditionally carried out in co-current downflow in fixed beds in trickle flow. Higher conversions are possible with a countercurrent hydrocracking operation. Problems with countercurrent operation, however, are excessive pressure drop and flooding limitations. To overcome these problems we need to consider larger-sized (say, 5 mm) "shaped" catalysts in the form of Raschig rings or Berle saddles (Trambouze, 1990).

D. REACTOR SUBSET III—CHOICE OF FLOW REGIMES

1. *Gas-Solid Systems*

The various flow regimes for gas-solid systems are shown in Fig. 4. 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 (see Fig. 11). 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 one year, fixed-bed operation is usually preferred. If the time interval is of the order of one week we usually opt for swing-type operation using two beds; 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 few hours, then moving-bed operations can be considered, such as in the continuous catalytic regeneration (CCR) technology for naphtha reforming. If the time between successive regenerations is of the order of less than one hour, then fluidized-bed operation is appropriate. 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), it is usually not advisable to fluidize it because of inevitable losses through cyclones.

Other reasons, distinct from catalyst deactivation, for choosing fluidized-bed operation could be the desire to use particles smaller than, say,

1 mm (such particles are usually not allowable in packed- or moving-bed operation because of excessive pressure drop). Sometimes, the desire to have a completely thermally backmixed system (Subset 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 (R-2 in Fig. 11), 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 “fast” fluidization 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. The choice of an “ideal” regime of operation for the FCC regenerator can be rationalized by an analysis of the gas-to-solid mass transfer characteristics of the regimes R-2, R-4, and R-5 of Fig. 11. For typical operating conditions in the FCC regenerator, the values of the overall volumetric mass transfer coefficient per reactor volume, $k_g a$, have been estimated; these are shown in Fig. 31 along with the pseudo first-order reaction rate constant for reaction of

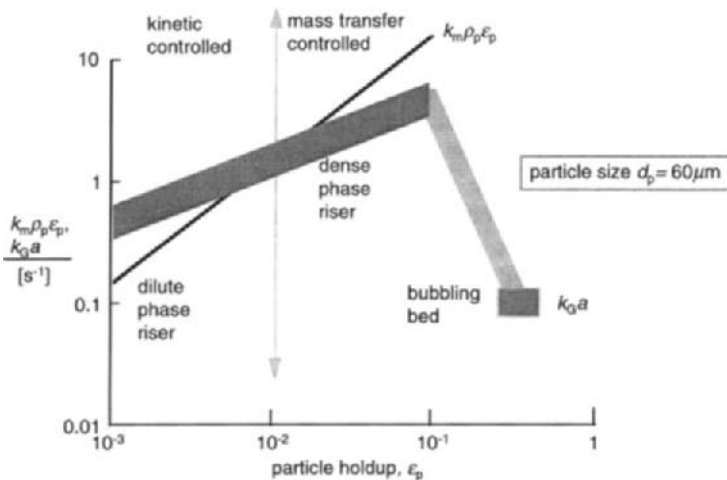


FIG. 31. Gas-to-solid mass transfer characteristics of various regimes of operation for FCC regenerators. R-2, R-4, and R-4 refer to the regimes sketched in Fig. 11. The kinetic data for coke burn off is taken from Hano *et al.* (1975). The gas-solids mass transfer coefficient for riser reactors is estimated from the Van der Ham *et al.* (1993) correlation. The estimation of volumetric mass transfer coefficient in fluid beds is from the model of Krishna (1981). Further details of the calculations presented in this figure can be found in Krishna (1993).

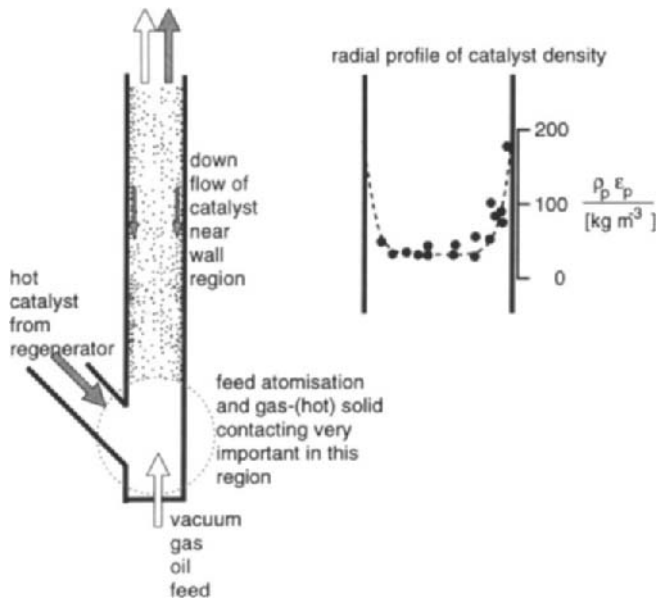


FIG. 32. FCC riser hydrodynamics. The solids concentration near the wall is considerably higher than at the center. Radial catalyst density profile measurements of Schuurmans (1980).

