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RECENT DEVELOPMENTS ON HYDROPROCESSING REACTORS

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1. ABSTRACT

The importance of hydroprocessing has been accelerated due to the imposition of stringent environmental regulations on petroleum products to achieve future goals of sustainability and cleaner environment, and the more demanding situation of middle distillates (mainly transportation fuels) against the availability of heavier and high sulfur crudes. Trickle-bed reactors (TBRs) are mostly used in hydroprocessing. Other types of reactors, such as moving bed reactors and ebullated-bed reactors (EBRs) are also used in the hydroprocessing. All of the above mentioned reactors are operated with cocurrent up or downflow of gas and liquid. TBRs have been most commonly studied over the last 30 years. The design and scale up of TBR is still not well understood, especially with respect to hydrodynamic parameters. Though the EBRs are gaining importance because of their flexibility in dealing with most types of heavy feedstock and the ease with catalyst replacement during operation, there are very limited studies available in literature for the design and scale up of the reactor. Recently, countercurrent operation in a structured catalytic packed bed is gaining importance for hydroprocessing in order to obtain higher conversions. The structured packed column, in which the catalyst particles are enclosed within

^a also at L.G.C. Toulouse in 2002.

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a wire gauze envelope, is a promising alternative for hydroprocessing. In this paper, an attempt has been made to present the state of art prevailing in structured catalytic packing for the design and scaleup of packed bed reactors operated countercurrently. The performance of the countercurrent catalytic packed bed reactor with different structured packing available in the literature and the conventional TBR with random catalytic packings is also compared. Recommendations have been made for future research in this area.

2. INTRODUCTION

Three phase reactors, consisting of flow of liquid and gas with a fixed bed of catalyst, have various applications, particularly in the petroleum industry for hydroprocessing of oils. Mainly trickle-bed reactors are used for this purpose. The petroleum refining industry is facing a tremendous challenge to meet the changing demand pattern for products and to cope with the increasingly stringent environmental regulations. As there is a depletion of conventional light and sweet crude, the crude oil will be more and more heavy in the near future – although the demand for middle distillates is showing an increase. As a result, an unbalanced situation between supply of crude oil and quality of demand of crude oil products (mainly transportation fuels) has been created. Table I shows the recent trend of the amount of residual portion ($>350^{\circ}\text{C}$ fraction) and amount of impurities (mainly sulfur) from different major sources. To overcome this situation, the importance of hydroprocessing will be enhanced, i.e. the application of catalytic reactors used in hydroprocessing will be greater. To process the heavier portion of crude oils, ebullated bed reactors are most applicable because of the ease with the catalyst replacement during operation. Moreover, today's drive toward greener environment leads to increasingly tight product and process specifications and imposes high demands on energy and cost effectiveness of the process. Though attempts have been made to solve society's high transportation fuel requirements with the help of alternative transportation fuels (and also alternative vehicles), very clean gasoline or diesel will still remain as the fuels of the future because of greater efficiency of gasoline or diesel engines compared to other alternative fuel engine (Piel, 2001). Therefore there is a need to look into the alternative type of reactor, which can meet stringent specifications as well as demands in addition to the further improvement of the existing reactors (like TBR) with respect to catalyst,

Table I
Amount of residue and impurities in different types of crude oils
in current trend

Type of crude oil	Yield on crude(vol%)	Sulphur content (wt%)	Metals content (ppm)
Arabian Heavy	55(>343°C)	2.8	14(Ni) and 3.7(V)
Arabian medium	50(>343°C)	2.4	9.5(Ni), 46(V), 4.8(Pb) and 6.8(Fe)
Dubai (UAE)	45(>350°C)	2	14(Ni) and 42(V)
Iranian Heavy	47(>347°C)	1.65	22.6(Ni), V(81), Sn(15) and Mg(8.8)
Iranian Light	43(>347°C)	1.35	
Zulum/Marjan (Saudi Arabia)	48(>343°C)	2.48	
Zakum(UAE)	44(>350°C)	1.05	
Zaire (Zaire)	56(>360°C)	0.13	17.8(Ni) and 1.5(V)
Siberian Light (Russia)	44(>350°C)	0.42	
Qatar Marine	40(>350°C)	1.57	
Skua (Australia)	44(>350°C)	0.06	0.5(Ni) and >0.5(V)
Bombay High (India)	34(>370°C)	0.17	1(Ni) and 0.3(V)

prediction of hydrodynamics, reactor internals and flow and temperature distribution inside the bed.

3. TRICKLE-BED REACTORS

Trickle-bed reactors are catalytic randomly packed fixed bed tubular devices traversed vertically downwards by a gas-liquid stream. This reactor configuration assures flexibility of operation and high throughputs of gas and liquid. Owing to a motionless catalyst bed, nearly plug flow is achieved in TBRs and in that respect they are superior to the other three-phase reactors where the catalyst is either slurried or fluidized (Al-Dahhan *et al.*, 1997). TBRs are usually operated at elevated pressures of about 2-30 MPa in order to slow down catalyst deactivation, increase the concentration of the gaseous component in the liquid phase, attain high conversion, achieve better heat transfer and handle of large gas volumes at less capital expensive. The reactor is widely used in many gas-liquid-solid catalytic industrial applications like petroleum (hydrotreatment (hydrodesulfurization, hydrodenitrogenation, alkylation etc.) and hydrocracking of petroleum fractions), petrochemical (hydrogenation of naphtha cracked main products for getting different usable products, hydrogenation of higher aldehydes, reactive distillation) and chemical industries (for oxidation and absorption purposes), in waste treatment, and in biochemical and electrochemical processing (Saroja and Nigam, 1996). Typical process conditions and hydrogen consumption in trickle-bed reactors for various hydrotreating processes are given in Table II (Nigam, 2000).

The philosophy of trickle-bed reactor design centers around the kinetics, the hydrodynamics and the liquid distribution. A large literature concerning the hydrodynamics of trickle-bed reactors under high pressure is available. Those hydrodynamic parameters are often interlinked with reaction conversion and selectivity, power consumption and interfacial mass transfer that take place in trickle-bed reactor. Numerous attempts are being made to model the hydrodynamics of trickle-bed reactors. They range from merely empirical correlations (Ellman *et al.* 1988,1990; Larachi *et al.*, 1991a; Iliuta *et al.*, 1999a,b) to physically sound models such as the slit (Holub *et al.*, 1992; Al-Dahhan *et al.*, 1998; Iliuta *et al.*, 2000), the permeability (Saez and Carbonell, 1985, Carbonell, 2000 and Nemeč *et al.*, 2001), the 1D CFD (Attou *et al.*,1999) models and model based on force balance (Tung and Dhir,

Table II
 Typical Operating Conditions for different Hydrotreating processes
 used in Trickle-Bed Reactors

Hydrotreating Process	Temperature (°C)	Hydrogen partial pressure (atm)	LHSV	Hydrogen consumption (Nm ³ /m ³)
Naptha	320	10-20	3-8	2-10
Kerosene	330	20-30	2-5	5-15
Atm. Gas Oil	340	25-40	1.5-4	20-40
VGO	360	50-90	1-2	50-80
ARDS	370-410	80-130	0.2-0.5	100-175
VGO HCR	380-430	90-200	0.5-1.5	150-300
Residue HCR	400-440	120-210	0.1-0.5	150-300

VGO: Vacuum Gas Oil

VGO HCR: Vacuum Gas Oil Hydrocracking

ARDS: Atm. Residue Desulfurization

Residue HCR: Residue Hydrocracking

1988; Narasimhan *et al.*, 2001). 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. The interactions of different hydrodynamic parameters are shown in Figure 1. It is established that pressure drop increases with the increase of operating pressure, gas mass flux, liquid mass flux and viscosity of the liquid phase. Pressure drop is also decreased with the increase of bed porosity and structure of the bed. The structure of the bed is dependent on the type of loading of catalyst (sock loading and dense loading). Though the dense loading gives higher pressure drop than that of sock loading, it improves the performance in trickle bed reactor. The H₂/hydrocarbon ratio reduces up to 40% in dense loading to get the same result keeping all other operating parameters the same with respect to sock loading (Nooy, 1984). Liquid holdup decreases with the increase of operating pressure. At relatively low gas mass flux, it decreases more rapidly than at

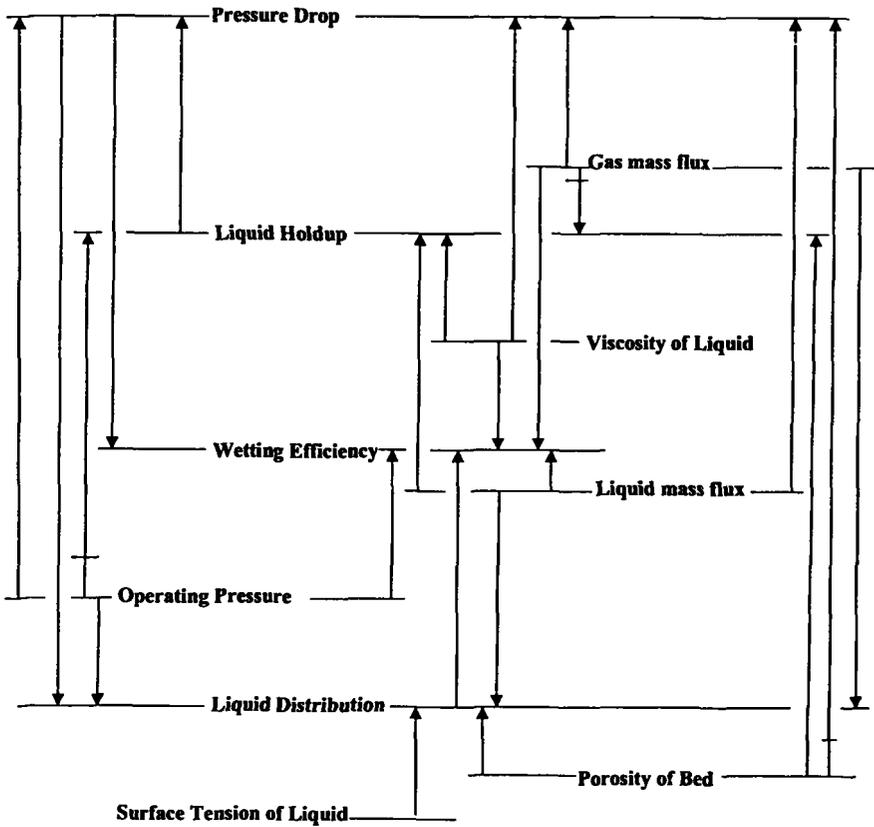


Fig. 1: Cause-effect diagram of different hydrodynamic parameters in trickle-bed reactors with the process variables and properties of gas and liquid (cause \rightarrow effect, increasing effect \rightarrow and decreasing effect $- \rightarrow$)

higher gas mass flux. Though at higher liquid mass flux, external wetting efficiency of the catalyst particles is not a crucial hydrodynamic parameter, it is important in TBR as it deals with very low liquid velocity. It has more importance in small scale TBRs, which are generally used for the development of better technology and catalyst evaluation because of the involvement of lower cost and safer operation (Chander *et al.*, 2001; Bej *et al.*, 2001). Wetting efficiency increases with increase of gas mass flux and operating pressure as these process variables increase spreading of liquid over catalyst particles due to increase in shear stress on the gas-liquid interface (Al-Dahhan and Dudukovic, 1995). The increase in liquid mass flux

increases the liquid holdup and wetting efficiency increases. Liquid distribution is an important parameter to obtain proper utilization of the catalyst. Properly designed liquid distributors, properly designed structure of catalyst and appropriate method of packing are necessary for getting uniform liquid distribution. In the recent literature, much work has been carried out on the development of a model for the estimation of pressure drop, liquid holdup, external wetting efficiency and liquid distribution in trickle-bed reactors, although there is no overall consensus for the acceptance of any definite method. With regard to these points, the published literature has been analyzed in the following.

3.1 Pressure Gradient and Liquid holdup

Accurate knowledge of two-phase frictional pressure drop and liquid holdup is essential for the design, scale-up and performance of trickle-bed reactors. The hydrodynamics are affected differently in each flow regime (Charpentier and Favier, 1975; Specchia and Baldi, 1977; Rao and Drikenburg, 1985; Xiao *et al.*, 2001). Of particular interest in the industry is the extensively used trickle flow encountered at low gas and liquid superficial velocities. Two-phase pressure gradient is defined as the variation of the internal pressure per unit reactor length. The pressure gradient is related to the mechanical energy dissipation due to the two-phase flow through the fixed bed of solid particles. It is needed in evaluating the mechanical energy losses, in sizing equipment for pumping and compression of the fluid (Tosun, 1984) and most of the other relevant design variables like gas-liquid, liquid-solid mass transfer and heat transfer are often estimated using the knowledge of two-phase frictional pressure drop and liquid holdup.

Liquid holdup (h_L) is defined as the volume of liquid contained in the bed per unit bed volume. It is a function of physical properties of the fluid phases and the bed characteristics. It is a basic parameter for reactor design, because it is related to other important parameters, namely pressure gradient, gas-liquid interfacial area, the mean residence time of the liquid phase, catalyst loading per unit volume, axial dispersion coefficient, mass transfer characteristics and heat transfer coefficient at the wall etc. The optimal value of liquid holdup is desirable for better performance of TBR as high value of liquid holdup will increase mass transfer resistance and too low value of liquid holdup will decrease the proper utilization of the catalyst bed. There are three different techniques for measuring liquid holdup in a laboratory trickle-bed reactor operated under high pressure: (i) tracer method, (ii)

drainage method and (iii) weighing method. Tracer method and drainage method give comparable value of liquid holdup and are recommended for measuring liquid holdup in TBR at high pressure operation (Al-Dahhan and Highfill, 1999; Nigam *et al.*, 2001; Pant *et al.*, 2000 and 2001). Nemeč *et al.* (2001a) had measured liquid holdup in trickle-bed reactors at high pressure (upto 7 MPa) with weighing method and recommended this procedure as it is less time consuming compared to other two methods and is less costly compared to tracer method. In addition to this, it will give both static holdup and dynamic holdup. The volumetric liquid-liquid mass transfer coefficients between dynamic and static zones and volumetric liquid-solid mass transfer coefficients between static liquid and porous particles can also be evaluated from tracer studies (Nigam *et al.*, 2002).

The correlations and models that have been established on the basis of atmospheric pressure data are summarized in the articles of Sai and Varma (1987), Ellman *et al.* (1988, 1990), Holub *et al.* (1993) and Saroha and Nigam (1996).

Investigations into pressurized trickle-bed reactors have been performed by Hasseni *et al.* (1987), Ellman *et al.* (1988, 1990), Wammes and Westerterp (1991), Wammes *et al.* (1991a, b), Larachi *et al.* (1991 a, b) and Al-Dahhan and Dudokovic (1994). These studies have shown that the hydrodynamic parameters are considerably affected by the gas density, and the correlations and models based on data at atmospheric pressure are not valid in the whole range of operating pressure.

