Process intensification in trickle-bed reactors

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Abstract

Process intensification (PI) is the strategy of making significant reductions in the size of a chemical plant in order to achieve a given production objective. Innovations in catalytic reactors, which constitute the heart of such process technologies, are often the preferred starting point. Trickle-bed reactors are multifunctional reactive systems (catalysts, reactors, etc.), and allow a unique way of achieving PI in the chemical process and refining industry. In this millennium, process intensification in trickle-bed reactors is essential to meet the ultra low specification of the transportation fuel. The process intensification by operating at elevated pressure and temperature, and better understanding of flow behavior (which also helps for better design and scaleup), inducing pulse and operating in countercurrent mode is discussed here. Recommendations have been made for the future research in this area.

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1. Introduction

Trickle-bed reactors (TBRs) are generally fixed bed catalytic reactors in which gas and liquid flow in cocurrent downward mode. The main application of TBR lies in the petroleum refining industry, more specifically in hydrefracking. Excellent reviews on trickle-bed reactors can be found in Ng and Chu (1987), Gianetto and Specchia (1992), Saroha and Nigam (1996), Al-Dahhan et al. (1997) and Dudukovic et al. (2002). The current status in trickle-bed reactors with respect to hydrodynamics and its effect on process intensification has been discussed. The development over the last 10 years has been mainly targeted in this review. The different hydrodynamic, mass transfer and heat transfer parameters on the performance of TBR are shown in Fig. 1. The drive to reduce air pollution has caused a myriad of new and proposed sulfur specifications. The restriction on impurities (mainly sulfur) in transportation fuel is going to be more stringent. The lower the specification of transport fuel, the tougher it gets. An integrated approach (catalyst selection, reactor design, process configuration) will be able to lead this situation. The process intensification will help to cope up the situation in addition to development of catalyst. Process intensification can be done by revamping the existing unit of TBR or a new unit of TBR with higher severed operating condition or installing alternative types of TBR. Though there is a lot of improvement on understanding the behavior of TBR, still it needs further progress to cope up with the present situation. Wettability of the catalyst has been explained based on contact angle of the liquid on the surface of porous particle as alternating patches of saturated pore and solid surface. The hysteresis behavior of hydrodynamics using this concept has also been explained.

Recent studies have demonstrated reactor performance improvement over the optimal steady state under forced time-varying liquid flow rates. In this mode of operation, the bed is periodically flushed with liquid, while the gas phase is...
fed continuously. The liquid adds a transport resistance for the gaseous reactant that is often rate controlling for sparingly soluble gaseous reactants. The liquid phase, however, is essential to the system and cannot be eliminated. By periodic operation of a trickle-bed reactor, the transport resistance for the gaseous reactant is periodically reduced. This phenomena and its contribution towards process intensification has been explained here.

Conventional hydrodesulfurization is carried out in countercurrent down flow trickle-bed reactors. The desulfurization reaction is product inhibited. As the reaction progresses down the reactor, the reaction slows down considerably for two reasons: (1) the hydrogen partial pressure reduces as hydrogen is consumed and (2) the H2S formed, inhibits the reaction rate. Deep desulfurization in conventional trickle-bed reactors is thus extremely difficult. However, if the trickle-bed reactor were to be run in counter-current flow mode, the major part of the catalyst bed would operate in an H2S lean mode thus allowing ultra-low sulfur levels to be achieved economically in the hydrocarbon liquid phase. One could conceive a multifunctional catalytic system that would allow counter flow trickle-bed operation without a high ΔP penalty. Ring-shaped catalysts have been used in some desulfurization processes such as SynSat, but the bed depths are small as ring-shaped catalysts cannot take much weight. Structured catalysts such as Sulzer’s Katapak-S or M-Series or the composite structured packing described above may be worthwhile investigation targets. The countercurrent operation and different structured packing used in the literature has been discussed here.

2. Trickle beds at elevated temperature and pressure

Trickle-bed reactors are operated at high pressures up to about 20–30 MPa in order to slow down catalyst deactivation, improve the solubility of the gaseous reactant, attain high conversion and achieve better heat transfer. Kinetics and/or thermodynamics of reactions conducted in TBRs require high temperatures, which in turn increase gas expansion and impede the gaseous reactant from dissolving sufficiently into the liquid. Elevated pressure acts against it and helps to improve the solubility. Effect of operating pressure on different hydrodynamic parameters (pressure drop, liquid holdup, and wetting efficiency) is important for designing and scaling up purpose. The main reason behind changing the values of hydrodynamic parameters with the increase of operating pressure lies on the energy dissipation. The energy dissipation is due to the resisting frictional forces at the packing surface and the driving forces on liquid flow. The driving forces consist of the pressure gradient, the gas–liquid interfacial drag and the gravitational force. A simple overall force balance on the gas phase shows that the pressure gradient is proportional to the gas–liquid interfacial drag. The pressure gradient depends, besides the bed characteristics, on the velocities of both phases and on the physicochemical properties of the flowing fluids. With the increase of pressure, only gas density changes of all physicochemical properties of the flowing fluids. Thus, for given gas and liquid velocities, a higher gas density produces a higher interfacial drag force or equivalently a higher-pressure gradient. The gravitational force depends on liquid density and is not affected by pressure in the usual operating range of TBRs (less than 30 MPa). Therefore, the effect of gas on the pressure drop can be split into an effect of the superficial gas velocity and another one due to gas density. Increased gas density leads to increased gas–liquid interaction and the higher pressure drop. With the increase of operating pressure, the liquid holdup decreases whereas wetting efficiency increases. With the increase of operating pressure, the operating range in trickle-flow regime also increases.