oxygen with coke: $k_m \rho_p \epsilon_p$. In the bubbling bed regime R-2, the reaction of oxygen with coke is governed by interphase mass transfer, while in dense- and dilute-phase riser transport, regimes R-4 and R-5, respectively, the reaction is kinetically controlled. Despite the large uncertainty in estimation of the $k_g a$ values, it is clear from Fig. 31 that the overall rate of reaction of oxygen is highest at particle hold-ups in the range 0.2–0.3, i.e., in the dense-phase riser transport (“fast” fluidization) regime. This explains the reason why modern regenerators adopt the fast fluidization regime. There is, however, a large degree of uncertainty in the scale-up of circulating dense-phase fluid beds. For the cracking reactor in FCC operations we should aim for pure plug flow of gas and catalyst in order to prevent overcracking of gasoline to light gases. Since backmixing of catalyst is undesirable, the dilute-phase riser transport regime, R-5 of Fig. 11, is normally chosen as the reactor configuration. A closer examination of the riser hydrodynamics (see Fig. 32) reveals that the concentration of solids near the wall of the riser is significantly higher than at the center and there is downflow of catalyst near the wall (Schuurmans, 1980). This higher catalyst concentration in the wall region leads to overcracking. There is a great economic incentive to devise a reactor configuration with

a closer approach to plug flow of catalyst. One possible solution is to have co-current downflow of gas and catalyst in the reactor, i.e., a “downer.” Other aspects of FCC operation which need attention are better feed atomization and gas–solid contacting at the feed inlet. We may consider pre-fluidization of the hot solids before allowing contact with liquid feed.

2. Gas–Liquid Systems

For upflow of gas through liquids, in vertical columns, there is complete correspondence of flow regimes; see Fig. 33. 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, our regime choice moves from left to right in Fig. 33. One possible starting point in the choice of the flow regime is consideration of the parameter β , already chosen in Subset I. Regimes to the left of the flow regime map of Fig. 33 correspond to high β (the choice for relatively slow liquid-phase reactions), whereas towards the right we have low β values (a choice for high rates of liquid-phase reactions). To achieve low β values we could, for example, operate in the spray regime in a tray column (see, e.g., Fig. 18). The

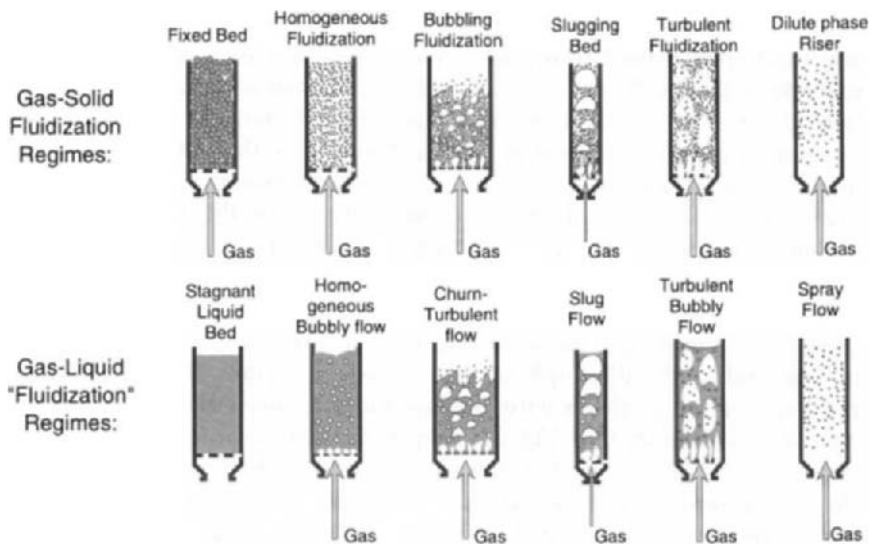


FIG. 33. Gas–solid and gas–liquid flow regimes in vertical columns with upflow of gas.

analogue of the turbulent or “fast” fluidization regime of gas–solids flow is the regime called turbulent bubbly flow in Fig. 33; this is the regime prevalent in air lift fermentors, for example. In air lift fermentors we aim 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 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).