The existing hydrodynamic models can be broadly classified into two different categories on the basis of empirical approach and theoretical approach.

3.1.1 Empirical Approach

The empirical approach is based on dimensional analysis to produce explicit correlations for pressure drop and liquid holdup using flow variables and packing characteristics or using the Lockhart-Martinelli parameter which was proposed for open horizontal tubes (Larkins *et al.*, 1961; Turpin and Hungtinton, 1967; Sato *et al.*, 1973; Midoux *et al.*, 1976; Clements and Schmidt, 1980; Sai and Varma, 1987; Ellman *et al.*, 1988, 1990; Larachi *et al.*, 1991a, b; Wammes *et al.*, 1991a, b; Xiao *et al.*, 2000, 2001 and Pina *et al.*, 2001). All correlations before 1990 were evaluated based on the atmospheric data. These correlations have several parameters for fitting the experimental results and these parameters are not universal constants. For the

prediction of pressure gradient, the correlation of Ellman *et al.* (1988) used four adjusted parameters, whereas Larachi *et al.* (1991a, b) have established more simple correlations of pressure gradient and total liquid saturation using five adjusted parameters to fit two-phase flow data. Wammes *et al.* (1991a, b) used a set of two correlations involving six adjusted parameters in order to predict simultaneously the pressure drop and the dynamic liquid saturation. Recently Pina *et al.* (2001) developed a correlation based on the Lockhart-Martinelli approach and tested with five different packings similar in shape and dimension to typical industrial catalysts (cylindrical pellets, raschig rings, extrudates) operating at high interaction regime.

3.1.2 Theoretical Approach

In this category, five distinct approaches have been used for the prediction of pressure-drop and liquid holdup in TBRs. These are (i) the relative permeability model (Sàez and Carbonell, 1985; Sàez *et al.*, 1986) (ii) the slit model (Holub *et al.*, 1992, 1993; Al-Dahhan and Dudukovic, 1994; Al-Dahhan *et al.*, 1998; Iliuta and Larachi, 1999) (iii) the model based on fundamental force balance (Tung and Dhir, 1988; Narasimhan *et al.*, 2002) (iv) the 1D-CFD model (Attou *et al.*, 1999; Souadnia and Latifi, 2001) (v) the F-function concept (Fourar *et al.*, 2001).

(i) **The relative permeability model:** In the relative permeability concept, Ergun's (1952) equation (which is basically for single-phase flow and arises from a momentum balance in an assumed pore geometry) has been modified to account for the existence of a second flowing phase. In the relative permeability model, Sàez and Carbonell (1985) utilized the volume-averaged momentum equations for steady, one-dimensional incompressible flow of gas and liquid to derive the equations for liquid holdup and pressure drop where inertial term has been neglected. The relative permeability of each phase has been correlated as a function of liquid saturation of each phase depending on the experimental results. First they correlated the relative permeabilities of gas and liquid phase as

$$k_l = \delta_l^{2.43} \quad (1)$$

$$\text{and } k_g = S_g^{4.90} \quad (2)$$

where δ_l is the reduced liquid saturation defined as

$$\delta_1 = \frac{\varepsilon_1 - \varepsilon_1^0}{\varepsilon - \varepsilon_1^0} \quad (3)$$

Levec *et al.* (1986) showed that the liquid phase relative permeability was best represented with the following expression

$$k_1 = \delta_1^{2.9} \text{ (for } \delta_1 \geq 0.2) \quad (4)$$

$$k_1 = 0.25 \delta_1^{2.9} \text{ (for } \delta_1 < 0.2) \quad (5)$$

Later, they added the dependence of gas phase velocity on the relative permeability of the gas phase and found the correlation (Lakota *et al.*, 2002),

$$k_1 = \delta_1^{2.92} \text{ (for } \delta_1 > 0.3) \quad (6)$$

$$k_1 = 0.40 \delta_1^{2.12} \text{ (for } \delta_1 < 0.3) \quad (7)$$

$$\text{and } k_g = S_g^n \quad (8)$$

where $n = \chi + 0.0478(Re_p)^{0.774}$

χ depends on the particle shape (for sphere, $\chi = 4.37$ and for extrudates, $\chi = 3.31$). Recently, Nemeč *et al.* (2001b) found that their experimental data could not fit well with the above correlation for relative permeability for the gas phase and obtained the following correlation based on their experimental results, which is only a function of gas phase saturation:

$$k_g = 0.5 S_g^{3.9} \quad (9)$$

where the dependence of gas phase velocity has been deleted, though there is a slight influence of it (Nemeč *et al.*, 2001b). Also the expression does not satisfy the upper theoretical limit at $S_g = 1$, where k_g should be equal to 1.

This approach, therefore, is semiempirical. As it is a modified Ergun equation, it requires the values of Ergun constants which have different values for different packings. It also requires accurate correlations for the relative permeabilities of the gas and liquid phase to obtain good results in the prediction of pressure drop and liquid holdup in TBR. Although the authors demonstrated a good correlation for the relative permeability of the liquid phase (Nemeč *et al.*, 2001b), it is difficult to get a good correlation for

the relative permeability of the gas phase due to complex dependence upon the gas phase saturation. It is to be noted that the effect of operating pressure on the pressure drop is only taken into account through liquid holdup parameter only. In this concept, the phase interaction terms are negligible, though, in reality, weak interfacial gas-liquid interaction prevails only at very low superficial gas and liquid velocities.

(ii) **Slit model:** The phenomenological slit model developed by Holub *et al.* (1992, 1993), Al-Dahhan and Dudukovic (1994) and Iliuta *et al.* (2000) involves momentum and mass balances for the local flow in the assumed geometry and mapping the average bed properties to the assumed geometry. It is also a modified form of the Ergun equation. Initially, Holub *et al.* (1992, 1993) modeled the complex geometry of the actual void space in the catalyst bed at the pore level by the much simpler flow inside a rectangular slit. In their model, the width of the slit is a function of bed porosity, the liquid was assumed to flow equally on the upper and lower surfaces, and the angle of inclination of the slit to the vertical axis is related to a tortuosity factor for the packed bed. The surface area per unit volume of solid in this rectangular slit was made equal to the surface area per unit volume of solid in the reactor. They introduced the concept of slip of the velocity and shear at the gas-liquid interface by introducing two slip parameters:

$$V_{i,G} = f_v V_{i,L} \quad (10)$$

and

$$\tau_{i,L} = f_s \tau_{i,G} \quad (11)$$

The resulting pressure drop and liquid saturation model of Holub *et al.* indicates zero shear stress at the gas-liquid interface. This result implies that the gas flow does not influence the liquid flow. However, the experimental studies of Wammes and Westerterp (1991), Wammes *et al.* (1991a,b), Larachi *et al.* (1991a, b, 1994) and Al-Dahhan and Dudukovic (1994) have shown that the gas flow has a considerable influence on the hydrodynamics of the trickle-bed reactor especially at high operating pressures. Al-Dahhan and Dudukovic (1994) validated the phenomenological model of Holub *et al.* (1992) based on their experimental data of pressure gradient and liquid holdup data obtained in the range of pressure of about 0.31-5 MPa. and found that it was not fitting well with the data in the high-interaction and high pressure regimes. Later, Al-Dahhan *et al.* (1998) obtained the correlations for

the slip parameters as a function of gas and liquid phase Reynolds numbers to fit high pressure data:

$$f_s = -4.4 \times 10^{-2} Re_G^{0.15} Re_L^{0.15} \quad (12)$$

and

$$f_v = -2.3 Re_G^{0.05} Re_L^{-0.05} \quad (13)$$

As both slip factors are negative, the above equation implies that the gas is moving in the direction opposite to the liquid and the stress on the gas is negative of the stress on the liquid, which is physically unrealistic (Carbonell, 2000). Recently, Iliuta and Larachi (1999) developed the double slit model which considers the distribution of totally dry slits in addition to the wet slits as in Holub *et al.* (1992, 1993). They used the same slip factors as Al-Dahhan *et al.* (1998) used in addition to another parameter for the distribution between liquid-full and dry slits. Later, Iliuta *et al.* (2002) developed the correlations of the slip factors in terms of gas Reynolds, liquid Reynolds, Froude, Weber, Lockhart-Martinelli and Stoke numbers based on their large database.

(iii) Model based on fundamental force balance: The fundamental force balance model developed by Tung and Dhir (1988) involves force balance equations in liquid and gas phase in an elemental reactor volume. Modeling has been done keeping in view the co-current up-flow and counter current mode of operation rather than the conventional down-flow mode practice in their work. Recently, Narasimhan *et al.* (2002) extended this approach with particle-gas drag, particle-liquid drag and liquid-gas interfacial drag in addition to taking into consideration the excess drag for the tortuosity effect. The liquid gas interfacial drag has been taken into account by first developing an expression for the drag on a single bubble/slug and then multiplying it by the number of bubbles/slugs per unit volume of the porous layer. The tortuosity corrects the gravity term in the liquid phase and gas phase force balance equation which has the expression

$$\tau = g \cos \theta - \mu g \sin \theta \quad (14)$$

where θ accounts for the distance traveled in the tortuous path and μ accounts for the excess loss in force due to drags on the liquid and liquid following the tortuous path. The expressions for θ and μ are obtained as:

$$\theta = \pi/2 \{1 - e^{-K(V_L + V_G)}\} \quad (15)$$

and

$$\mu = (k_1 - k_2)/(V_L + V_G) \quad (16)$$

The values of K , k_1 and k_2 are dependent on the physical properties of the system. The model has been tested with the available experimental results of the literature and found to be an excellent match with the model's prediction.

(iv) 1D-CFD model: Recently, Attou *et al.* (1999) developed a model based on macroscopic mass and momentum conservation laws in which the drag force has a contribution of both particle-liquid and gas-liquid interactions. The liquid-solid and gas-liquid interaction forces are formulated on the basis of the Kozeny-Carman equation by taking into account the presence of liquid films and the gas-liquid slip motion. The gas-liquid interaction forces are generated due to the gas-liquid drag for the relative motion between the liquids and the force by which the gas pushes the liquid against the solid particles. To do the calculations for the drag forces, they have used the Ergun coefficients as 180 and 1.8, though these coefficients are depended on geometrical characteristics for each type of packing as reported by Holub *et al.* (1993). Attou *et al.* (1999) found reasonable agreement with the experimental results of Larachi *et al.* (1991a), Al-Dahhan *et al.* (1994) and Wammes *et al.* (1990, 1991). Nemeč *et al.* (2001b) verified the model of Attou *et al.* (1999) with their own experimental results from 41 mm diameter reactor operating up to 7 MPa with spherical particles and extrudates. They have shown that the model does not predict well with the constant value of Ergun constants i.e. 180 and 1.8, and the optimized Ergun constants offer a better prediction. Attou (1999) has shown the limitation of the model, i.e., that the model does not predict well (mean relative error for prediction of pressure > 0.3 and that for prediction of liquid saturation > 0.15) at low D/d_p ratio (less than 12-14) due to the column wall effect.

Souadnia and Latifi (2001) have developed a 1D CFD model based on the Eulerian approach which consists of volume averaged continuity and momentum equations for each flowing phase. Previously, Propp *et al.* (2000) also developed the model using the same approach having three governing equations; conservation of mass, conservation of volume and momentum equation:

$$\frac{\partial(\varepsilon\rho_i S_i)}{\partial t} + \nabla \cdot (\rho V_i) = 0, i = G, L \quad (17)$$

(S_i = saturation of phase I)

$$\sum S_i = 1, i = G, L \quad (18)$$

and

$$\rho \left(\frac{\partial V_i}{\partial t} + V_i \cdot \nabla V_i \right) = \nabla p_i - \rho g + F_i + \nabla \cdot (\tau + R_i), i = G, L \quad (19)$$

(F_i = drag force exerted by phase i , τ_i and R_i are volume averaged viscous stress tensor and pseudo-turbulence stress tensor of phase i , respectively)
Neglecting the inertial term, the above equation becomes:

$$V_i = -k \left(\frac{k_{ri}}{\mu_i} \right) (\nabla p_i - \rho g), i = G, L \quad (20)$$

The capillary pressure has been neglected by Souadnia and Latifi (2001) for obtaining simpler governing equations, whereas Propp *et al.* (2000) have solved with the consideration of the capillary pressure. The gas phase is assumed as an incompressible in both works. The drag force coming in the momentum equation is evaluated following an expression given by Sàez and Carbonell (1985) which is based on the concept of relative permeability of each phase, discussed earlier. They have compared their experimental results with the model's predictions in terms of ϕ_L and χ_L , where

$$\phi_L = \sqrt{\frac{(\Delta P / H)_{LG}}{(\Delta P / H)_L}} \quad (21)$$

and

$$\chi_L = \sqrt{\frac{(\Delta P / H)_L}{(\Delta P / H)_G}} \quad (22)$$

In Figures 4 and 5 of Souadnia and Latifi (2001), it is clear that the model predicts well at higher superficial gas velocity, i.e. at higher ϕ_L and lower χ_L , whereas at low gas superficial velocity, the prediction by the correlation of Midoux *et al.* (1976) and Tosun (1984) is better than this model. The work of Propp *et al.* (2000) was significant with respect to the CFD approach, although it was not compared with real experimental data. However, they have shown the effect of capillary pressure, Ergun equation and variable porosity on liquid saturation of TBR in the cylindrical coordinate system.

(v) **F-function concept:** Fourar *et al.* (2001) developed the model for the prediction of liquid saturation and pressure drop in TBRs with the help of Forchheimer's equation originally employed to explain inertia deviations in Darcy's law for single phase flow. They have modified the single phase Forchheimer equation by multiplying a phasic F-function (that depends on fluid saturation) with superficial velocity of each fluid. Obviously, here the inertial force has been taken into account, though the capillary forces are neglected for getting the pressure gradients in both phases to be identical. In their model, they have determined liquid saturation from the modified Forchheimer equation for each phase and the following expressions of F function for each phase:

$$F_L = \frac{1}{\beta^2} \quad (23)$$

and

$$F_G = \frac{1}{(1-\beta)^2 + 2\mu_G / \mu_L \beta(1-\beta)} \quad (24)$$

After calculating liquid saturation, they have calculated F_L with the above expression and the pressure gradient is determined using the modified Forchheimer equation for liquid phase. They have tested the model with the experimental results of Larachi *et al.* (1991a) and found the prediction of pressure gradient within average error of 22% and that of liquid saturation within 8%.