A large number of studies have been reported in the literature on the various hydrodynamic aspects of trickle-bed reactors. Though most of the research studies before 1990 have been performed at atmospheric pressure (Sai and Varma, 1987; Ellman et al., 1988, 1990), a considerable number of investigations have been performed in pressurised trickle-bed reactors after that period (Wammes et al., 1991; Al-Dahhan et al., 1998; Larachi et al., 1991; Nemec et al., 2001 and Guo and Al-Dahhan, 2004).

Numerous attempts are being made to model the hydrodynamics of trickle-bed reactors. It ranges from merely empirical correlations (Ellman et al. 1988,1990; Larachi et al., 1991; Iliuta et al., 1999a,b) to physically sound models (Holub et al., 1992; Al-Dahhan et al., 1998; Iliuta et al., 2000; Säez and Carbonell, 1985; Carbonell, 2000; Nemec et al., 2001; Attou et al., 1999; Tung and Dhir, 1988
Table 1
Comparison of theoretical models for the prediction of hydrodynamics in TBR

<table>
<thead>
<tr>
<th>Authors</th>
<th>Model</th>
<th>Characteristics of the model</th>
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| Saez and Carbonell (1985)      | Relative permeability model     | 1. The model is based on Ergun’s equation  
2. The relative permeability of each phase has been correlated as a function of liquid saturation of each phase depending on the experimental results  
3. The gas–liquid interaction term has been neglected. |
| Holub et al. (1992, 1993); Al-Dahhan and Dudukovic (1994); Al-Dahhan et al. (1998); Iliuta et al. (1999b) | Slit model                      | 1. The complex geometry of the actual void space in the catalyst bed at the pore level has been represented by the much simpler flow inside a rectangular slit.  
2. It is modified form of Ergun equation  
3. Initially it is considered zero shear stress at the gas-liquid interface. Later Al-Dahhan et al. (1998) expressed the gas and liquid phase slip parameters as a function of gas and liquid phase Reynolds numbers. |
| Tung and Dhir (1988); Narasimhan et al. (2002); Kundu et al. (2003c) | Model based on fundamental force balance | 1. It involves force balance equations in liquid and gas phase in elemental reactor volume.  
2. The gas–liquid interfacial drag has been taken into account  
3. The tortuosity effect corrects the gravity term in the liquid phase and gas phase force balance equations |
| Attou et al. (1999)            | 1D-CFD model                    | 1. These models are based on macroscopic mass and momentum conservation laws.  
2. The liquid–solid and gas-solid interaction forces are formulated on the basis of Kozeny–Carman equation.  
3. Model does not predict well at low D/dp ratio (< 12–14) due to column wall effect.  
4. The gas–liquid interfacial drag has been considered. |
2. Drag force is evaluated using concept of relative permeability of each phase as proposed by Saez and Carbonell (1985) |
| Fourar et al. (2001)           | F-function concept              | 1. This model is based on Forchheimer’s equation originally employed to explain the inertia deviations in Darcy’s law for single phase flow.  
2. Phasic F-function is multiplied with superficial velocity of each fluid. |
| Jiang et al. (2002) and Gunjal et al. (2003) | k-fluid model                   | 1. The Eulerian CFD model, the flow equations are solved for the kth fluid.  
2. The drag exchange coefficients are obtained from the Holub model. |

No consensus has emerged as to whether general approaches yielding pressure drop with acceptable accuracy can be recommended (Larachi et al., 2000). This is ascribable to many causes, among which the following are most frequently mentioned: (i) the complexity of the gas–liquid flow patterns prevailing in trickle beds, (ii) the lack of accurate descriptions of two phase flow interactions, (iii) the complex relationship between trickle bed hydrodynamic characteristics, fluids and bed properties, and interfacial interactions, (iv) the restricted range of the experimental data, and of the models/correlations derived thereof, usually reported for individual studies.

In the category of physically sound models, six distinct approaches have been used for the prediction of hydrodynamics in TBRs. These are (i) the relative permeability model (Sæz and Carbonell, 1985) (ii) slit model (Holub et al., 1992, 1993; Al-Dahhan and Dudukovic, 1994; Al-Dahhan et al., 1998; Iliuta et al., 1999b) (iii) model based on fundamental force balance (Tung and Dhir, 1988; Narasimhan et al., 2002) (iv) 1D-CFD model (Attou et al., 1999; Souadnia and Latifi, 2001) (v) F-function concept (Fourar et al., 2001) (vi) CFD model (Jiang et al., 2002; Gunjal et al., 2003). Salient features of each model are figured in Table 1.

Process intensification in trickle-bed reactors is always carried out with the operation at high pressure and high temperature. When the process needs more conversion with respect to HDS, HDM and HDN, trickle-bed reactors are operated at high pressure and high temperature. Also in the case of hydrocracking, TBRs are operated at very high pressure and temperature to get the extreme severity. The total operating pressure is set by the design pressure of the unit and it cannot be increased to the desired operating pressure beyond the design pressure. So the existing unit by increasing operating pressure and temperature can be operated up to the level of design pressure and temperature to get process intensification.
3. Wettability and porosity

In TBRs, flow of gas–liquid over porous catalyst particle is extremely complex. Liquids may or may not wet the surface completely. Some important reactor design parameters like pressure drop, liquid holdup and wetting efficiency affected by this external surface coverage of the particle or spreading of liquid over the particle. Here change in wettability refers to the change in liquid flow, which increases or decreases fractional coverage of the particle, i.e., wetting efficiency.