While in the foregoing we have stressed the analogies between gas–solid and gas–liquid flow regimes, there are some important practical differences in the hydrodynamics of these systems. The operating window for the homogeneous fluidization regime for gas–solid systems is extremely narrow, and it is normally not possible to design a commercial reactor to operate in a stable manner in this regime. The situation is somewhat different for gas–liquid systems; the homogeneous bubbly flow regime is a common choice for gas–liquid systems because of the much wider operating window with respect to gas velocity. The churn-turbulent flow regime of gas–liquid flow is characterized by the presence of large fast-rising bubbles, typically 50 mm in size, co-existing with small, about 5 mm sized, bubbles (Krishna *et al.*, 1993). These fast-rising bubbles, akin to the bubbles in a gas–solids fluid bed, cause the contents of the reactor to be churned up (*i.e.*, backmixed) and reduce the efficiency of gas–liquid contact. At the regime transition point we should experience a sharp decrease in the reactor performance; this is indeed found to be the case in practice for the Fischer Tropsch synthesis reaction where the liquid phase additionally contains fine catalyst particles (see Fig. 34). The importance of properly selecting the flow regime is demonstrated by this example.

3. Gas–Liquid–Solid Systems

Here the solid phase could be a catalyst or an inert packing material. If the solid phase is the catalyst, the first question to answer is whether to transport the solids or not; the considerations leading to this decision are entirely analogous to those for the gas–catalyst system and relate to the time interval between successive regenerations. If it is decided not to transport the solids *i.e.*, to choose fixed beds, we have the following options (see also Fig. 30):

- (i) Co-current downflow of gas and liquid,
- (ii) Co-current upflow of gas and liquid, and
- (iii) Countercurrent flow of gas and liquid.

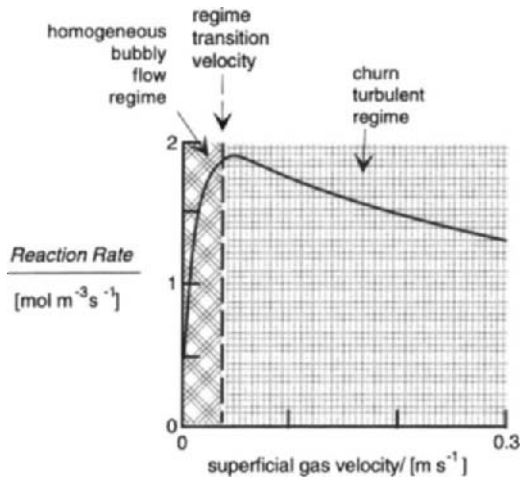


FIG. 34. Rate of reaction of syngas ($A = CO + H_2$) as a function of superficial gas velocity for Fischer-Tropsch synthesis in the slurry phase. Adapted from Krishna (1993)

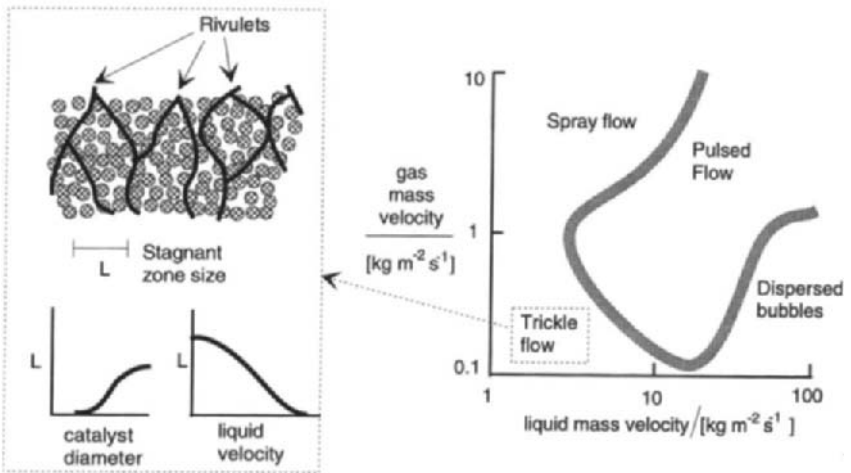


FIG. 35. Flow regime map for co-current downflow of gas and liquid through packed beds.