Comparison of theoretical models

Carbonell(2000) has given a complete comparison of the relative permeability model, slit model and 1D-CFD model (Attou *et al.*, 1999) by presenting the tables of comparison of the respective workers for the above mentioned models. It is true that there is not much difference between these models in terms of mean relative error as small differences between different workers may be encountered in the error of the experimental measurements due to the difficulty in packing the same bed with a variety of packing materials and liquids with different viscosity and surface tension. Larachi *et al.* (2000) compared the prediction of pressure drop and liquid holdup for the different theoretical models (the relative permeability model, slit model and 1D-CFD model by Attou *et al.*, 1999) with their database. They came to the conclusion that the extended slit model by Iliuta *et al.* (1998) gives the best performance for the prediction of pressure drop in terms of mean relative error, though the prediction of liquid holdup is almost the same for all the models (within 20% mean relative error). The model of Attou *et al.* (1999) can be considerably improved by taking different Ergun constants in single phase flow for different packings and neglecting the inertial terms (Larachi *et al.*, 2000 and Nemeč *et al.*, 2001b). Though the slit model and the relative permeability model predict pressure gradient and liquid holdup within a considerable margin of error, there are some adjustable constants having complex behavior, which makes it difficult to handle these two models. The models based on fundamental equations like 1D-CFD models and models based on fundamental force balance equations can be integrated with more complex behavior associated with the chemical reactions, mass transfer and heat transfer. These models can also be extended for the prediction of other hydrodynamic considerations like flow distribution, wetting efficiency and flow regime transition. Since these models are based on fundamental approach and contain mechanistic details of the system, they have a wider range of applicability, unlike the models based on the correlations, which are system specific.

3.2 Wetting Efficiency

External wetting efficiency, f , is an important design and scale up parameter, which is essential in determining the degree of catalyst utilization in trickle-bed reactors. It is defined as the area of the catalyst effectively wetted by the liquid flowing down the bed. The mass transfer between the

internal liquid and the liquid flowing down the bed occurs through this area. It is a function of flow rate of gas and liquid, operating pressure, physical properties of liquid and diameter of the catalyst. In many reactions in trickle-bed reactors, one of the main reactants is nonvolatile (e.g. in hydroprocessing, one of the reactants is liquid and nonvolatile at the operating pressure in almost all cases), so that a reaction can occur only on the wetted surface of the catalyst. In that case, partial wetting of the catalyst will decrease the reaction rate. Though at high superficial liquid velocity in the presence of flow of gas, the external wetting efficiency of the catalyst in a commercial trickle-bed reactor should be close to unity, strictly speaking, trickle-bed reactor deals with very low superficial liquid velocity. Consequently, external wetting efficiency of the catalyst has great importance in the performance of trickle-bed reactors. Moreover, poor initial distribution of the liquid can cause partial wetting of the catalyst (Kundu *et al.*, 2001). Low value of external wetting efficiency is a major problem with pilot scale trickle-bed reactors which are used for scaling-up and scaling-down of commercial trickle-bed reactors (Sie, 1991, Sie and Krishna, 1998 and Chander *et al.*, 2001).

In the literature, the external wetting efficiency of the catalyst in trickle-bed reactors has been obtained from a chemical method based on reaction rates, dynamic tracer technique and dissolution, dye adsorption and magnetic resonance technique. The dynamic tracer technique is preferred over the method based on the reaction rate as the latter method requires an adequate reactor model (Llano *et al.*, 1997), whereas the tracer technique allows the determination of wetting efficiency in actual beds under operating conditions (Al-Dahhan and Dudukovic, 1995). Pironti *et al.* (1999) have given a non-intrusive method for the calculation of wetting efficiency which requires only the knowledge of two-phase pressure drop, liquid holdup and Ergun's constant characteristics of the packing.

A complete review of the different methods for the measurement of wetting efficiency in trickle-bed reactor and its different forms of definitions based on those methods has been presented by Pironti *et al.* (1999). All authors have expressed wetting efficiency in terms of the ratio of two-phase operation and liquid-filled operation (completely wetted). For calculating wetting efficiency, they have measured the intra-particle effective diffusivity (Colombo *et al.*, 1976; Dudukovic, 1977; Baldi and Gianetto, 1979; Al-Dahhan and Dudukovic, 1995), the apparent adsorption equilibrium constant (Schwartz *et al.*, 1976), the volumetric mass transfer coefficients (Herskowitz

and Mosseri, 1983) and the liquid-solid drag force (Pironti *et al.*, 1999). Recently, Sederman and Gladden (2001) measured wetting efficiency using 2D and 3D magnetic resonance imaging from the extent of surface wetting by quantifying the number of liquid rivulets. Their work is important in the sense that this is the first direct measurement of wetting efficiency in TBRs. It should be mentioned that there are many correlations available in literature (e.g. Ring and Missen, 1991, Larachi *et al.*, 2001, Al-Dahhan and Dudukovic, 1995) for the prediction of external wetting efficiency in trickle-bed reactors based on the experimental results. Recently, Iliuta and Larachi (1999) and Iliuta *et al.* (1999b) have estimated the external wetting efficiency based on the slit model (Holub *et al.*, 1992 and 1993) considering the gas-liquid interaction.

3.3 Liquid Distribution

Liquid distribution plays an important role in determining the reactor performance in trickle-bed reactors. To guarantee uniform liquid distribution in a trickle-bed reactor has been a tough problem that has drawn much attention. The liquid tends to flow preferentially along the existing filaments where the porosity is high. The introduction of gas flow into the liquid-solid system smoothens the liquid distribution to some extent due to the competition between liquid and gas phase for the interstitial pore space (Sarooha *et al.*, 1998).

A TBR may not have uniform flow pattern throughout the reactor. It may be operating in the trickle flow regime at the top but pulse flow may exist in the lower portion of the reactor. This is due to the fact that pulses start forming at the bottom of TBR due to lower pressure while maintaining trickle flow at the top of TBR. This form of nonuniformity in flow pattern does not affect the TBR performance as it occurs in a small region of the flow map.

But global liquid maldistribution can greatly jeopardize the operation of a TBR. Improper liquid distribution will result in non-optimal use of a catalyst, rapid deactivation of a part of a catalyst by creating hot spots or thermal instability that means improving flow distribution increases capacity and cycle length for existing plants. In highly exothermic reactions, the liquid is vaporized and the heat generated is not carried away by the liquid leading to rapid deactivation of the catalyst. The role played by the initial liquid distribution at the top of the bed is of decisive importance. A poorly designed liquid distributor can have a serious impact on the performance of TBR. The

method of packing of the catalyst particles, particularly the cylindrical extrudates, also affects the liquid distribution in TBR. If the cylindrical extrudates are packed with their major axis pointing downward towards one side of the reactor, the liquid will be flowing towards that side of the reactor (Ng and Chu, 1987). Al-Dahhan *et al.* (1995) reported that the essential requirement of the packed bed is to ensure reproducibility of the packing. This is because even if a uniform liquid distribution is achieved at the distributor, significant bypassing (channeling) and/or segregation could occur due to the improper direction of the catalyst and fines are packed. The effect of prewetting of the catalyst bed is significant on the liquid distribution as reported by Lutran *et al.* (1991), Ravindra *et al.* (1997), Jiang *et al.* (2000) and Kundu *et al.* (2001).

So liquid distribution in trickle-bed reactors mainly depends on three factors:

- (i) structure of the packed bed
- (ii) gas-liquid-solid interaction
- (iii) design of distributor

Under the structure of the packed bed, the liquid distribution is dependent on (i) Porosity distribution (ii) D/d_p ratio (iii) H/d_p ratio (orientation problem) (iv) Height of the catalyst bed (v) Method of loading: convex loading, concave loading and randomly loading (sock and dense loading).

Numerous studies on porosity distribution in randomly packed beds are available (Mantle *et al.*, 2001, Stephenson and Stewart, 1986 for experimental studies and Spedding and Spencer, 1995 for computational study). These experimental and computational studies have shown that the porosity is higher near the vicinity of the wall and it fluctuates significantly in the near wall region (width of about 4 to 5 particle diameters). The magnitude of fluctuations is a strong function of a ratio of column diameter to particle diameter (for $D/d_p > 15$, fluctuations are within 1% whereas for lower values of D/d_p , fluctuations may rise up to 30%). Mueller (1991) has proposed a correlation for radial variation of axially averaged porosity as a function of column diameter, particle diameter and average porosity. This correlation is fairly general and represents the available experimental data with a reasonable accuracy.

$$\varepsilon_p = \varepsilon_B + (1 - \varepsilon_B) J_0(ar^*)e^{-br^*} \quad (25)$$

where

$$a = 8.243 - \frac{12.98}{(D/d_p + 3.156)} \text{ for } 2.61 \leq D/d_p \leq 13.0 \quad (26)$$

$$a = 7.383 - \frac{2.932}{(D/d_p - 9.864)} \text{ for } 13.0 \geq D/d_p \quad (27)$$

$$b = 0.304 - \frac{0.724}{D/d_p} \quad (28)$$

$r^* = r/d_p$ and J_0 is zeroth order Bessel Function. r is the distance from the wall.

Jiang *et al.* (2001) have shown that axial porosity variation is close to Gaussian distribution function. The value of standard deviation of such distribution decreases with increase in the ratio of column diameter to particle diameter and eventually approaches zero for small (compared to column diameter) particles.

At a large ratio of D/d_p , there will also be smaller portion of wall and larger inner part of the catalyst bed which will decrease the nonuniform distribution of liquid. Conversely, at a small ratio of D/d_p , the flow will be uneven due to the large portion of the wall. This effect is called the wall effect. Herskowitz and Smith (1978) suggested the value 18 of D/d_p ratio above which the wall effect can be eliminated. Al-Dahhan and Dudukovic (1994) suggested the value of 20 and Saroha *et al.* (1998) reported the value of 25 of D/d_p ratio.

The dependence of gas-liquid-solid interaction on liquid distribution implies mainly the gas and liquid mass fluxes and physical properties of liquids (surface tension etc.). Liquid distribution in a trickle-bed reactor can be improved by radial dispersion, giving better utilization of the bed. Radial dispersion takes place at the points where the catalyst particles touch each other. Low radial dispersion often gives channeling. Uneven catalyst loading and nonuniform liquid inlet distribution can also give channeling.

The design of liquid distributors in commercial hydroprocessing reactors is well explained by Jacobs and Milliken (2000). Three main factors are considered during the designing of the liquid distributor: (i) Center to center spacing, which is directly proportional to particle size, is chosen at an optimum value so that radial mixing compensates for maldistribution, (ii) Liquid discharge pattern and (iii) Wall coverage, in which the problem arises due to the absence of distributors located close to the reactor wall. Jacobs and

Milliken (2000) compared the performances of three types of distributors, namely, riser tray, conventional bubble cap tray and modified bubble cap tray in terms of overall catalyst utilization. They have concluded that the modified bubble cap tray reached an overall catalyst utilization of over 92% at all bed lengths they investigated. This is due to the combination of improved discharge pattern by the presence of ring shaped discharge pattern (which has the tendency to diffuse the liquid both radially inward and upward) and increased wall coverage.

Different procedures for studies of liquid distribution in trickle-bed reactors have been reported. It has been summarized in Table III. Although some liquid distribution studies mostly use the collector at the outlet of the bed due to its simplicity in carrying out the experiments, there is a chance of flow redistribution at the exit region. So recent studies have emphasized the tomographic technique and video imaging technique which provide the information of flow distribution more quantitatively and are useful for the validation of the CFD model (Jiang *et al.*, 1999). Marcandelli *et al.* (2000) suggested the RTD technique for the liquid distribution studies in a commercial reactor which is also quantitative. They also reported that liquid collectors and tomography are not good techniques for the liquid distribution studies in a commercial reactor due to unavailability of quantitative information and low spatial resolution with inapplicability in porous medium respectively.

Different models describing the liquid distribution in trickle-bed reactors exist in the literature. The diffusion model introduced by Stanek *et al.* (1981) assumed that the irrigation flux satisfies the diffusion equation, which could be solved for a variety of inlet flow distribution. The 'percolation approach' used by Crine *et al.* (1979) and Meilli and Scriven (1991) assumed the flow distribution in the bed to be a stochastic process. The liquid was distributed on the network by randomly choosing the bonds in the structure that have flowing fluid. This model has a limit for small particles as no direct relationship exists between the network and bed structure. Zimmerman and Ng (1986) modeled the liquid distribution assuming hypothetical "computer generated" packings of equally sized spheres based on developed wetting criteria. The above models do not consider the effect of particle prewetting, although it has a significant influence on liquid distribution. Jiang *et al.* (1999) developed a model assuming a number of interconnected cells called "Discrete cell model (DCM). The gas and liquid distribution is assumed to be governed by the minimization of total energy dissipation rate in DCM. The

Table III
Investigations of liquid distribution in trickle-bed reactors

Authors	Systems	Geometric characteristics	Method	Range of velocities
Herskowitz and Smith (1978)	Air-water+tenside	D=0.0408-0.114 m, H=0-0.7m, $d_p=0.00258-0.0111$ m, $D/d_p=4.4$ Granules, spheres, cylinders	Annular collector 3, 4 or 5 annulars	L=1-5 kg/m ² .sec G=0.001-0.05 kg/m ² .sec
Lutran et al. (1991)	Water+tenside (liquid only)	Square cross section (0.0603 m, H=0.1905 m, $d_p=0.003-0.006$ m, $D/d_p=17-33$ Glass spheres	X-ray tomography	L=3.2-9.1 kg/m ² .sec
Berner and Zuideweg (1978)	Water+alcohol (liquid only)	D=0.2 m, H=0.05-0.3 m, $d_p=0.01-0.03$ m, $D/d_p=7-20$ Raschig Rings	Collector 177 zones	L=0.5-8.9 kg/m ² .sec
Moller et al. (1996)	Air-water+tenside	D=0.144 m, H=0.77 m, $d_p=0.0016$ m extrudates or 0.016*0.011 m perforated cylinders, $D/d_p=10-90$	Collector 8 zones	L=2-8 kg/m ² .sec G=0-0.07 kg/m ² .sec

Borda et al. (1987)	Air-water+CMC	D=0.072 m, H=0.85m, d _p =0.0048-0.0075 m, D/d _p =9.6-15 Cylinders or Raschig rings	Annular collector 3 or 4 annulars	L=2-20 kg/m ² .sec G= 0.016- 0.1kg/m ² .sec
Sylvester and Pitayagulsarn (1975)	Air-water	D=0.15 m, H=0.15-0.91m, d _p =0.0032-0.0063 m, D/d _p =24-48 Cylinders or Intalox saddles	Annular collector 6 annulars	L=3.6-19.7 kg/m ² .sec G= 0.04-0.78 kg/m ² .sec
Hock et al.(1986)	Liquid only	D=0.5 m, H=0-2 m, d _p =0.0010-0.005 m, D/d _p =10-50 Raschig or Pall rings, Intalox saddles	Collector 657 zones and 24 at the wall	L=5-15 kg/m ² .sec
Toye et al. (1996)	Air-water	D=0.6 m, H=2 m, d _p =0.05 m, D/d _p =12	X-ray tomography	L=0-10 kg/m ² .sec