External wetting efficiency (i.e., fraction of external area of catalyst effectively wetted by the liquid flowing down the bed) of the catalyst is an important feature in trickle-bed operation as it gives an indication of the extent of catalyst utilisation. It is a function of flow rates of gas and liquid, operating pressure, physical properties of liquid and diameter of the catalyst. The external wetting efficiency of catalyst in trickle-bed reactor has been obtained experimentally from a chemical method based on reaction rates, dynamic tracer technique and dissolution and dye adsorption technique. Many authors have used the dynamic tracer technique (Al-Dahhan and Dudukovic, 1995, 1996; Ring and Missen, 1991; Mills and Dudukovic, 1981), which allows the determination of wetting efficiency in actual beds under operating conditions. Llano et al. (1997) has determined the wetting efficiency using reaction method. In reality, the reaction method requires an adequate reactor model, the main difficulty of which lies in axial dispersion.

There are two approaches to predict the wetting efficiency in TBR. In one approach, it is expressed as the ratio of particle-liquid drag forces in two-phase flow and liquid-filled operation. Assuming the whole liquid flowing as a falling film and the gas phase as a continuous phase in the trickle-bed reactor configuration, point force balances are applied to the two flowing phases. Gas and liquid flow configurations in a unit volume cell representing cross-sectionally averaged flow conditions are shown in Fig. 2. The annular configuration has been postulated here, but such a force balance should be equally applicable to other flow regimes, provided the effect of flow regimes is accounted elsewhere.

In the figure, Particle–gas drag force, $F_{PG}$ is opposed by an equal and opposite force applied by the particles on the other side of the liquid layer. $F_I$ is the drag force on the gas as a result of relative motion between the two phases (Narasimhan et al., 2002). The force balance on the gas phase is given by:

$$\{(dP/dZ) + \rho_G g \tau \} \alpha \epsilon = F_{PG} + F_I. \quad (1)$$

The term $\alpha$ is the gas saturation, which is defined as the volume of gas present in a void volume of the reactor and may be obtained from the difference of the value of unity and the liquid saturation, $\beta$. The liquid phase force can also be broken into two components $F_{PL}$ and $F_{PG}$. The first component $F_{PG}$ is simply a reaction to the force by which the gas pushes the liquid against the particles. The second component $F_{PL}$ represents the force acting on the particles due to the liquid motion. The force balance on the liquid then yields

$$\{(dP/dZ) + \rho_L g \tau \} (1 - \alpha) \epsilon = F_{PL} - F_I. \quad (2)$$

$F_{PG}$, $F_{PL}$, and $F_I$ represent the drag forces per unit of total bed volume. The model for particle-liquid and particle-gas drag was obtained from the modified Kozeny–Carman equation. The model equations are elaborated in Narashiman et al. (2002).

Another approach for quantifying wetting efficiency is based on the understanding of liquid movement over the porous catalyst (Khanna and Nigam, 2002). Recent efforts by Starov et al. (2002a–c, 2003) have provided a valuable insight into the mechanics of the process based on Brinkman’s equations for description of flow inside the porous layer and by lubrication and continuum theory for liquid drop flow over it (Starov, 1983; Teletzke et al., 1987). That analysis is extremely useful for conditions where a fixed amount of liquid (drop) is put on porous substrate. In trickle-bed reactors, a continuous flow of liquid is maintained along with gas flow. It is therefore essential to understand the intricacies between porous surface and movement of liquid on it to develop better understanding of the above design parameters/hydrodynamic parameters in TBR.

Khanna and Nigam (2002) tried to improve the understanding of liquid movement on porous catalyst using a conceptual model. They modeled the surface of porous particle as alternating patches of saturated pore and solid surface. With increasing wettability the wetting efficiency increases as the contact line advances on solid surface and eventually merges with neighbouring rivulets. One starts with a wetting efficiency of I (Fig. 3) and film morphology as in stage A, increase in wettability results first in a regular increase (Stage B) in the wetting efficiency followed by a small...
decrease (the first transition, B → C) and then again a regular increase (Stage C) followed by a sudden vertical increase (the second transition, C → D) and once again a regular increase (Stage D). When the catalyst wettability decreases, the contact line starts decreasing and will result in a reduction of the wetting efficiency. The retracting contact line retracts on a wetted surface unlike on a dry surface. After reaching the edge of the liquid filled pore, it becomes stationary so that any more retraction is very difficult, which leads to unusually high wetting efficiency (Stage D → E, Fig. 3). If non-homogeneities are present in the form of completely wettable saturated pore and partially wettable solid patches, film rupture happens showing a sudden dip in wetting (Stage F in Fig. 3). Depending on whether the wettability change forces the contact line to move across a saturated pore or a solid surface the wetting efficiency will change at either faster or slower rates (Fig. 4). They found that microscopic wettability of solid catalyst has a direct effect on thickness of the liquid film that covers the solid catalyst. Higher wettability would translate into thinner films.

From the above argument it is shown that pore has a prominent role on enhancement of liquid spreading and on pinning or holding back of liquid during retraction. Maiti et al. (2004b) supplemented the above argument by using the experimental observation of Ravindra et al. (1997) and in house study of Arora (2002). Also in the light of the above pore level conceptual framework of Khanna and Nigam (2002) it was assumed that porosity should play a role in hysteresic behavior of TBR. Therefore hysteresic observation was re-examined to improve the understanding of the hysteretic behavior of trickle-bed reactor.