Let us first consider co-current downflow of gas and liquid (Fig. 30a); for this case the flow regime map is shown in Fig. 35. The most commonly used regime of operation is the trickling flow regime. To achieve good wetting of catalyst, the superficial liquid velocity has to be of the order of 10 mm/s (see Trambouze *et al.*, 1988). Another possible solution to overcome the problem of liquid stagnancy in trickle beds is to increase the gas velocity and operate under pulsing flow conditions. For laboratory columns operating in the pulsing flow regime, it has been shown that the stagnant zones are swept away by the pulses (Blok *et al.*, 1983), resulting in better contacting and mass transfer. It is, however, not certain that commercial units, typically of diameters greater than 2 m, can be made to operate in the pulsing flow regime. Another aspect which needs to be taken into account when choosing the flow regime of operation is the influence of system pressure on flow regime transitions. Increased-pressure operation tends to stabilize the trickle flow regime, and the transition to the pulsing flow regime is “delayed” (Wammes, 1990).

Another strategy to avoid the wetting and stagnancy problems associated with co-current downward trickle flow is to opt for co-current upflow; the various flow regimes are shown in Fig. 36 (Shah, 1979). We normally choose the bubble flow regime. The IFP technology for HDM utilizes this regime of operation.

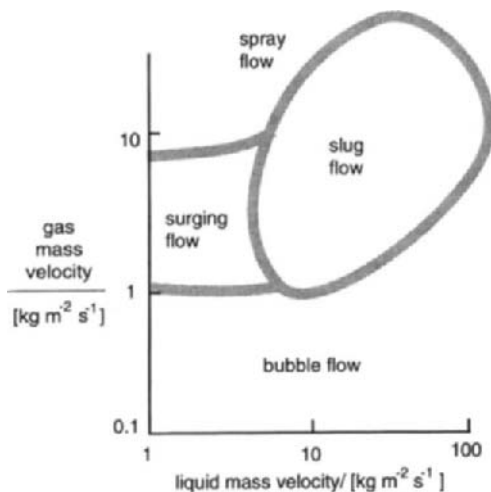


FIG. 36. Flow regimes in co-current upflow of gas and liquid through a packed bed of solids. Adapted from Shah (1979).

The analysis in Subset II may point to the choice of countercurrent operation through a packed bed. The most commonly used regimes here are trickle flow and bubble flow. The possibility of flooding places an important constraint on the choice of the operating gas and liquid flow velocities. The pressure drop is significant for small catalyst particles; this precludes countercurrent operation unless shaped catalyst particles are used.

Three-phase fluidized beds and slurry reactors (see Figs. 30g–l) in which the solid catalyst is suspended in the liquid usually operate under conditions of homogeneous bubbly flow or churn turbulent flow (see regime map in Fig. 33). The presence of solids alters the bubble hydrodynamics to a significant extent. In recent years there has been considerable research effort on the study of the hydrodynamics of such systems (see, e.g., Fan, 1989). However, the scale-up aspects of such reactors are still a matter of some uncertainty, especially for systems with high solids concentration and operations at increased pressures; it is for this reason that the Shell Middle Distillate Synthesis process adopts the multi-tubular trickle bed reactor concept (*cf.* Fig. 30e). The even distribution of liquid to thousands of tubes packed with catalyst, however poses problems of a different engineering nature.

IV. Closing Remarks

In this article we have advocated the use of a systematic, structured approach to reactor selection. The reactor selection exercise is conveniently split into three, separate, sequential decisions on the following subsets, or attributes:

Subset I: Volume-to-surface area of each phase

Subset II: Contacting flow pattern of the phases

Subset III: Multiphase flow regimes.

For each of these subsets we have further provided a checklist of reactor parameters that need to be examined. The choice of each item in the checklist is made on the basis of a wish list, set up right at the beginning of the reactor selection exercise. Figure 37 presents a summary of the reactor attributes and considerations along with a commonly used “wish” list. In the discussions we have stressed the point that a disciplined approach may unravel novel ways of improving reactor performance; this has been demonstrated by means of several examples.