Table III (continued)

Authors	Systems	Geometric characteristics	Method	Range of velocities
Reinecke et al.(1996a, 1996b, 1998)	Air-water	D=0.12 m, H=2 m Spheres and monoliths	Capacitance tomography	
Ravindra et al.(1997)	Air-water	Rectangular (0.06*0.08 m) H=0.2 m Glass beads ($d_p = 0.0016$, 0.0035 and 0.0057m) and Alumina particles ($d_p =$ 0.0019, 0.0035 and 0.0063m)	Dye adsorption method and Collector (16 zones)	L=1-8 kg/m ² .sec G=0.05 kg/m ² .sec
Saroha et al. (1998)	Air-water	D=0.152 m, H=2 m, $d_p = 0.0015$ m, D/ $d_p = 100$ H=0.55 m	Annular collector 6 collectors	L=0.7-5 kg/m ² .sec G=0-0.027 kg/m ² .sec
Jiang et al.(1999)	Air- coloured water	2D trickle-bed reactor (0.072*0.009m), H=0.288m, $d_p = 0.003$ m, Glass beads	Video imaging method	L=1.48-3.52 kg/m ² .sec G=0.059 kg/m ² .sec

Li et al.(2000)	water	Rectangular (240*240 m ²) Glass beads (0.006 m and 0.020 m diameter)	Collector 144 zones	L=0.29 kg/m ² .sec
Marcandelli et al. (2000)	Air-water	D=0.1-0.3 m, H= 1.3-3m, d _p = 0.002m glass beads (ε=0.41), 0.0067m ceramic beads, polylobe extrudates (ε=0.58), D/d _p = 15-150	pressure drop measurement method, RTD method, local heat transfer measurement, capacitance and collector method (9 zones)	L=1-8 kg/m ² .sec G=0.001-0.83 kg/m ² .sec

Table III (continued)

Authors	Systems	Geometric characteristics	Method	Range of velocities
Kundu et al.(2001)	Air-water and water+surfactant, air-kerosene, air-ethylene glycol	D=0.152 m, H=0.62 m, $d_p=0.0045$ m extrudates ($\epsilon=0.47$), 0.003m spheres($\epsilon=0.36$), 0.0073m tablet($\epsilon=0.42$), 0.0053m holed tablet($\epsilon=0.48$), 0.0034m trilobe extrudates($\epsilon=0.53$), $D/d_p=30-50$	Annular collector 6 annulars	$L=0.69-7.31$ kg/m ² .sec $G= 0-0.043$ kg/m ² .sec
Boyer and Fanget (2002)	Heptane	D=0.06 m, $d_p= 0.00166$ m ($\epsilon=0.36$)	gamma ray tomography	$L=0.7-11.9$ kg/m ² .sec

effect of particle wetting has been taken into account by incorporating the contribution of capillary pressure. They have compared the effect of liquid distributor and effect of pre-wetting through the parameter “liquid maldistribution factor” along the bed calculated by DCM. The effect of liquid distributors on liquid flow maldistribution is significant in the upper half of the bed. After a certain height of the packed bed, it is not possible to minimize the liquid flow maldistribution with the uniform distributor. Pre-wetting of the bed improves the liquid distribution to a large extent in the upper half of the bed.

3.4 Structured catalytic packing with cocurrent downward flow

Versteeg *et al.*(1997) tried the structured packing (KATAPAK™) to obtain better performances in trickle bed reactors., They have compared the performance of TBR for a hydrogenation of α -methylstyrene with the structured packing coated with a thin alumina layer and paladium and the randomly packed 3 mm alumina sphere with paladium. 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. Another work of structured packing in cocurrent downward mode was reported by Nijhuis *et al.* (2001) with monolithic catalyst. In contrast to the results of Versteeg *et al.* (1997), they have reported better performance in terms of productivity of the monolithic catalyst for the hydrogenation of α -methylstyrene and better selectivity for the hydrogenation of benzaldehyde to benzylalcohol. 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.

4. EBULLATED BED REACTORS

Ebullated bed reactors are three-phase reactors in which catalysts are in suspension and the addition and removal of catalysts are present. It is most applicable in exothermic reactions and for feeds (e.g. vacuum residue) which are difficult to process in a fixed-bed or plug flow reactor due to high level of metals and asphaltenes or when more conversion is required. The expansion rate of the bed is kept at 1.3 to 1.5 under normal industrial conditions. EBRs can be operated at a higher temperature and at a slightly higher velocity than fixed bed reactors. The advantages of this reactor are (i) uniform temperature, (ii) high heat transfer rates, (iii) catalyst replacement and (iv) much lower pressure drop. The disadvantages are (i) backmixed flow and the volume of the reactor is not fully utilized, (ii) catalyst attrition due to motion, (iii) higher consumption of catalyst than fixed bed and (iv) difficult to scale-up.

Though the first commercial ebullated bed process, known as the H-Oil process, was originally developed in 1960 by a joint development of HRI and City services, very few published reports concerning EBR have yet been made. The works on residence time distribution studies of the liquid phase (Kressmann *et al.*, 2000), hydrodynamics study in cold flow EBR (Kam *et al.*, 1999) and catalyst attrition (Kam *et al.*, 2001) are available in the open literature. Kam *et al.* (1999) studied the hydrodynamics in a EBR having a diameter of 0.15 m and a total height of 4.5 m. Air, H-oil hydrotreating catalysts and heavy kerosene were used as gas, solid and liquid phases respectively. They have measured the axial pressure profile at different superficial liquid velocity, gas holdup and normalized bed expansion with two types of catalyst having different length. The interaction of different hydrodynamic parameters of EBR are never studied which will be helpful for scaling up of EBR. Recently, Kressmann *et al.* (2000) studied the residence time distribution of the liquid phase in EBR using argon 41 as a radiotracer and evaluated liquid holdup at different axial positions and at different gas flow rates. They have also shown the flow regime map for an industrial EBR. The liquid holdup, evaluating from the radiotracer study, was increased slightly axially as the solid density is higher at the bottom of the reactor and at the top of the reactor, the hydrodynamics is closer to that of the bubble column reactor. The process parameters that are directly affecting the hydrodynamics of EBRs (i.e. the flow rates of the liquid feed, gas feed and ebullation) should be varied more to get a thorough dependency.

The study of catalyst attrition in EBR, which reduces the reactor efficiency, has been given attention in the works of Kam *et al.* (2001). The continuous settling and rising of catalysts in ebullated-bed, interparticle impacts, fracture and abrasion cause attrition with the consequent production of fines. Kam *et al.* (2001) obtained more fines production at higher flow rate of gas and liquid in the same process time and also the maximum daily fines production at higher flow rates is high.

5. COUNTERCURRENT CATALYTIC PACKED BED REACTORS

Packed beds with countercurrent operation are being widely used in gas absorption and desorption, distillation, gas extraction and liquid liquid contacting (Shah, 1979). They are also used as entrainment separators and for the removal of dust, mists and odours. 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 demonstrated very low-pressure drop, because of large voidage in the bed. A number of papers have been published (Bravo *et al.*, 1986, Colazo *et al.*, 1991, Spiegel and Meier, 1992, Suess and Spiegel, 1992, Rocha *et al.*, 1993, Brunazzi and Paglianti, 1997a and 1997b, Launaro and Paglianti, 1999, Covatorta *et al.*, 1999 and Stockfleth and Brunner, 1999) dealing with the subject of pressure drop, mass transfer, liquid holdup and mixing for the above mentioned packings.

A catalytic packed bed reactor, with countercurrent mode where reaction takes place and having a very large surface area to volume ratio, is a suitable alternative to trickle-bed reactors. Trickle-bed reactors (which have cocurrent downward flow of gas and liquid through a randomly packed catalyst bed) cannot be operated in a countercurrent mode because of excessive flooding. In that case, it is necessary to search for structured catalyst packed beds, which will show less pressure drop without much affecting the rate of reaction. The spatial position of the catalyst material in a reactor with structured catalyst packings is controlled on the scale that is relevant for momentum, mass and heat transfer.

The comparison of this countercurrent operation with conventional trickle-bed reactors has been summarised in Table IV.

The main advantages in countercurrent packed bed catalytic reactors are:

Table IV
 Comparison of countercurrent and cocurrent operation in catalytic packed bed reactor in different situations

Process	Countercurrent Operation	Cocurrent Operation	Comments
1. Hydrodesulfurization of heavy oils and gas oil	Major part of the bed is in H ₂ S lean regime and protects from inhibition by H ₂ S formed in larger part of the bed.	Most part of the bed is under H ₂ S rich regime and its inhibiting effect is strongest in the region where the refractory sulfur compounds have to be converted which calls for the highest activity of the catalyst.	Countercurrent operation is favoured with respect to product inhibition and a large heat of reaction.

<p>2. Hydrogenation of aromatics in petroleum oils</p>	<p>Hydrogen pressure is highest at the exit end of oil of the bed and in this part temperature can be lowered and we can use more active, less sulfur tolerant catalysts in downstream part of catalyst, which will favor the chemical equilibria for this reaction.</p>	<p>Hydrogen partial pressure will be lowest at the reactor outlet due to combined effect of pressure drop, hydrogen consumption & reduction of hydrogen purity as gaseous byproducts (H_2S, NH_3 & H_2O) will increase along the path.</p>	<p>Countercurrent operation is preferred in the view of equilibrium limited conversion and product inhibition.</p>
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Table IV (continued)

Process	Countercurrent operation	Cocurrent operation	Comments
3. Hydrocracking	Major part of the bed is in NH_3 (a byproduct of hydrodenitrogenation reaction) lean regime which favors the reaction by protection from the inhibition of NH_3 and also H_2S .	Major portion of the bed is under NH_3 and H_2S reach condition. Particularly NH_3 strongly suppresses the activity of the acidic function of the hydrocracking catalyst.	For high conversions, countercurrent operation will show great advantages by omitting two separate reactor stages.
4. Reactive Distillation (a combined unit operation of heterogeneous catalytic reaction and multistage distillation)	It has been recognized as a proven technology for the reaction alongwith separation of the products which favors the conversion normally limited by Chemical equilibrium.	It has the applications in conventional process, which involves reaction followed by separation.	Countercurrent is favorable with respect to capital investment and specific chemical reaction, mainly equilibriumlimited reaction.

5. Operation of randomly packed catalyst bed	It is limited to low velocities far below those of industrial interest due to excessive pressure drop and flooding problem.	Used in downward mode in industry with less degree of conversion, inhibition effect of SO ₂ and NH ₃ on catalyst resulting less performance	Cocurrent is favorable due to occurrence of flooding & excessive pressure drop in countercurrent mode.
6. Operation of structured catalytically packed bed	It can be operated at much higher superficial gas and liquid velocities without flooding problem. Target should be to design shape of catalyst packing to reduce the momentum transfer between the two phases at the minimal expense of mass transfer.	No necessity as this mode with randomly packed catalyst bed is feasible and it will be costly in respect of capital investment without any benefit.	Countercurrent is favorable, but feasibility of this novel reactor concept and design of commercial scale reactor still to be done.

- (i) The concentration of gas impurities which are formed in the reaction is less in most parts of the bed. Figure 2 shows the partial pressure of H_2S along the bed length in cocurrent and countercurrent operation for hydroprocessing (Gosselink, 1998). This favours the conversion normally limited by the chemical equilibrium and also enables handling more difficult feed stock to obtain higher conversion (Trambouze, 1990).
- (ii) The countercurrent operation gives more favourable flat axial temperature profile (Van Hasselt *et al.*, 1997).
- (iii) Countercurrent operation provides the highest catalytic activity and hydrogen purity in that part of the bed where it is needed to convert the least reactive compounds. (Krishna and Sie, 1994).

Other advantages are a large surface area for vapor-liquid mass transfer, a high ratio of number of active sites to reactor volume and an easy catalyst handling (Sundmacher and Hofmann, 1996).

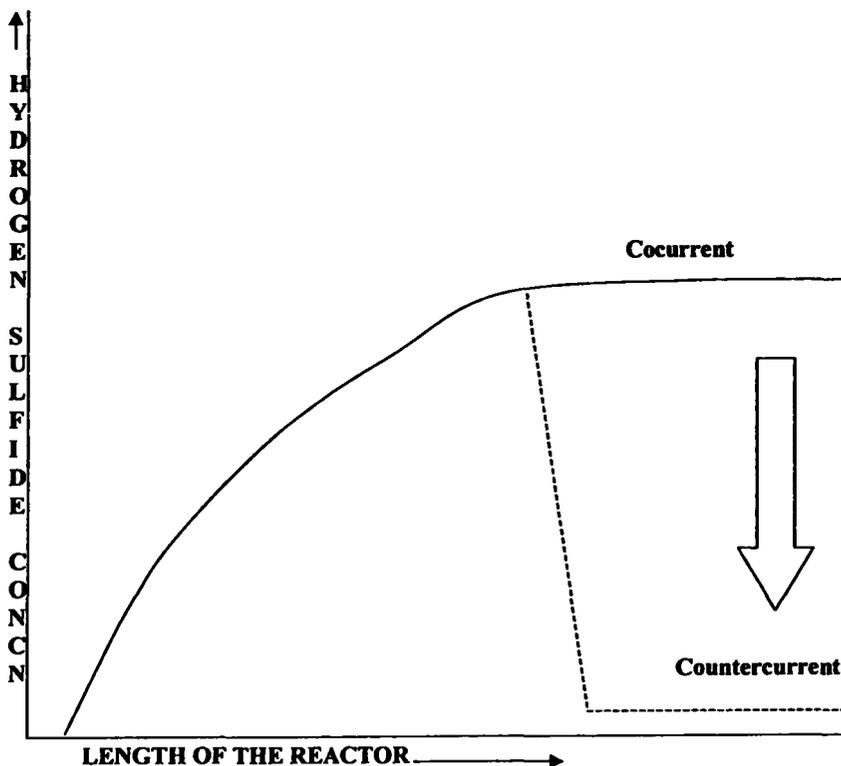


Fig. 2: Concentration of H_2S along the bed length of cocurrent and countercurrent packed bed reactor (graph not in scale)

5.1 Countercurrent operations-different types of structured catalytic packing

Many workers (Zheng and Xu, 1992, Xu *et al.*, 1997, Subawalla *et al.*, 1997, Levens *et al.*, 1997, Van Hasselt *et al.*, 1997, Sie and Levens, 1998, Moritz and Hasse, 1999, Ellenberger and Krishna, 1999, Oudshoorn *et al.*, 1999 and Higler *et al.*, 1999) have analyzed the countercurrent operation in a fixed catalytic bed reactor with a view to studying pressure drop, liquid holdup, residence time distribution and mass transfer. In arriving at their correlations of 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
4. Katamax packing
5. Catalytically active packing material in the form of raschig ring
6. Three-levels-of-porosity (TLP) packing
7. Monolithic catalysts

It has been found that the pressure drop in the reactor with TLP and internally-finned-monolith (IFM) catalyst is 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 reactors with TLP and IFM catalyst is also higher compared to that of conventional TBR. Table V summarises the works on structured catalytic packing.