4. Pore induced hysteresis

In the light of recent work by Khanna and Nigam (2002), Arora (2002) and Maiti et al. (2004) whereby porosity is shown to play a major role in spreading and retraction of liquid, it was expected that porosity of the packing material is likely to play a major role in hysteretic behavior of TBR. Therefore hysteretic behavior of TBR was re-examined in the above pore level conceptual framework.

The performance of TBR depends mainly on two hydrodynamic parameters viz., pressure drop across the reactor and liquid hold-up inside the reactor. The performance of the reactor is mostly predicted by using experimentally developed empirical/semi empirical correlations for these parameters. Recently a more fundamental approach was proposed to predict hydrodynamic parameters like pressure drop, liquid hold-up and wetting efficiency considering
gas–liquid–particle interaction and tortuosity factor (Narasingh et al., 2002; Kundu et al., 2003c). These developments are chronicled in reviews of (Zhukova et al., 1990; Gianetto and Specchia, 1992; Saroha and Nigam, 1996; Al-Dahhan et al., 1997; Sie and Krishna, 1998; Kundu et al., 2003b; Maiti et al., 2004a). Predictions of these correlations and actual performance of TBR differ significantly in many cases. One of the major contributors to these differences has been existence of hysteresis in pressure drop and liquid holdup at same liquid and gas flow rate in TBR (Kan and Greenfield, 1978, 1979; Ravindra et al., 1997).

It has been reported that this hysteresis depends on three factors viz., startup conditions, the mode of operation and the type of packing material (Ravindra et al., 1997). The startup conditions refer to the state of the system with respect to initial prewetting or non-prewetting of the solid packing by the liquid. The mode of operation refers to how the desired flow has been attained whether by increasing the flow of fluid from a low value or decreasing it from a high value. The type of packing material refers to it being porous or nonporous. Among all these studies, only one study (Ravindra et al., 1997) has looked at the influence of all the three control parameters. In all these studies hysteresis has been attributed to the difference between advancing and receding contact angle in rivulet and film flow of liquid over the solid packing. The porous/nonporous nature of the packing though being taken as one of the control parameters has not been taken into consideration. An attempt has been made to examine this role based on the framework proposed by Khanna and Nigam (2002) and subsequent analysis of Maiti et al. (2004b).

5. Induced pulsing

Sometimes process intensification of a trickle-bed reactor can be obtained by forced no steady operation. For process intensification it is required to improve the mass transfer characteristics of the limiting reactant. Simultaneously, flow maldistribution and the formation of hot spots must be prevented or at least controlled. If we can control the wetting efficiency as a function of time and utilizing the advantages associated with pulsing flow, it is possible to meet the demands for process intensification.

Unsteady operations can be performed in one of two ways

- in the slow mode, where with a time interval of the order of minutes periodic changes of liquid feed rate and/or reactant concentration are forced;
- in the fast mode where short pulses of liquid, in the order of seconds, travel through the column.

TBRs are usually operated at steady-state conditions. Recent studies have demonstrated reactor performance improvement over the optimal steady state under forced time-varying liquid flow rates. In this mode of operation, the bed is periodically pushed with liquid, while the gas phase is fed continuously. This on-off feed strategy increases reactor performance in case the limiting reactant is in the gas phase. During the liquid flush, heat and products are removed from the catalyst, while in between flushes, the gaseous reactants can more easily adsorb on the catalyst. The overall mass transport rate of the limiting gaseous reactant to the catalyst is increased. Haure et al. (1989) and Lee et al. (1995) used this concept for the oxidation of SO$_2$ to sulfuric acid. They reported the increase in oxidation rates up to 50%. During the periodic operation, higher bed temperatures were encountered compared to steady-state operation (see Fig. 5 for temperature variation in the catalyst bed, adopted from Boelhouwer, 2001). Only half of the rate enhancement could be attributed to these higher temperatures. The additional improvement is due to an increase in the mass transfer of oxygen to the catalyst. The duration of the flush is determined by the time needed to fully regenerate the catalyst.

To demonstrate the advantages of periodic operation on a reaction, in which both the gas and liquid phase contain reactants, the hydrogenation of $\alpha$-methyl styrene was studied by Lange et al. (1994); Castellari and Haure (1995); Gabarain et al. (1997) and Lange et al. (1999). These studies reported the increase in reaction rates up to 400%. Recently, Urseanu et al. (2004) compared the performance of TBR with the periodic operated TBR for hydrogenation of $\alpha$-methyl styrene over 2 wt% Pd/C catalyst in a pilot scale reactor at temperature of 40 $^\circ$C and pressure of 0.2 MPa. They obtained an increase of 50% in reaction rate in periodic operation.

Periodic operation results in significant increase in production capacity and conversion compared to steady state operation for gas-limiting reactions. For liquid limiting reactions, steady state operation is superior to periodic operation. The optimal durations of the high and low liquid feed are strongly interdependent.

A fast cycling of the liquid feed is most effective in terms of production capacity, conversion and selectivity. With increasing cycled liquid feed frequency, the time average concentration of the liquid phase reactant inside the catalyst
increases and the time-average concentration of the product decreases. High concentrations of liquid phase reactant result in high reaction rates for the desired reaction. Low concentration levels of the product lead to low reaction rates for the undesired reaction.

Process intensification using periodic operation of TBR is obvious with respect to liquid distribution, temperature distribution and overall reactor performance. So far this technique has not found any commercial application in hydroprocessing.