Reactor Attributes	Considerations
<p>Reactor Sub Set I: (Volume/Surface area)</p>	<ul style="list-style-type: none"> - effectiveness factor - influence of intra-particle transport on selectivity - thermal stability - gas-liquid reaction regime (slow, fast pseudo first order or instantaneous)
<p>Reactor Sub Set II Contacting Flow Pattern</p> <p>(a) Ideal RTD of each phase</p> <p>(b) Staged injection of reactants</p> <p>(c) In-situ separation of products from reaction zone</p> <p>(d) Counter-, Co- or Cross-current contacting</p>	<ul style="list-style-type: none"> - To mix or not to mix ? - thermal stability - selectivity in complex reaction sequence - selectivity - thermal quenching - flammability limits - shift reaction equilibrium -selectivity -reaction equilibrium -pressure drop -flooding - catalyst deactivation and frequency of regeneration
<p>Reactor Sub Set III Choice of Flow Regime</p> <ul style="list-style-type: none"> - packed/moving bed - homogeneous G-S fluidization = bubbly flow in G-L systems - heterogeneous G-S fluidization = churn turbulent flow in G-L systems - circulating G-S fluid bed = air lift G-L reactor - G-S riser transport = G-L spray system 	<ul style="list-style-type: none"> - realisation of decisions in SubSets I and II - interphase transfer - heat removal capability - backmixing characteristics of individual phases - scale-up know-how - catalyst deactivation rates and frequency of regeneration

- Wish List**

 - ease of scale-up
 - ease of operation
 - freedom from instabilities and runaways
 - environmental acceptability
 - maximum conversion of reactants
 - maximum selectivity to desired products
 - low capital and operating costs
 - intrinsically safe process
 - minimum hold up of hazardous materials

FIG. 37. Summary of reactor selection methodology. The “wish” list is used to arrive at various “decisions” on the three reactor subsets. In arriving at the decisions there are several reactor engineering parameters which need to be taken into account; these are listed under “considerations.”

The systems approach presented here has been mainly developed for application within the petroleum and petrochemical industries and, therefore, is restricted to continuous "steady-state" processing on a large scale. It is worthwhile examining the extension of these concepts to unsteady-state processing and batch operations. Also, there may be other ways to structure the reactor selection problem to suit one's own work environment and technology culture.

Notation

a	interfacial area per unit reactor volume, m^{-1}
d_p	particle diameter, m
C_A^*	molar concentration of component A which is in equilibrium with the bulk gas phase, mol m^{-3}
C_{Bb}	molar concentration of liquid phase component B, mol m^{-3}
D_{eff}	effective diffusivity within catalyst particle, $\text{m}^2 \text{s}^{-1}$
D_l	liquid-phase diffusivity, $\text{m}^2 \text{s}^{-1}$
E	enhancement factor for gas-liquid reaction
F	dimensionless parameter $F \equiv (D_{Bl}C_{Bb})/(D_{Al}C_A^*)$
H_{CO_2}	Henry coefficient for CO_2 , $\text{mol m}^{-3} \text{Pa}^{-1}$
Ha	Hatta number $Ha \equiv \sqrt{k_1 D_l}/k_l$
k_g	gas-phase mass transfer coefficient, ms^{-2}
k_1	pseudo first-order reaction rate constant for homogeneous liquid-phase reaction, s^{-1}
k_l	liquid-phase mass transfer coefficient, ms^{-1}
k_m	pseudo first-order reaction rate constant for catalytic reaction, defined per kilogram of catalyst, $\text{m}^3 \text{kg}^{-1} \text{s}^{-1}$
L	characteristic length of particle, m
NTU	number of overall gas phase mass transfer units
R	gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
Sel	Selectivity for absorption of hydrogen sulfide from a gaseous mixture in presence of carbon dioxide
S_p	external surface area of particle, m^2
T	temperature, K
ΔT_{max}	maximum temperature rise in catalyst pellet, K
T_o	surface temperature of catalyst pellet, K
V_p	volume of particle, m^3

Greek Letters

β	ratio of liquid phase volume to volume of diffusion layer $\beta \equiv \epsilon_l/\delta_l a$
δ_l	thickness of diffusion layer of liquid phase $\delta_l \equiv D_l/k_l$, 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
ϕ	Thiele modulus for spherical particle

$$\phi \equiv \frac{d_p}{2} \sqrt{\frac{k_m \rho_p}{D_{\text{eff}}}}$$

ϕ_{gen} generalized Thiele modulus

$$\phi_{\text{gen}} \equiv \frac{V_p}{S_p} \sqrt{\frac{k_m \rho_p}{D_{\text{eff}}}}$$

Subscripts

A	referring to component A, usually in gas phase
B	referring to component B, usually in liquid phase
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
p	referring to particle
1	pseudo first-order parameter

Superscript

* referring to equilibrium value

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