The criteria for development of all structured catalytic packings require the reduction of momentum transfer between the two phases at the minimal expense of mass transfer, which will result in minimizing 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). Figure 3 shows the percentage of different resistances encountered in the case of hydroprocessing (Sie and Krishna, 1998). 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

Table V
Different works on structured catalyst packings

<u>Name of the Workers</u>	<u>Experiments</u>	<u>Comments</u>
Sundmacher and Hofmann (1994) 8X8 mm Glass supported precipitated polymer(GPP) packing	Study of fluid dynamic behaviour with pure MeOH and pure MTBE using GPP catalyst packing	(i) A varying liquid holdup along the packing was observed (ii) The predicted height of the flooded zone can be upto 50% of the packing height.
Xu et al. (1997) Two types of cylindrical catalyst bundles with outside diameters of 70 mm and 200 mm and a height of 150mm	Effect of superficial gas velocity on pressure drop and liquid holdup	(i) correlations for pressure drop and liquid holdup developed (ii) Three flow regimes-film regime, bubble regime and emulsification regime were identified
Moritz and Hasse (1999) Seven katapak-s laboratory scale packings each having length 193.5 mm, diameter 70mm and wire thickness 0.25mm.	(i) Develop a model for pressure drop and liquid holdup of katapak-s in different flow regime (ii) Study of liquid phase RTD	(i) The calculated and observed pressure drop are within deviation of 20%. (ii) At liquid load below load point, effect of gas velocity is about linear. (iii) Below load point, the interaction between stagnant zones & dynamic zones increases with increase in liquid flow rate and at above load point, the RTD curve becomes broad and asymmetric due to bypassing of the liquid.

<p>Ellenberger and Krishna (1999) Two types of katapak-s packing having similar geometry but different hydraulic diameters (7 & 20 mm). The catalyst particles used inside the sandwiches consist of 1mm glass sphere.</p>	<p>(i) study of hydrodynamics and liquid phase mixing (ii) Develop a model for pressure drop of katapak-s packing (iii) Measurement of liquid phase Residence Time Distribution(RTD).</p>	<p>(i) The pressure drop in katapak-s packed column is about three orders lower than that of conventional Trickle Bed Reactor. The observed & calculated pressure drop is within deviation of 20%. (ii) The measured liquid phase RTD is same irrespective of whether the tracer is injected in packed channel or open channel.</p>
<p>Higler et al.(1999) Two types of katapak-s packing having similar geometry but different hydraulic diameters (7 & 20 mm). The catalyst particles used inside the sandwiches consist of 1mm glass sphere.</p>	<p>(i) Measurement of liquid phase residence time distribution and its CFD simulation (ii) Study of liquid phase mass transfer by CFD technique</p>	<p>(i)The values of the axial dispersion coefficient are practically independent of the column diameter and depend only on Re_L. The measured value of axial dispersion coefficient is 50 times lower than the calculated value from CFD, due to high degree of bypassing of the liquid through open channel. (ii) Mass transfer due to mixing within the sandwich structures mainly occurs at the crossovers and is practically independent of the liquid flow velocity.</p>

Table V (continued)

<u>Name of the Workers</u>	<u>Experiments</u>	<u>Comments</u>
Oudshoorn et al. (1999) A piece of stainless steel wire mesh coated with a binderless film of zeolite crystals	(i) Preparation of catalyst (ii) Feasibility of ETBE synthesis using this catalyst.	(i) This structured catalyst has a good potential for ETBE production through reactive distillation
Sie (1997) (i) Alumina Extrudates of 1.5 mm. dia., staggered configuration (a) 8 layers of troughs, layer thickness, d=30 mm, (b) 16 layers of troughs, layer thickness, d=11 mm. (ii) Alumina Extrudates of 1.5 mm. Dia., 8-16 layers, staggered and in-line configuration	(i) Effect of no packing and dry condition, packed and dry condition & packed and wet condition on pressure drop ($\phi_{L-5.4} \text{ kgm}^{-2} \text{ s}^{-1}$) (ii) Effect of configuration of the TLP packing on gas pressure drop	(i) Pressure drop is lowest at the empty conditions of the troughs, pressure drop is increased at filled condition of the troughs & further increased with flowing of liquid as the cross section for the flow of gas is reduced. (ii) In-line configuration gives lower pressure drop as the resistance of flow of gas is more through zig-zag path in staggered configuration.

<p>Van Hasselt et al. (1997)</p> <p>(a) 3 basket layer (each basket 110*30*30mm., gap between two baskets=6mm. & gap between outside basket and wall=4mm.)</p> <p>(b) 4 basket layer (two central basket having dimension 110 *30 *30 and other two 110* 15* 30, gap between two central baskets=6mm. & for other two is 7mm). Below each layer redistributer and between two sides of each layer & the column wall a wall wiper is present.</p>	<p>(i) Effect of gas flow on pressure drop at different liquid flow rates.</p> <p>(ii) Effect of gas mass flux on liquid hold up & liquid weight in packing at different liquid mass flux.</p> <p>(iii) Effect of gas mass flux on pressure drop at different catalyst shape as well as at empty condition.</p> <p>(iv) Flooding limit of different TLP configuration.</p>	<p>(i) Pressure drop in TLP reactor is very low and effect of liquid flow rate on pressure drop is small.</p> <p>(ii) Effect of gas flow on liquid hold up is very less.</p> <p>(iii) Pressure drop across empty basket & basket filled with particles are the same with a liquid flow rate, but less in empty condition at without liquid flow condition.</p> <p>(iv) The measured flooding ranges for different number of layers (upto 18 layers) for 3 basket & 4 basket layers are well above the flow rates used in commercial Trickle Bed Hydrotreater.</p>
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Table V (continued)

<u>Name of the Workers</u>	<u>Experiments</u>	<u>Comments</u>
<p>Van Hasselt et al. (1999b)</p> <p>Alumina Extrudates of 0.0016m. Dia.& glass beads of 0.003m dia.</p>	<p>Develop a model to describe pressure drop in TLP reactor</p>	<p>Four contributions to pressure drop</p> <p>(i) frictional loss in the channels between baskets in a layer, (ii) contraction losses due to change in void fraction, (iii) expansion losses due to change in void fraction and (iv) losses due to zig-zagging of the gas phase for staggered configuration.</p> <p>Laminar and turbulent contributions to pressure drop are included in the model. The calculated dry pressure drop matches with measured value within 20% accuracy.</p>
<p>Van Hasselt et al. (1999a)</p> <p>Alumina Extrudates of 0.0016m. Dia.& glass beads of 0.003m dia.</p>	<p>Develop a model to describe the liquid holdup in TLP reactor.</p>	<p>(i) liquid bed holdup is higher compared to TBR due to repeated occurrence of capillary effects.</p> <p>(ii) measured value & calculated values of bed holdup matches good.</p> <p>(iii) residual holdup matches well with literature value.</p> <p>(iv) the residual bed holdup for TLP reactor is equal to that in TBR regardless of bed height of TLP.</p>

<p>Van Hasselt et al. (1999c) Glass beads of 0.003 m. dia.</p>	<p>Gas-liquid-phase residence time distribution</p>	<p>(i) Gas & liquid phase residence time distributions of different TLP packings measured. (ii) The liquid phase RTD model that considers each catalyst layer as a no. of stirred tanks and the liquids falling from layer to layer as plug flow reactor, correctly predicts the influence of layer distance on Pe_L. (iii) Gas phase RTD model is best described by tank-in-series (TIS) model due to mixing in between every two layer for the variation of the flow area of the gas phase.</p>
<p>Levens et al. (1997) Internally finned tube with inner diameter of 4.5mm</p>	<p>Effect of gas flow on pressure drop at different liquid velocities in a internally finned tubes and unfinned tubes (number of tubes=19)</p>	<p>(i) Characterisation of flow regime in internally finned tubes and unfinned tubes. (ii) Relatively large transition regime obtained that allows to operate close to the initial flooding limit without risking abrupt changes in the hydrodynamic state</p>

Table V (continued)

<u>Name of the Workers</u>	<u>Experiments</u>	<u>Comments</u>
Levens et al. (1999b) Internally finned monolith(IFM) with a diameter of 43mm	(i) Hydrodynamic and mass transfer study (ii) Develop a model for pressure drop and liquid holdup	(i) Operation area of industrial reactors ($U_{LS} < 0.03 \text{ m/sec}$ & $U_{OS} < 0.3 \text{ m/sec}$) lies comfortable within the wavy annular flow regime (ii) The volumetric mass transfer coefficient is of the same order of magnitude ($0.03 - 0.16 \text{ sec}^{-1}$) compared to Trickle Bed Reactor.
Levens et al. (1999c) A monolith consisting of 44 channels, the diameter of the channel=4.62mm & the height of the fins= 1.07mm	Develop a model to describe the mass transfer in an IFM	The model underpredicts the mass transfer in the upper part of the monolith while overestimates the mass transfer in the lower part of the monolith.

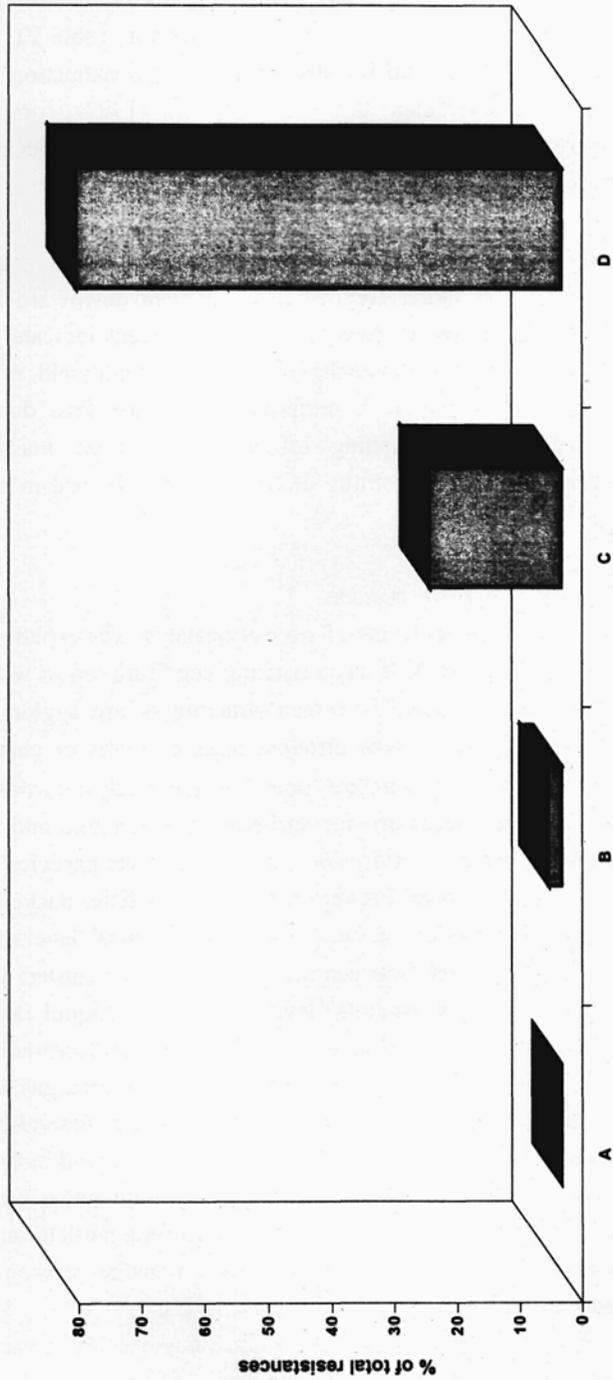


Fig. 3: Relative magnitude of mass transfer resistances in a typical case of hydroprocessing (A-from bulk gas to G/L interface, B-from G/L interface to bulk liquid, C-from bulk liquid to external catalyst surface, D-intra-particle diffusion and reaction).

catalyst (Froment and Bischoff, 1990). Table VI gives the overall view of the structured catalysts. Among these structured catalysts in Table VI, two types of structured catalysts are used for absorption and gas extraction processes having porosity greater than 0.9. Iluita *et al.* (1997) compared the performance of two modes of operation-cocurrent and countercurrent using randomly packed raschig ring having a porosity of 0.69. Total and dynamic liquid holdup in cocurrent downward flow is the same as that in countercurrent flow, but the mass transfer coefficient values for countercurrent flow are larger compared to cocurrent downward flow. The high pecllet number values for two-phase countercurrent indicate that axial mixing due to axial dispersion is negligible. To obtain high yield, if plug flow is desired, 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.

5.1.1 Three-levels-of-porosity reactor

The concept of the three-levels-of-porosity catalyst was explained by Sie (1997), as shown in Figure 4. It has a packing configuration in which small catalyst granules are contained in screen structure or are agglomerated to macroporous larger bodies. Three different sizes of pores or channels are present in this system: (i) nanometre 'pores' inside catalyst particles which have high surface area necessary for sufficient reaction rate and in which molecular transport occurs by diffusion i.e. "microporous particles" level of porosity, (ii) millimeter 'pores' between the catalyst particles packed in a bed through which liquid flows down, i.e., "interstitial channels" level of porosity and (iii) finally, the channels between the various beds or clusters constitute centimeter 'pores' i.e. "gas conduits" level of porosity. Liquid flows down through the beds driven by gravity and gas flows up, preferentially around the beds driven by a small pressure difference. In this concept, gas and liquid flow countercurrently in separate channels with regular intervals, i.e., the reduced pressure drop is obtained at the expense of gas-liquid mass transfer efficiency. This will not be a problem, because the simultaneous presence of gas and liquid and their continuous intimate contact on a particle scale is not necessary for reactions where gas-liquid mass transfer resistance is of relatively minor importance (Van Hasselt *et al.*, 1997).