6. Filtration and induced pulsing

A promising perspective to forced periodic operation concerns the stretching of the life cycle of trickle-bed hydrotreaters experiencing plugging due to fines deposition in some petroleum industry operations. Such situations occur for instance when the clay-containing Athabasca oil sand bitumen are refined in trickle-bed hydrotreaters. Plugging develops and leads to progressive obstruction of the catalyst bed that is often accompanied with a rise in pressure drop. Although the fines concentration lies typically in the 100 ppm range, the cumulative effect of several months of refining operation diverts the catalyst bed from its catalytic function to that of a huge filter. In these conditions, the unit is often shutdown to unload the plugged catalyst bed for replacement with a pristine one.

One important aspect during plugging that could be exploited in forced periodic operation is the ability to enhance the release of deposited fine particles from pore bodies within the porous bed due to hydrodynamic (non-Brownian fines) or colloidal (Brownian fines) forces. The release of fines is known to be a threshold process, that is, a minimum perturbation is required to detach the fines from the pore surface. This could be in terms of a critical hydrodynamic stress so that the released fine particles while flowing with the liquid phase can either re-adhere to the collector surface, flow without capture, or get entrapped downstream at the pore constrictions.

Iliuta and Larachi (2005a,b) analyzed theoretically the benefits of forced induced pulsing on the mitigation of fines plugging in trickle beds operating under hydrotreating conditions. For this purpose, a dynamic multiphase flow deep-bed filtration model was established which incorporates physical effects of porosity and effective specific surface area changes due to fines deposition/release, gas and suspension inertial effects, and coupling effects between the filtration parameters and the interfacial momentum exchange force terms. The release of the fine particles from the collector surface was assumed to be induced by the colloidal forces in the case of Brownian fines ($d_f < 2 \mu m$) or by the hydrodynamic forces in the case of non-Brownian fines. The parameters of the pulsing sequence are the base and pulse liquid velocities ($v_{lb}, v_{lp}$) and the corresponding durations ($t_b, t_p$) as shown in Fig. 6. The pressure drops are normalized with respect to that with a clean fines-free liquid under identical conditions. In Fig. 7 pressure drop simulations indicate that for non-Brownian fines, periodic operation reduces the specific solid deposit, and thus plugging, in the reactor as opposed to normal trickle-bed operation, viz., steady-state suspension feed flux. Fig. 8 represents the effect of fine diameter on pressure drop. The larger the fine diameter the more intense their detachment from collectors. On the contrary, liquid flow rate induced pulsing affects only very slowly the attenuation of plugging in trickle-bed reactors when the suspension is composed of Brownian fine particles. However, instead of liquid flow rate induced pulsing, liquid flow shear shocks, consisting of alternating immaculate liquid feed with the suspension at constant flow rate, accelerate the detachment of the Brownian particles which has been shown in Fig. 9.

Liquid forced induced pulsing might contribute in alleviating possible conversion drop offs in hydrodesulfurization. This can be due to the superimposed mass retardation brought about through the build-up of fines around the
catalytic collecting particles. Thick and/or densely packed deposits would eventually impede access of dissolved hydrogen and sulfur-bearing molecules to the inner catalyst intra-granular porosity. Thus, induced pulsing might play a positive effect when non-Brownian fines are involved in the deposition process as the deposit layer is likely to be eroded as inferred from the reduction of bed pressure drop, vide supra. On the contrary, it is not expected that induced pulsing would yield beneficial conversion effects in the case of Brownian fines. Simulations were thus attempted to check such contentions for model catalytic hydrodesulfurization of dibenzothiophene over sulfided CoO–MoO3/Y-Al2O3 catalyst at high temperature/pressure in a trickle-bed reactor operating under filtration (Iliuta et al., 2005). Fig. 10 shows the predicted outlet dibenzothiophene conversion plotted as a function of influent fines concentration for two different values of fines diameter after 485 min and constant liquid flow rate operation. Dibenzothiophene conversion is lower the higher the fines feed concentration. This is due to the fact that higher values of overall specific deposit ensue generating more mass transfer resistances, though not too severe, in the solid deposit. This is reflected in the lower values of the effectiveness factors due to the additional mass transfer resistance of the external deposit. However, as can be seen in Fig. 10, fine particles deposition influences only slightly the trickle-bed reactor catalytic performance regardless of whether Brownian or non-Brownian fines are concerned. These results seem to indicate that forced liquid induced pulsing is beneficial exclusively from the standpoint of

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**Fig. 8.** Pressure drop rise at different values of fine diameters ($c_0 = 0.1 \text{ g/L}$; periodic operation: $v_{lp} = 0.009 \text{ m/s}$, $v_{lb} = 0.003 \text{ m/s}$).

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**Fig. 9.** Bed-averaged transient specific deposit ($c_0 = 1.0 \text{ g/L}$) under liquid flow shear shock ($c_0 = 0.0 \text{ g/L}$) for Brownian fine particles ($d_f = 1 \mu\text{m}$). $v_g = 0.1 \text{ m/s}$ in all cases.

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**Fig. 10.** Effect of fine particles deposition process on dibenzothiophene conversion at $t = 485 \text{ min}$ ($T_{in} = 598 \text{ K}$, $P_{in} = 10 \text{ MPa}$): (a) $d_f = 5 \mu\text{m}$, (b) $d_f = 1 \mu\text{m}$.
hydraulics by delaying plugging and pressure drop rise. Its effects are only secondary in terms of catalytic reactions because fines-deposition outer-particle diffusion remains reasonably fast.

7. Artificial gravity with strong inhomogeneous magnetic fields

Improvement of chemical processes is a continuous task in multiphase catalytic systems where a number of factors can be optimized for improving process efficiency (e.g., catalyst wetting efficiency, selectivity, etc.). It is believed that magnetic fields could open up very attractive new applications.