Van Hasselt *et al.* (1999d) carried out a case study of HDS of vacuum gas oil using three different reactor configurations – a conventional cocurrent

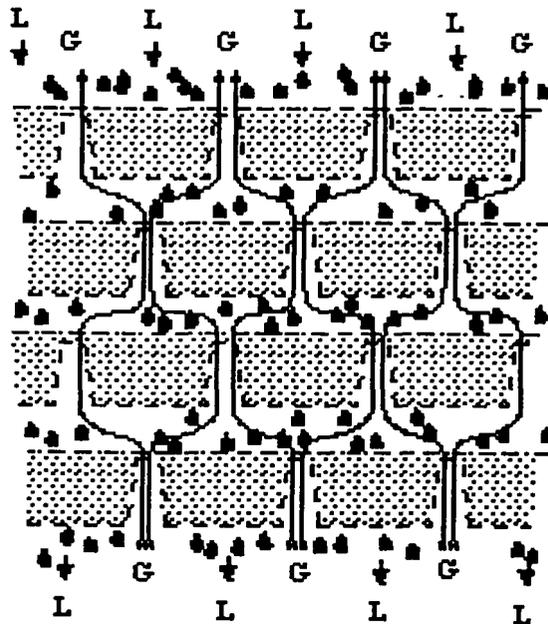


Fig. 4: The Three-Levels-of-Porosity Reactor (Van Hasselt *et al.*, 1997)

TBR (TBR, CO), semi-countercurrent TBR (TBR, SC) and the countercurrent operation using IFM and TLP packing designed for 98% conversion. The different configurations are shown in Figure 5. A comparison of concentration of H_2S as well as temperature along the length of reactor was reported. At the starting part of all reactors, the temperature drops steeply and then rises in a moderate manner due to fast heat transfer in the quench sections followed by subsequent reaction sections. The concentration of H_2S also fluctuates in the beginning due to discontinuity in mass transfer effectiveness. The balance between reaction rate and mass transfer determines the overall shape of H_2S (l) profile. At the initial part of the catalyst bed, the concentration of H_2S (l) increases due to higher reaction rate. In countercurrent, it will be more predominant, as H_2S is transferred from the gas to the liquid and upstream heat transfer from the gas phase will increase the reaction rate, which further increases the H_2S (l) concentration in the liquid. The concentration of H_2S in liquid as a function of catalyst bed length is shown in Figure 6. In this type of reactor, the reduced mass transfer by this typical structured packing causes the undesirable accumulation of H_2S in liquid in the first of the second reactor in the two-reactors- in-series system

Table VI
Different types of structured packing used for catalytic packed bed countercurrent operation

Type of Catalyst	Porosity	Dia. of Catalyst Particles(m)	Dia. of tower(m)	Height of the Bed (m)	System used	U_G and U_L
Sulzer CY(Gas extraction)	0.9584	0.0002215	0.035	0.9	Water+ CO ₂ , Aqueous surfactant solution+CO ₂	-
Helic-R (Absorption)	>0.9	0.00254, 0.00381, 0.00508 and 0.01016	0.00381, 0.01016	0.985 2	Air-water, air-SO ₂ - aqueous soln. of NaOH, air-CO ₂ saturated soln	-
Catalyst Bundles	0.7	0.0003-0.0012	0.6	0.6	Air-water	0.6-3m/sec and 5-25m ³ /m ² hr
TLP	0.41 0.368	1.6X10 ⁻³ m cylindrical-Al ₂ O ₃ extrudates and glass beads with a dia. 3X10 ⁻³ m	0.11m.	0.03, 0.09, 0.1 0.12, 0.15 and 0.21	Air-water	0-0.6m/sec and 0-0.0069m/sec

Katapak-S	0.7953	0.001m glass sphere	0.1	1.8	Air-water	0-1.6m/sec & 0-0.02m/sec, 0-1.6m/sec and 0- 0.05 m/sec
Katapak-S	0.8018	0.001m glass sphere	0.24	1.705	Air-water	- and 3-33m ³ /m ² hr
Rachig ring (random packing)	0.69	0.007	.051	0.920	Air-Isopar. L Air-water	0.028-0.38m/sec and 0.005- 0.011m/sec
Internally finned monolith	0.75	0.00462 m (diameter of each channel),0.00107m (height of each fin), 0.000497m. (thickness of the fin and the wall)	0.048- 0.05	0.5, 1.0 and 0.06	n-decane-air, water-air sucrose solution-air	0-1.5m/sec and 0- 0.06m/sec
GPP packing (8x8 mm rings)	0.49	0.0052 m (effective diameter)	0.053	0.51	Methanal-isobutene	

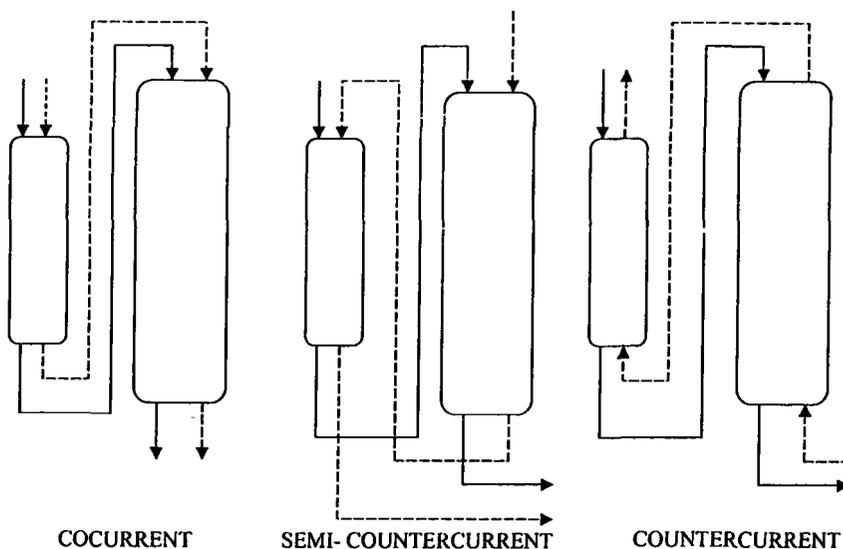


Fig. 5: Different modes of operation of catalytic fixed bed reactor used by Van Hasselt *et al.*, 1999d (—► liquid flow and - - -► gas flow)

(Van Hasselt *et al.*, 1999d). The mass transfer in TLP reactors is lower compared to TBR, but the value is not low enough to obtain high conversion. Though the pressure drop is lower compared to conventional trickle bed reactors, the surface to volume ratio of catalyst as well as the feasibility in the industrial scale operation needs to be verified.

5.1.2 Monolithic reactor

The monolithic reactor is a fixed bed reactor consisting of support structure. This support structure is a block with a large number of parallel channels (up to 225 channels/cm²) with diameters in the order of 1mm. The channels are quadratic, rectangular or triangular. The catalysts are positioned to the channel walls. Cybulski and Moulijn (1994) have reviewed the applications of monoliths for chemical processes. The main advantages are: (1) low pressure drop, (2) higher catalyst utilisation and improved selectivity due to short diffusion distance inside the thin layer of the catalyst, (3) enlarged gas/liquid contact area, (4) low mass transfer resistance, (5) the absence of maldistribution problems (provided the liquid is properly distributed at the inlet, (Nijhuis *et al.*, 2001), (6) easy scale-up and safer operation, (7) the high thermal stability of the ceramic material and the ceramic material is inert so that no undesired consecutive or back reaction

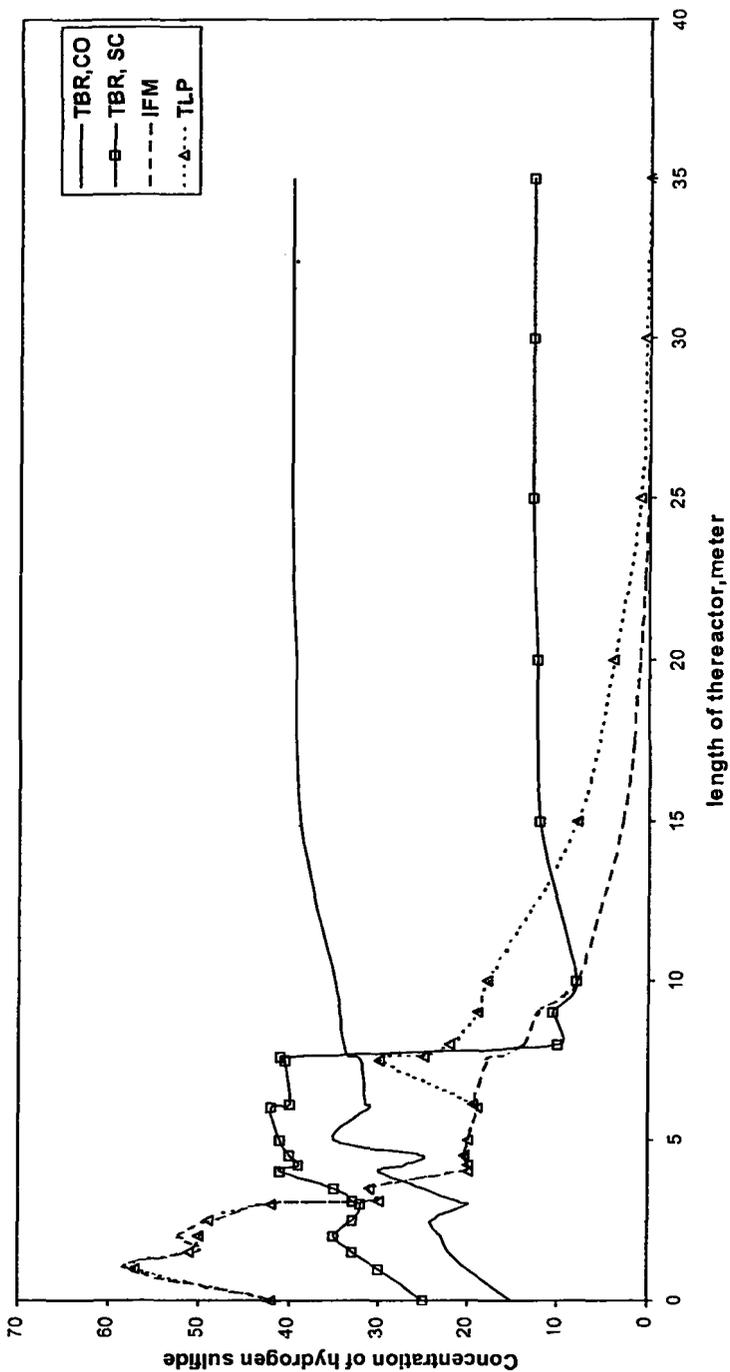


Fig. 6: Concentration of hydrogen sulfide along the length of different modes of operation

has to be considered outside the catalyst region (Frauhammer *et al.*, 1999). Flow regime in a monolithic reactor with cocurrent downward flow of gas and liquid was reported (Mewes *et al.*, 1999). The model for pressure drop of this reactor was also developed. Countercurrent flow of gas and liquid in these narrow channels will be very tough as the liquid flow in a downward mode will block as a film against the upflowing gas and will be pushed upward by the gas as a slug. The internally finned monolith reactor is a new concept of a three phase catalytic reactor in which the gas flows up under a very low pressure gradient, not obstructing the liquid from flowing down as a falling film. In this structure, the liquid will flow through space between the fins, provided the liquid wets the solid surface as usual. Thus the flow of liquid and gas occurs in separate paths in the same channel. The channel diameter is about 4 mm. Due to its geometry, catalyst loading and surface to volume ratio is comparable to 3 mm pellets randomly packed. The decreased mass transfer caused by the laminar flow of liquid and gas is not considered as a problem since the intended applications concern diffusion limited reactions such as desulfurisation, denitrogenation and dearomatization. Another potential application can be found in reactive distillation. Its main advantage is that it has a high degree of freedom over void fraction and the specific surface area so that there will be a good adjustment of reaction and mass transfer rate as well as catalyst and reactor utilisation. Different structures of the IFM are shown in Figure 7 (Lebens *et al.*, 1999a). Hydrodynamic studies with decane and air in single and multiple internally finned reactors have shown (Levens *et al.*, 1997) that countercurrent flow of gas and liquid is possible at velocities which are of industrial interest. When the liquid is distributed evenly, pressure drop and flooding limits are the same for a bundle as for a single tube. The flooding behaviour of gas-liquid countercurrent flow in this reactor was reported (Levens *et al.*, 1997). Characterisation of flow regimes in this reactor is distinguished by seeing the effect of increasing gas velocity with a constant liquid flow. Levens *et al.* (1999b) measured the flooding, pressure drop, liquid holdup and mass transfer characteristics in internally finned monoliths having 44 square channels. The diameter of each channel was 4.62mm, the height of each fin was 1.07 mm and the thickness of the fins and the walls was 0.497mm. Although the operational area of industrial reactors lies within the wavy film regime in IFM reactors, the gas-liquid volumetric mass transfer coefficient in IFM reactors is of the same order of magnitude compared to trickle bed reactors. However, its surface to volume ratio is not comparable with an

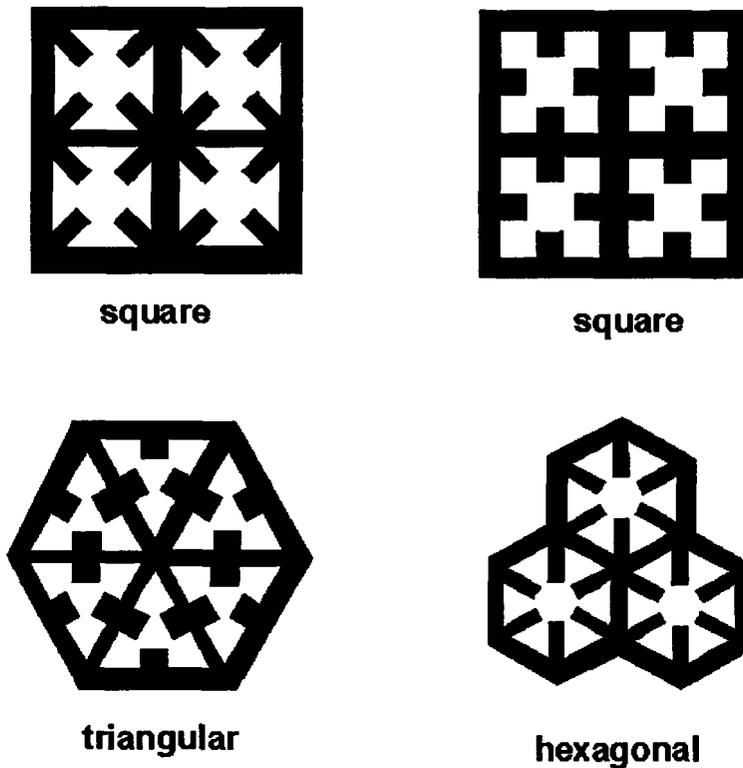


Fig. 7: Different structures of internally finned monolith catalyst.

industrial reactor, where in general a high catalyst loading is necessary. Van Hasselt *et al.* (1999d) studied the performance of two reactors in series having diameter 3m and 5m are operated in three different modes – cocurrent, semicountercurrent and countercurrent (packed with TLP packing or IFM packing) for HDS of VGO using Co-Mo- Al₂O₃ catalyst at a desired conversion of 98%

5.1.3 Flow regimes

In a countercurrent fixed reactor with cylindrical catalyst bales, three flow regimes exit: film regime, bubble regime and emulsification regime (Xu *et al.*, 1997). They were identified visually and by pressure drop method. Figure 8 shows the different flow regimes in catalyst bales (structured catalytic packing) and raschig ring (randomly packed). It is cleared from the figure

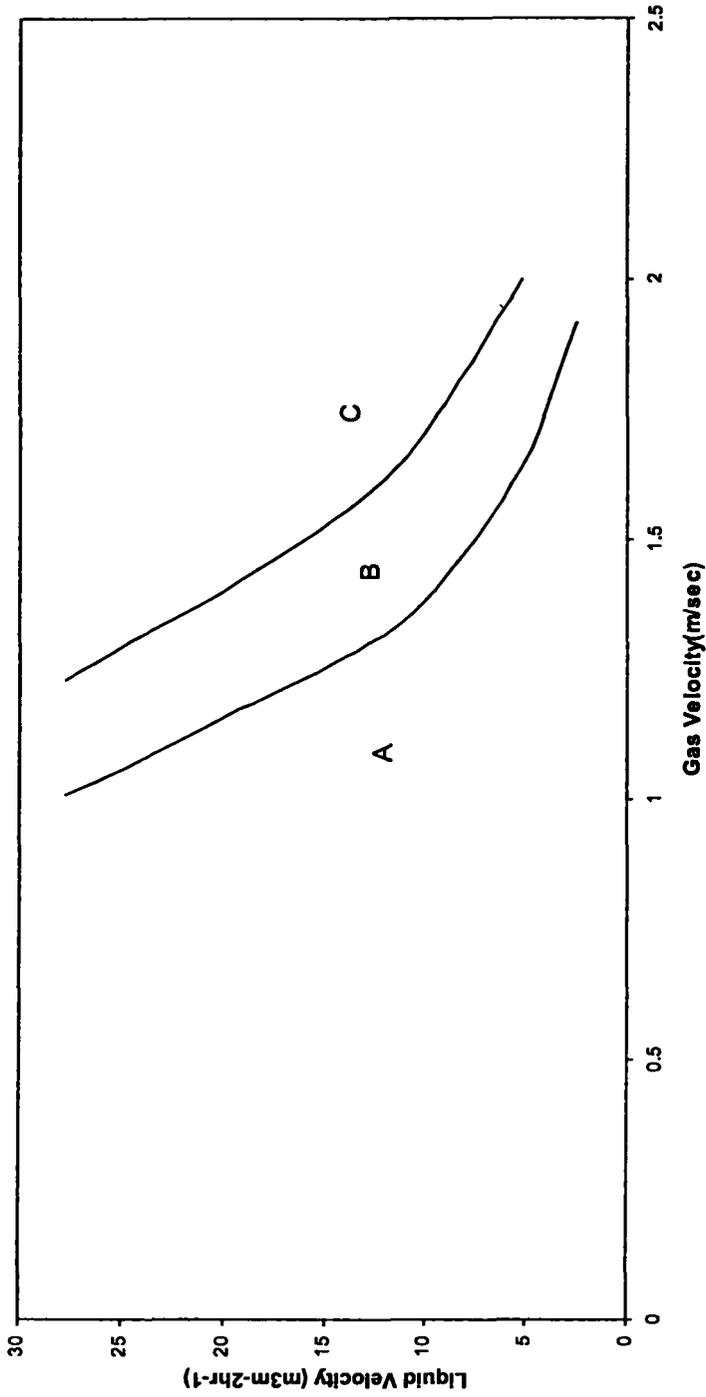


Fig. 8: Flow Regime Transition in catalyst containing bales (A= Film Regime, B= Bubble Regime, C= Emulsification Regime)

that the film flow regime for catalyst bales has covered wide range of gas and liquid flow rates compared to that of trickle flow regime for raschig ring.

Three flow regimes in Katapak-S (see Figure 9 for the structure of Katapak-S) can be distinguished (Moritz and Hasse, 1999): (i) Flow regime A, below load point: in this regime, the catalyst particles are generally completely wetted, though the space between the catalyst particles is not totally filled by the liquid. Stagnant liquid zones may exist in the catalytic structure, which may cause side reactions. (ii) Flow regime A*, load point: The space between the catalyst particles is totally filled with liquid. Here the surface tension between liquid and the wire gauze prevents the liquid from leaving the structure sideward. (iii) Flow regime B, above load point: The catalytic sandwich is completely filled with liquid and the excess liquid will flow outside the sandwich as a bypass, leading to maldistribution.

Three flow regimes are found in the internally finned monolith reactor as stated in Levens *et al.* (1997). The flow regimes are: (i) Wavy annular film

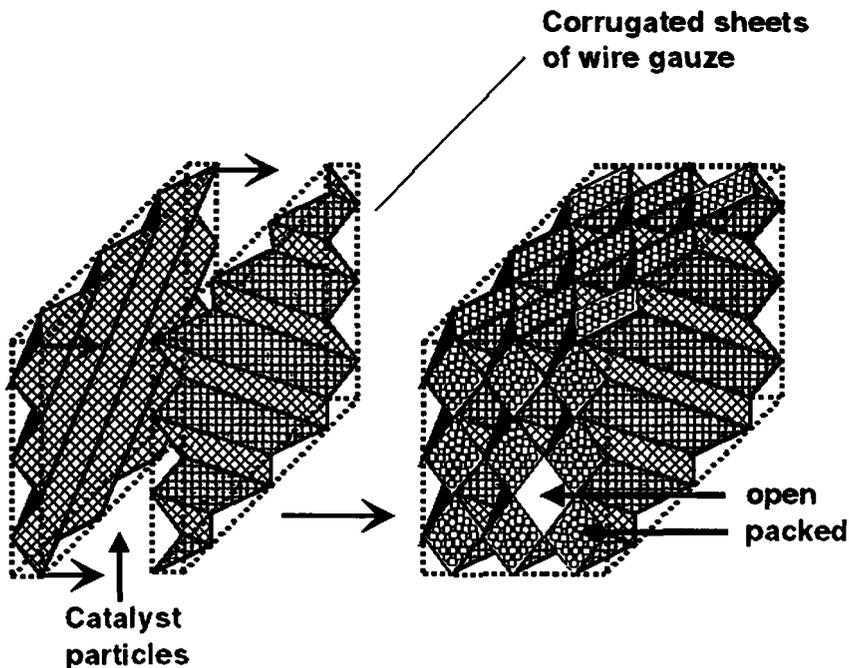


Fig. 9: Schematic drawing of Katapak-S structured packing with catalyst particles inside envelopes (from Ellenberger and Krishna, 1999).

flow regime: in this flow regime liquid falls down as a film with either ripples or waves and pressure drop is proportional to superficial gas velocity. (ii) Transition flow regime: here pressure drop starts to increase more than proportional with the superficial velocity of gas. Liquid plugs, formed at the liquid outlet, are carried upwards with the gas phase in this flow regime, and (iii) Total flooding regime: here the liquid behaves very chaotically, resulting in a combination of liquid downflow, upward slug flow and even downward slug flow.

5.1.4 Pressure drop

Most correlations for pressure drop in structured catalytic packing are reported separately in dry bed and wet bed conditions. Pressure drop characteristics of catalyst bundles, IFM, TLP and Katapak-S packing were analyzed. Table VII shows the overview.

Pressure drop for cylindrical bundles is explained by Xu *et al.* (1997). It can be seen that superficial gas velocity at flooding point is decreasing as the liquid superficial velocity increases because of more resistance of gas flow by liquid.

Pressure drop for IFM that is operated in wavy film regime, assuming that both liquid and gas flows are laminar, is explained by Levens *et al.* (1999b). A set of two-dimensional elliptic partial differential equations (PDEs) can be obtained from Navier-Stokes equations (Bird *et al.*, 1960) describing the relation between pressure drop, liquid hold up, and fluid velocities. Two-dimensional PDEs are

$$\nabla^2 (\mu_F \nabla \mu_{F2}) = dp/dz + g\rho_F, \text{ where } F = G, L \quad (29)$$

The above equations are valid for steady flow of an incompressible Newtonian liquid with constant viscosity and must be solved simultaneously for two sub-domains containing liquid and gas respectively. For irrigated pressure drop, the above two dimensionless PDEs give a good match with experimental value varying within a $\pm 20\%$ interval.

For TLP packing the proposed pressure drop model is based on the Channel model. Four contributions to pressure drop are taken into account (Van Hasselt *et al.*, 1999b):

- (I) Frictional loss in the channels between the baskets in a layer.
- (II) Contraction losses due to change in voidage.
- (III) Expansion losses due to change in voidage.
- (IV) Losses due to zigzag path of the gas phase (staggered configuration).

Contributions for expansion and contraction are taken together. For calculation of dry pressure drop, the number of occurrences of friction (i.e. n_f) were calculated by varying the bed height (n_f) on in-line configuration (i.e. $n_{zz}=0$) at a constant number of expansion-contraction (n_{ec}). Thus n_f and n_{ec} are calculated. Then fitting pressure drop vs. superficial gas velocity across the in-line configuration, turbulent contribution to friction (C_{Tf}) and expansion-contraction ($C_{T_{ec}}$) and laminar contributions to friction (C_{Lf}) were obtained. Keeping C_{Tf} , $C_{T_{ec}}$ and C_{Lf} constant and changing the configuration from in-line to staggered zigzag contribution ($C_{L_{zz}}$ and $C_{T_{zz}}$) are obtained. It is found that the calculated dry pressure drop matches with measured value within accuracy $\pm 20\%$ (refer to Table VII for details).

For the irrigated pressure drop, there is no such model, which directly gives the pressure drop.

For Katapak-S structure Moritz and Hasse (1999) and Ellenberger and Krishna (1999) described the pressure drop characteristics depending upon the flow regime.

Dry pressure drop: Moritz and Hasse (1999) reported an expression to predict dry pressure drop in Katapak-S structured packing. A similar expression was also obtained by Ellenberger and Krishna (1999). However the value of constants C and D were different as they depend on the characteristics of the structured packing.

Irrigated pressure drop: Moritz and Hasse (1999) described the irrigated pressure drop depending upon the flow regime. These are as follows:

1. Pressure drop upto the load point and below the flooding point (regime A)
2. Pressure drop above the load point and below flooding point (regime B)
3. Pressure drop near the flooding point (regime C),

whereas Ellenberger and Krishna (1999) described the irrigated pressure drop of this packing in two conditions:

- (I) Below a maximum superficial liquid velocity, $U_{L, PC, max}$ (defined as that flow rate at which liquid will flow only in the packed channel, not in the open channel).
- (II) Above the $U_{L, PC, max}$.

For condition (I), i.e. in the range $U_L < U_{L, PC, max}$, the pressure drop is equal to the dry pressure drop of the packing as the gas flow through the open channel is not hampered by liquid flow. This is the same as in the flow

Table VII
Pressure drop correlations in structured packings

Packing	Correlation	Remarks
Catalyst Bales	$\Delta P_b = au^b$ for dry condition ($L=0$), $a=171.2$, $b=1.790$ and $\ln(\Delta P_w/Z) = au^b ZL^c$ for $L>0$ and below the flooding points, $a=5.539$, $b=0.330$, $c=0.048$	The measured value is within $\pm 10\%$ of the simulated value
IFM	$-(dp/dz)_d = 2B\mu_c u_c / d_{it}^2$ Where B is a constant which depends on velocity profile, $B=15.4$.	There is no such correlation for calculating wet pressure drop.
TLP	$\Delta P_b = C_L V_o + C_1 V_o^2 = (n_f C_{Lf} + n_{ec} C_{L,ec} + n_{zz} C_{L,zz}) V_o^2 + (n_f C_{Tf} + n_{ec} C_{T,ec} + n_{zz} C_{T,zz}) V_o^2$ The subscripts 'L' and 'T' stand for laminar flow and turbulent flow respectively and 'f' for friction, 'ec' for expansion and contraction and 'zz' for zigzagging. 'n' is the no of times that friction, expansion-contraction or zigzagging occurs in a given length of the TLP packing.	For wet pressure, there is no such correlation, which directly gives the pressure drop.

<p>Katapak-S</p>	<p>$\Delta P_D = f_1 \rho_c \Delta H (W_G / \epsilon \cos \alpha)^2 / 2d_h$, the friction factor $f_1 = C Re_{G,A}^D$ and $Re_{G,A} = W_G d_h / \nu_G$. C & D are the fitting parameters for the dry pressure.</p> <p>Regime-A</p> <p>$\Delta P_{A,1} = f_2 \Delta P_D$ with $f_2 = K h_A^L$ and $h_A = E Fr_{L,A}^F / Re_{L,A}^G$, where $Fr_{L,A} = W_{L,eff}^2 / (\epsilon^2 g d_h)$ and $Re_{L,A} = W_{L,eff} d_p / (1-\epsilon) \nu_L$. K, L, E, F and G are fitting parameters.</p> <p>Regime-B</p> <p>$\Delta P_{B,1} = f_3 \Delta P_{A,1}$ with $f_3 = Q \{ \epsilon_R (h_B - h_A) \}^{-R}$. Where $h_B = h_A^* + M Fr_{L,B}^N / Re_{L,B}^P$. Q, R, M, N & P are fitting parameters.</p> <p>Regime-C</p> <p>The pressure drop is calculated using a cubic polynomial:</p> <p>$\Delta P_{II} / \Delta H = X (W_G - W_{G,max})^3 + Y (W_G - W_{G,max}) + Z$</p> <p>X is the fitting parameter.</p> <p>Above $U_L > U_{L,FC,max}$ (Moritz & Hasse, 1999).</p> <p>$\Delta P / L = \Delta P_D \exp[1.3 \epsilon_{Loc} (Re_{Loc} / Fr_{Loc})^{0.3}]$ and $\epsilon_{Loc} = 2.8 (Fr_{Loc}^3 / Re_{Loc})^{0.3}$</p> <p>$Re_{Loc} = V_{Loc} \rho_L d_p / \eta_L$, $Fr_{Loc} = V_{Loc} / (g d_h)^{0.5}$, $V_{Loc} = U_{Loc} / (\epsilon_{Loc} \sin \alpha) = (U_{L,FC,max}) / (\epsilon_{Loc} \sin \alpha)$ and $\epsilon_{Loc} = \epsilon_L - \epsilon_{L,FC,max}$</p>	<p>The pressure drop ($\Delta P_{A,1}$) was described as a function of dry pressure drop and it is almost equal to dry pressure drop.</p> <p>ΔP_{II} starts with the pressure drop Z at $W = W_{G,max}$ and increases with the same slope as ΔP_I ends.</p>
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regime A predicted by Moritz and Hasse (1999). For condition (II), liquid will flow through the packed channel as well as through the open channel forming a liquid film. Consequently the space for gas flow decreases and thus pressure drop increases.