External inhomogeneous strong magnetic fields are able to vary the gravity conditions for both diamagnetic and paramagnetic flowing materials. The magnetization force exerted by the magnetic field is a body force proportional to the local magnetic field and magnetic field gradient \((B_z dB_z/dz)\) as well as to the body magnetic susceptibility \((\chi)\). The sign of this force could be negative or positive, depending on magnetic susceptibility of materials and on magnetic field gradient sign. The resultant force acting on the material is the sum between the magnetization force and the gravitational force \(g(1 + \chi/\rho g\mu_o B_z dB_z/dz)\) and \(g\) being the artificial gravity factor. When such resultant is zero \((\gamma = 0)\), levitation occurs, and around which microgravity (small net downward resultant force), hypergravity (upward resultant force, \(\gamma > 1\)) or hypogravity \((\gamma < 1)\) take place as represented in Fig. 11.

The experiments performed in true low gravity conditions are expensive and demand complicate installations. Powerful superconducting magnets constitute adequate proxies for ground experimentations to mimic (extra-terrestrial) artificial gravity environments.

Microgravity conditions could be obtained for both paramagnetic and diamagnetic fluid materials submitted to inhomogeneous magnetic fields. Wakayama et al. (2001) obtained microgravity values of 0.04 g for a solution of cobalt chloride and 0.5 g for water. Iliuta and Larachi (2003) developed a two-phase flow model that takes into consideration the magnetic field effect on gas–liquid trickle flow. The main hydrodynamics parameters (liquid holdup, pressure drop and wetting efficiency) have been shown to be influenced by the magnetic field.

Preliminary calculations and experimental data conducted at Laval University revealed that inhomogeneous and strong magnetic fields applied to trickle bed reactors are capable of affecting hydrodynamics and might thus improve process performances. A superconducting NbTi solenoid magnet was used to obtain a 9 T maximum magnetic induction and a product gradient in the range of \(\pm 650 T^2/m\). A mini trickle-bed reactor was positioned in the maximum positive product gradient region \((+650 T^2/m)\). The water–air–glass beads (1 mm) system was used at different flow rates where liquid holdup and...
pressure drop were measured and compared to the case with no magnetic field.

Fig. 12a,b compares the evolution of liquid holdup and pressure drop at various air and water flow rates with active and inactive magnetic field. Positive-gradient inhomogeneous magnetic fields promote larger values of liquid holdup (and thus wetting efficiency in trickle flow regime) and two-phase pressure drop. These trends have been rationalized as follows:

- Water, being diamagnetic, exhibits a negative magnetic susceptibility for which the prevailing artificial gravity factor $\gamma = 0.52$ is propitious to hypogravity in the liquid. Hypogravity in liquid favors longer liquid residence times thus also larger liquid holdups.
- Air, being paramagnetic, exhibits a positive magnetic susceptibility for which the resulting $\gamma = 17.0$ promotes rather gas hypergravity. Hypergravity in gas favors more gas-liquid interactions and thus pressure drop is expected to increase under inhomogeneous magnetic fields.

8. Structured geometries

8.1. Structured catalytic packing with cocurrent downward flow

Versteeg et al. (1997), Ellenberger and Krishna (1999) tried the structured packing (KATAPAK™), shown in Fig. 13, to obtain better performances in trickle-bed reactors. They have compared the performance of TBR for a hydrogenation of $z$-methylstyrene with the structured packing coated with a thin alumina layer and the randomly packed 3 mm alumina sphere with palladium. The gas and liquid flow were in cocurrent downward mode in both cases. The overall performances of trickle-bed reactors did not improve significantly in trickle-flow conditions for the change of catalyst packing from the randomly packed spherical particles to structured catalyst packing (KATAPAK™). They reported that the increase in physical absorption rate due to better mass transfer characteristics of structured packings compared to dumped packings was eliminated to a certain extent in reactive system due to the enhancement effect of heterogeneous reactions in trickle-flow operation. Nijhuis et al. (2001) reported structured packing in cocurrent downward mode with monolithic catalyst. In contrary to the results of Versteeg et al. (1997), they have reported the better performance in terms of productivity of the monolithic catalyst for the hydrogenation of $z$-methylstyrene and better selectivity for the hydrogenation of benzaldehyde to benzyalcohol. Though this type of reactor may be advantageous for some specific reactions, it cannot be useful, in general, considering the point of catalyst utilization per reactor volume and mass transfer driving force. Fig. 14 represents catalyst structures frequently used in monolithic reactors.

9. Countercurrent catalytic packed bed reactors

Packed bed with countercurrent operation with respect to gas and liquid phases is being widely used in gas absorption and desorption, distillation, gas extraction and liquid–liquid contacting. They are also used as entrainment separators and for the removal of dust, mists and odors. This type of bed consists of packing, which has porosity greater than 0.9 (such as raschig ring, pall ring, nutter ring, saddle type, tellurates, mellapak, intalox metal tower packing). These packings demonstrate very low-pressure drop, because of large voidage in the bed. Countercurrent operation with catalytic
packed bed where reaction takes place and having very large surface area to volume ratio has also been attempted to use for some processes. The higher momentum transfer between gas and liquid phase in countercurrent operation with packed catalyst bed having small catalyst particles causes flooding at very low velocities. This problem can possibly be overcome by increasing the porosity of the catalyst bed and/or by making separate paths for the flow of gas and liquid.

Hydroprocessing operations play an important role in refining industry to remove obnoxious impurities such as sulfur and nitrogen from various petroleum fractions as well as to convert the heavier fractions into lighter ones. These operations are generally carried out in multiphase cocurrent trickle-bed reactors in which the liquid hydrocarbon and the gaseous hydrogen pass in a downward way through a fixed bed of solid catalyst. However, these reactors have their own limitations (Sie, 1997; Sie and Krishna, 1998; Van Hasselt et al., 1997; Sie and Lebens, 1998). For example, for the case of hydrodesulfurization (HDS), the concentration of hydrogen sulfide, an inhibitor for the HDS of the refractory sulfur compounds, increases along the downward axial length of the reactor. As a result, the concentration of H$_2$S becomes higher at the bottom zone of the reactor where the desulfurization of the most refractory sulfur compounds takes place. In addition, the concentration of hydrogen becomes lower in this zone of the reactor thereby slowing down the rate of desirable hydrogenation reactions. The temperature of the catalyst bed at the lower part of the reactor also becomes higher which is not desirable for a number of reactions.

All these drawbacks of a cocurrent trickle-bed reactor can be overcome if the reactor is operated in a countercurrent mode in which the liquid hydrocarbon flows from top to bottom and the hydrogen passes in an upward way from the bottom of the reactor. The countercurrent operation of a fixed bed reactor is promising to get high conversion and to maintain higher driving force for concentration throughout the reactor length (Kundu et al., 2003a). Moreover, it can reduce the build up of the inhibitory byproducts at the bottom zone of the reactor (Trambouze, 1990). The countercurrent mode of operation is also advantageous in order to obtain a more desirable temperature profile in the reactor.

9.1. Countercurrent operations-different types of structured catalytic packing

Many workers (Zheng and Xu, 1992; Xu et al., 1997; Subawalla et al., 1997; Lebens et al., 1997; Van Hasselt et al., 1997; Sie and Lebens, 1998; Moritz and Hasse, 1999; Ellenberger and Krishna, 1999; Oudshoorn et al., 1999; Higler et al., 1999 and Kundu et al., 2003a) have analyzed the countercurrent operation in a fixed catalytic bed reactor with a view to study pressure drop, liquid holdup, residence time distribution and mass transfer. In deriving their correlations or models for hydrodynamic parameters, different workers have used different types of packings. The packings used are listed below:

1. Cylindrical catalyst bundles (catalyst containing bales).
2. Katapak-s configuration of sulzer.
3. A binderless film of zeolite crystals on common structured distillation packing.
5. Catalytically active packing material in the form of raschig ring.
6. Three-levels-of-porosity (TLP) packing.
7. Monolithic catalysts.
8. Spiral coils.

It was also observed that the pressure drop in the reactor with spiral coils, TLP and internally finned-monolith (IFM) catalyst was very much less than random catalyst used in the trickle-bed reactor for the same flow rate of gas and liquid. The operating range for the flow rate of gas and liquid in reactor with spiral coils, TLP and IFM catalyst was also higher compared to that of conventional TBR.

The criteria for development of structured catalytic packings require the reduction of momentum transfer between the two phases at the minimal expense of mass transfer, which will result to minimize the flooding. This will not affect the rate of reaction, because it has been found that intraparticle diffusion resistance is very large compared to gas–liquid and liquid–solid mass transfer resistance (Sie, 1997). The solubility of hydrogen is very high in petroleum fractions and the reactions are carried out at high pressure. As a result, the liquid is saturated with the gas. Also the liquid side and liquid-solid side resistances are negligible with respect to the resistances offered inside the catalyst (Froment and Bischoff, 1990). Table 2 gives the overall view of the structured catalysts. Among these structured catalysts listed in Table 2, two types of structured catalysts are used for absorption and gas extraction processes having porosity greater than 0.9. Ilituta et al. (1997) compared the performance of two modes of operation-cocurrent and countercurrent using randomly packed Raschig ring having porosity 0.69. Total and dynamic liquid holdup in cocurrent downward flow was same with that in countercurrent flow, but the mass transfer coefficient values for countercurrent flow were higher compared to cocurrent downward flow. The high Péclet number values for two-phase countercurrent operation indicate that axial mixing due to dispersion was negligible. To obtain high yield, plug flow desired, and a pulse flow regime is preferred to a trickle flow due to extra advantages like increased wetting efficiency, enhanced mass transfer coefficients and improved uniformity of flow through the bed in pulse flow regime.