The hysteresis of pressure drop was observed in a countercurrent fixed bed reactor with glass beads and ceramic raschig rings (Wang *et al.*, 1998). The hysteresis of pressure drop originates from the nonuniformity of gas-liquid flow in a countercurrent fixed bed reactor. Figure 10 compares the pressure drop of different structured packings – TLP and Katapak-S ($L=6.9 \text{ kgm}^{-2} \text{ sec}^{-1}$) and IFM ($L=5 \text{ kgm}^{-2} \text{ sec}^{-1}$) where TLP has lower pressure drop compared to Katapak-S at the same gas and liquid velocity.

5.1.5 Liquid holdup

Liquid holdup of TLP, the cylindrical bales, Katapak-S, IFM and GPP packings were described. The effect of liquid superficial velocity and gas superficial velocity on liquid holdup was studied. The total holdup in TLP reactors consists of three parts: (i) intra-particle holdup inside the porous particles, (ii) bed holdup outside the particles in a bed, (iii) excess holdup outside the catalyst bed (Van Hasselt *et al.*, 1999a). The bed holdup consists of (i) free draining holdup: volume of drained liquid per unit of void reactor volume, (ii) residual bed holdup, β_{res} : volume of liquid located at the contacting points of the particles. Excess holdup consists of liquid on the reactor internals and reactor wall and liquid falling from bed to bed. A model for bed holdup in TLP reactors was developed assuming that the bed holdup consists of two parts: (i) below the capillary rise height (h_c) the interstitial pores will be completely filled ($\beta = 1$), (ii) above this height holdup is determined by a liquid film spreading over the particles, which can be described by correlations for single phase trickle flow. For cylindrical catalyst bales, the correlation for estimating the dynamic liquid holdup below the turning point (at that superficial gas velocity where dynamic liquid velocity increases quickly) is (Xu *et al.*, 1997)

$$h_d = a u^b L^c \quad (30)$$

where $a = 0.0336$, $b = 0.0109$ and $c = 0.429$ for this packing.

It was found that the dynamic liquid holdup increases with the increase of liquid superficial velocity and increases slowly with the increase of gas superficial velocity, when it is in lower range. The dynamic liquid holdup

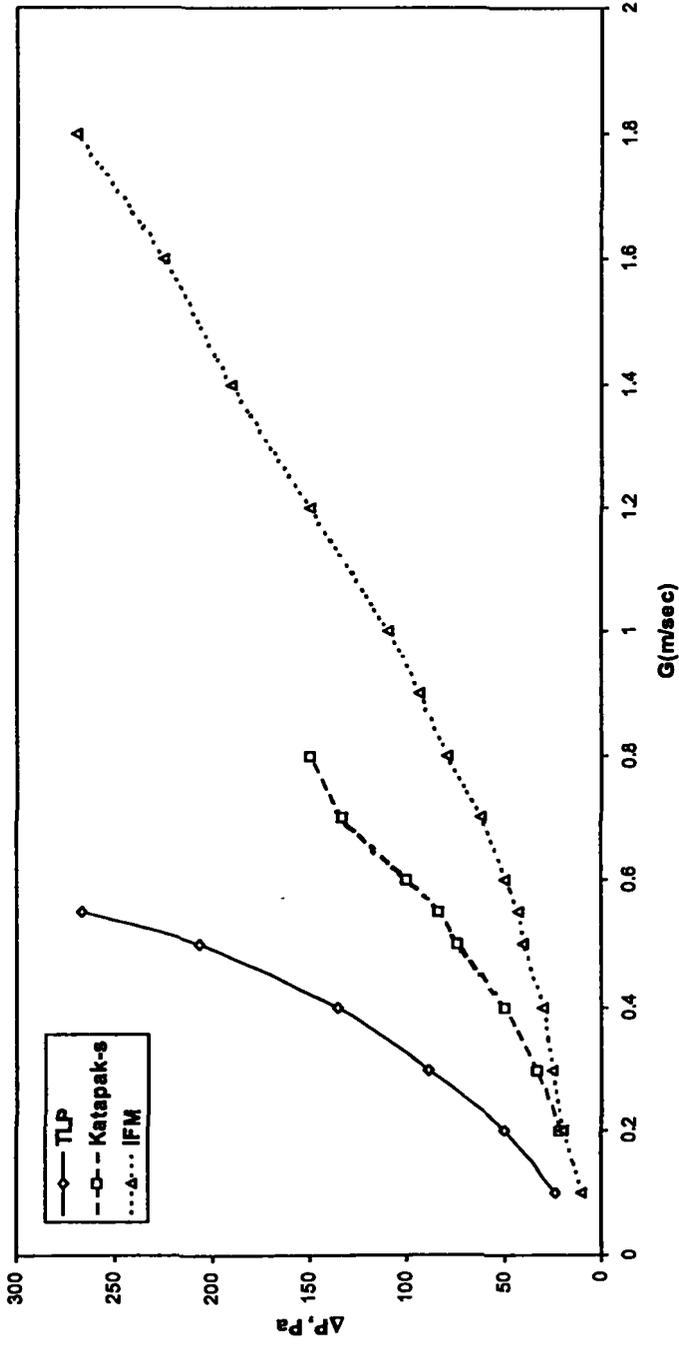


Fig. 10: Pressure drop for different structure packings (for TLP and Katapak-S, $L=6.9\text{kg/m}^2\cdot\text{sec}$ and for IFM, $L=5\text{kg/m}^2\cdot\text{sec}$)

increases quickly after a certain gas superficial velocity. The correlations for liquid holdup of Katapak-S packing have been described previously with pressure drop correlations (in Table VII). The model for liquid holdup in IFM reactor was developed by Levens *et al.*, 1999b. The experimental value of dynamic holdup in IFM reactor matches with calculated value at low NLS (ReLS/GaL). At high NLS, the model overestimates the experimental value. Total liquid holdup in GPP packings fluctuates with the vapour mass flux density. This was explained by Sundmacher and Hofmann (1994) and the characteristics of the vapour distributor is responsible for that fluctuation.

5.1.6 Residence time distribution studies

Residence time distribution (RTD) studies were carried out in Katapak-S and TLP structured catalytic packings. The residence time behaviour of these two types of structured packing does not depend on the moderate gas load.

Liquid phase residence time distribution studies in Katapak-S were reported by Ellenberger and Krishna (1999), Moritz and Hasse (1999) and Higler *et al.* (1999). The effect of liquid load on residence time distribution curve shows that the curve is comparatively narrow with a tailing due to the presence of stagnant zones at liquid load below the load point. At liquid load near the load point the RTD curve becomes narrower without tailing. At high liquid load (above the load point) the RTD curve becomes broad and asymmetric due to the bypass of liquid (Moritz and Hasse, 1999). The axial dispersion coefficient of the liquid phase is determined by fitting the measured response to

$$E(t/\tau) = 1/[2(\pi t/\tau Pe)^{0.5}] \exp[-(1-t/\tau)^2/(\pi t/\tau Pe)] \quad (31)$$

The calculated axial dispersion coefficient is practically independent of the column diameter and depend only on $Re_{L,H}$ (Reynolds number in terms of hydraulic diameter) (Higler *et al.*, 1999). The measured liquid phase RTD is the same for the cases where the tracer is injected in the packed channel or in the open channel. This implies that there is a very good exchange between the liquid in the open channel and packed channel. Axial dispersion coefficient for this structured packing is higher than that in the conventional trickle bed reactor due to bypassing of the liquid in the open channels (Ellenberger and Krishna, 1999). Van Baten *et al.* (2001) studied radial liquid phase residence time distribution in a Katapak-S structure. The radial dispersion coefficient in a Katapak-S structure was about one order of

magnitude higher than that in cocurrent down flow trickle-beds, which is desirable for prevention of the formation of hotspots in the reactor. A liquid phase RTD model for TLP packing was developed that considers each catalyst layer as a number of stirred tanks, and the liquid jets falling from layer to layer as plug flow reactors. This model predicts the influence of layer distance on Pe_L (Van Hasselt *et al.*, 1999c). An experimental RTD curve shows that the reactor wall has a strong influence on RTD, as the RTD curve has a tail despite the use of wall wipers, which means that there is a liquid bypass along the reactor wall. The laminar flow in the IFM will introduce some axial dispersion; a cascade of monoliths will reduce this effect (Levens *et al.*, 1999a). The Peclet number values for the structured catalytic packing is greater than that of noncatalytic packing. This is desirable as reaction is also occurring in catalytic packing.

5.1.7 Gas- Liquid mass transfer

There are studies on the gas-liquid mass transfer in structured catalytic packing by Subawalla *et al.*(1997), Levens *et al.*(1999c), Higler *et al.*(1999) and Van Hasselt *et al.* (2001). Subawalla *et al.* (1997) studied mass transfer in reactive distillation bale packing. They developed a model based on liquid film flow over the area of packing and falling liquid drops. The gas-liquid volumetric mass transfer coefficient, k_La , in an internally finned monolith reactor was calculated for a wider range of liquid and gas flow by Levens *et al.* (1999c). It was found that k_La varied between 0.03 and 0.16sec⁻¹ and the value of k_La in IFM is not much less than that of conventional TBR. Higler *et al.* (1999) showed that the mass transfer within the sandwich structure of Katapak-S packing was dominated by the mixing experienced at the cross-overs and was independent of the liquid velocity. Van Hasselt *et al.* (2001) modeled gas-liquid mass transfer in TLP as a combination of the mass transfer in the liquid jets that fall from one catalyst bed to another and the mass transfer at the faces of baskets. They obtained the value of volumetric mass transfer coefficient for the baskets about 16% to the overall mass transfer, which indicates that mass transfer mainly takes place at the surface of the liquid jets. They also showed the higher value of k_La per volume solids of TLP reactor than that of TBR after a certain length.

6. CONCLUDING REMARKS

For the last 30 years, much attention has been paid to pressure drop, liquid holdup, wetting efficiency and mass transfer characteristics in trickle-bed reactors. There are many correlations and theoretical models for the prediction of hydrodynamics in TBR. The correlations cannot be used, in general, as these are generated based on some sets of individual experiments. Although we have made significant progress in modeling the hydrodynamics of TBR theoretically, still the prediction of some hydrodynamic parameters like pressure drop in TBR is not altogether accurate due to the complex of gas-liquid flow pattern and their interaction. The theoretical models like Attou *et al.* (1999), Souadnia and Latifi (2001), Propp *et al.* (2000), Fourar *et al.* (2001) and Narasimhan *et al.* (2002) should be preferred for the modeling. Some of them are CFD based models and some of them have the capability for fitting into CFD code. These models also offer the inclusion of more complex behavior associated with chemical reactions and mass transfer. More recently, Jiang *et al.* (2002a and b) have modeled the multiphase flow in TBRs using the Eulerian k-fluid CFD approach. All the drag forces physically present are taken into account. The effect of interfacial tension and wetting of the packing has also been considered.

For the measurement of wetting efficiency in TBR, the magnetic resonance imaging (MRI) method can be applied due to its direct way of measurement, though it is expensive. Among the other methods, tracer technique seems to be logical. The theoretical modeling of wetting efficiency is lacking in the literature. Only the double slit model (Iliuta *et al.*, 1999b and 2000) and the model developed by Pironti *et al.* (1999) are present. Recently, many works on the problems of liquid and gas distribution inside the bed have been reported. Theoretical modeling on liquid distribution in TBR is rare. Only the DCM model of Jiang *et al.* (1999) is available for the description of liquid distribution in TBR. The investigation of microscaling fluid distribution in TBR is still required. Though the EBR configuration is a promising reactor to cope with the emphasis on the conversion of less valuable streams (e.g. residue hydroconversion) into transportation fuel, the published literature on the fundamental aspects of EBR is very sparse. Attention should be given to that point.

The different structured catalyst packings are discussed. The hydrodynamic studies of structured packings such as catalyst particles,

sandwiched between corrugated sheets of wire gauze, and catalyst bales are reported with large diameter column at atmosphere pressure. For some structured packings like TLP and IFM packings, the hydrodynamic, RTD and mass transfer studies are performed using very small diameter column (less than 12 cm). It is interesting that pressure drop in structured catalytic packing is low compared to conventional TBR. The experiments should be carried out in large diameter columns with more catalyst layers to compare with the present results.

Structuring the catalytic packing creates more flexibility for fine tuning and optimising the reactor performance by controlling the position of the catalyst material. This is why more works on the invention and development of structured catalytic reactor packings are required. Studies with real liquids are also required. These types of structured catalytic packing are promising reactor configurations for hydroconversion, which are operated at high pressure (30-200 bar), so fluid dynamic behavior should be studied at high pressure. Lastly, the major disadvantages of the countercurrent hydroprocessing in commercial applications are due to hardware limitations. The catalyst loading is 20-25% by volume in countercurrent operation (though less catalyst volume is necessary for the countercurrent operation for getting the same conversion), whereas in TBR, the catalyst loading is 60-70% by volume. There is, therefore, a need to develop improved hardware configurations that allow countercurrent contacting of gas and liquid in the presence of small size catalyst particles and also when the catalyst loading is above 50% by volume. TLP and IFM structured packing can also be applied industrially where the catalyst loading can be obtained above 50% by volume.

NOTATIONS

a_K	=	specific surface area of Katapak-S packing
d_h	=	hydraulic diameter, meter
d_p	=	equivalent particle diameter, m
$D_{ax, L}$	=	axial dispersion coefficient, m^2/sec
$Fr_{L, B}$	=	$\{(W_B - W_A) a_K\} / g$
L	=	length of the reactor, m
ΔP_D	=	Dry pressure drop
ΔP_w	=	Wet pressure drop

- $Pe = U_L L / (\epsilon_L D_{ax,L})$,
 $Re_{L,B} = (W_B - W_A^*) / V_L a_K$
 $U_L =$ Superficial liquid velocity, m/sec
 $V_{L,OC} =$ interstitial liquid velocity in open channel, m/sec
 $W_{L,eff} = W_L^* / \cos \alpha$
 $W_L^* =$ liquid velocity at liquid point
 $W_{G,max} =$ gas velocity at 80% of the maximum capacity

Greek letters:

- $\alpha =$ angle of inclination of the flow channel i.e. corrugated sheet,
 $\epsilon =$ void fraction of the packing, m^3 void/ m^3 reactor
 $\epsilon_{LOC} =$ liquid holdup in the open channels
 $\epsilon_{L,PC,max} =$ maximum liquid holdup of the packed channels
 $\rho_L =$ density of liquid, kg/m^3
 $\eta_L =$ dynamic viscosity, Pa. sec
 $\epsilon_L =$ Liquid holdup
 $\tau =$ mean residence time = $L / (U_L / \epsilon_L)$

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