The commercial applications of the catalytic packed bed countercurrent operation are AROSAT process—where a relatively small catalyst bed is operated in the countercurrent mode at the tail end of a conventional trickle-bed reactor to allow deeper hydrodenitrogenation and SYNSAT
<table>
<thead>
<tr>
<th>Type of catalyst</th>
<th>Porosity</th>
<th>Dia. of catalyst particles (m)</th>
<th>Dia. of tower (m)</th>
<th>Height of the bed (m)</th>
<th>System used</th>
<th>$U_G$ and $U_L$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulzer CY (Gas extraction)</td>
<td>0.9584</td>
<td>0.0002215</td>
<td>0.035</td>
<td>0.9</td>
<td>Water + CO$_2$, Aqueous surfactant solution + CO$_2$</td>
<td>—</td>
<td>Stockfleth and Brunner (1999)</td>
</tr>
<tr>
<td>Catalyst Bundles</td>
<td>0.7</td>
<td>0.0003–0.0012</td>
<td>0.6</td>
<td>0.6</td>
<td>Air–water</td>
<td>0.6–3 m/s and 0.6–33 m$^3$/m$^2$ h</td>
<td>Xu et al. (1997)</td>
</tr>
<tr>
<td>TLP</td>
<td>0.41, 0.368</td>
<td>$1.6 \times 10^{-3}$ m cylindrical $\gamma$-Al$_2$O$_3$ extrudates and glass beads with a dia. $3 \times 10^{-3}$ m</td>
<td>0.11 m.</td>
<td>0.03, 0.09, 0.1, 0.12, 0.15 and 0.21</td>
<td>Air–water</td>
<td>0–0.6 m/s and 0–0.006 m/s</td>
<td>Van Hasselt et al. (1999)</td>
</tr>
<tr>
<td>Katapak-S</td>
<td>0.7953, 0.8018</td>
<td>0.001 m glass sphere</td>
<td>0.1 0.24</td>
<td>1.8 1.705</td>
<td>Air–water</td>
<td>0–1.6 m/s and 0–0.02 m/s, 0–0.1 m/s and 0–0.05 m/s</td>
<td>Ellenberger and Krishna (1999)</td>
</tr>
<tr>
<td>Katapak-S</td>
<td>0.001 m glass sphere</td>
<td>0.6</td>
<td>1.355</td>
<td></td>
<td>Air–water</td>
<td>— and 3–33 m$^3$/m$^2$ h</td>
<td>Moritz and Hasse (1999)</td>
</tr>
<tr>
<td>Rachig ring (random packing)</td>
<td>0.69</td>
<td>0.007</td>
<td>0.051</td>
<td>0.920</td>
<td>Air–water</td>
<td>0.028–0.31 m/s and 0.005–0.013 m/s</td>
<td>Iluuta et al. (1997)</td>
</tr>
<tr>
<td>Internally finned monolith</td>
<td>0.75</td>
<td>$0.00462$ m (diameter of each channel), $0.00107$ m (height of each fin), $0.000497$ m (thickness of the fin and the wall)</td>
<td>0.048–0.05</td>
<td>0.5, 1.0 and 0.06</td>
<td>n-decane–air, water-air and 30 wt% sucrose solution–air</td>
<td>0–1.5 m/s and 0–0.06 m/s</td>
<td>Lebens et al. (1999)</td>
</tr>
<tr>
<td>GPP packing (8 × 8 mm rings)</td>
<td>0.49</td>
<td>0.0052 m (effective diameter)</td>
<td>0.053</td>
<td>0.51</td>
<td>Methanal–isobutene</td>
<td></td>
<td>Sundmacher and Hofmann (1994)</td>
</tr>
</tbody>
</table>
process—where the similar configuration is used for hydrodesulfurization of gas oil with aromatic saturation.

Process intensification can be obtained using countercurrent fixed bed catalytic reactors. There is a need to design a perfect hardware of structured configuration with a higher catalyst volume/reactor volume ratio, industrially equivalent operating range and better contact between two flowing phases.

10. Conclusion

The process intensification in trickle-bed reactors is necessary in “More Miles with fewer Emissions” age. Periodic operation with respect to liquid flow may help in getting process intensification especially for gas-limiting reactions or for petroleum applications where filtration and bed plugging are serious threats. Understanding of flow behavior inside the catalyst bed is always helpful for better designing and scaleup of TBR. The much less focused “wettability of catalyst” has been discussed here based on contact angle of the liquid on the surface of porous particle as alternating patches of saturated pore and solid surface. The hysteresis behavior is also explained on the basis of the concept of wettability. Non-conventional research on magnetic-driven process intensification is worth exploring for mini trickle-bed reactors especially in non-petroleum applications such as in fine and pharmaceuticals chemical processes. The alternative type of TBR which can handle more impure reactants and get much more conversion is countercurrent catalytic packed bed reactor and the current status of this configuration is discussed here.

11. Future recommendation

1. A possible improvement of liquid distribution and wetting efficiency by cycling the liquid feed has been reported in the literature. There is no existing literature of experimental results on distribution of flow during cycled liquid-feed conditions as well as wetting characteristics of the catalyst in periodic operation.

2. There are mainly experimental studies in laboratory scale trickle-bed reactors reported in the literature. No systematic studies concerning the effect of column diameter on pulsing flow hydrodynamics are reported in the literature.

3. Though countercurrent catalytic packed bed reactor is a promising alternative, it still requires suitable hardware of the structured packing, which will have optimum value of catalyst volume/reactor volume and mass transfer between gas and liquid. Experimental studies with large diameter column are desired.

4. Wetting efficiency could be correlated in terms of interfacial phenomena based on movement of advancing and receding contact line. This has the potential to explain the physics at micro-level in TBR.

5. Quantitative relation could be drawn between hydrodynamic parameters and pore induced liquid movement over solid surface with change of wettability.

6. The present understanding can be exploited in study of periodic operation of TBR where wettability changes in cyclic way.

Notation

- \( B_z \) local magnetic field
- \( d_f \) diameter of fine
- \( F_I \) drag force on the gas
- \( F_{PG} \) particle–gas drag force
- \( F_{PL} \) the force acting on the particles due to the liquid motion
- \( P \) pressure
- \( t_b \) base duration
- \( t_p \) pulse duration
- \( v_{lb} \) base liquid velocities
- \( v_{lp} \) pulse liquid velocities

Greek letters

- \( \alpha \) gas saturation
- \( \beta \) liquid saturation
- \( \gamma \) artificial gravity factor
- \( \varepsilon \) bed void fraction
- \( \mu_0 \) absolute magnetic permeability of vacuum, H/m
- \( \tau \) shear Stress term
- \( \chi \) body magnetic susceptibility

References


