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Muthanna H. Al-Dahhan
Missouri University of Science and Technology, aldahhanm@mst.edu

Milorad P. Duduković

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CATALYST WETTING EFFICIENCY IN TRICKLE-BED REACTORS AT HIGH PRESSURE

MUTHANNA H. AL-DAHHAN and MILORAD P. DUDUKOVIĆ
Chemical Reaction Engineering Laboratory, Chemical Engineering Department, Campus Box 1198, Washington University, One Brooking Drive, St. Louis, MO 63130-4899, U.S.A.

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Abstract—Trickle-bed reactors are widely used in industrial high pressure operations (up to 30 MPa). The knowledge of catalyst wetting efficiency as a function of operating conditions is needed for relating laboratory and pilot scale reactor data to large scale reactor operation. The available predictions of the wetting efficiency rest on data collected at atmospheric pressure. In this study a phenomenological analysis has been developed to relate the wetting efficiency with operating conditions such as reactor pressure, gas and liquid flow rate. Experimental data for the wetting efficiency at high pressure have been obtained via a tracer technique. The data support the developed model which can be expressed by the following correlation:

$$\eta_{CE} = 1.104\, Re_L^{1/3} \left[\frac{1 + [(\Delta P/Z)/\rho_L g]}{Ga_L} \right]^{1/9}.$$

This correlation is also in good agreement with the data correlated previously at atmospheric pressure and provides the means for assessing liquid-catalyst contacting at all operating pressures.

INTRODUCTION

Trickle-bed reactors (TBR), are fixed beds of catalyst particles, contacted by the cocurrent downflow of gas and liquid. They are used widely in industry (e.g. petroleum, petrochemical and chemical industries, pollutant abatement, biochemical and electrochemical processes). The vast majority of industrial trickle-bed reactors operate at high pressure, up to about 20–30 MPa (3000–4000 psig) in order to slow down catalyst deactivation, improve the solubility of the gaseous reactant, attain high conversion and achieve better heat transfer. Various flow regimes that exist in trickle-bed reactors depend on the superficial mass velocities, fluid properties and bed characteristics (Zhukova *et al.*, 1990; Holub, 1990; Gianetto and Specchia, 1992) and can be lumped into two basic ones: the low interaction regime (trickle flow regime) and the high interaction regime (pulse, spray, wavy, bubble, and dispersed bubble flow regimes). In the trickle flow regime the catalyst is either partially externally wetted ($\eta_{CE} < 1$) or fully externally wetted ($\eta_{CE} = 1$) as illustrated in Fig. 1. Incomplete catalyst wetting in laboratory and pilot plant trickle-bed reactors, operated with the same catalyst shape and sizes used in the industrial reactors, is the result of low liquid velocities.

The internal liquid-catalyst contacting efficiency (i.e. the fraction of pore volume in the particles that is filled with liquid) is usually equal to unity due to capillary effects. In contrast, the external catalyst wetting efficiency (i.e. the fraction of particles external area wetted by the flowing liquid) increases monotonically with the liquid mass velocity and is unity only at high liquid velocities. This external catalyst contacting efficiency is an important design and scale up parameter which is essential in determining the degree of catalyst utilization in trickle-bed reactors (Dudukovic and Mills, 1986). The reaction rate over externally incompletely wetted packing can be greater or smaller than the rate observed over completely wetted packing. This depends upon whether the limiting reactant is present only in the liquid phase or in both gas and liquid phases. For instance, if the reaction is liquid-limited and the liquid reactant is nonvolatile, such as occurs in many hydrogenation processes, then a decrease in the catalyst-liquid contacting reduces the surface for mass transfer between the liquid and the catalyst causing a decrease in the reaction rate. However, if the liquid reactants are volatile, and significant heat effects are also present, then, a gas phase reaction can occur on the dry area of the catalyst and consequently a higher reaction rate is observed. Such higher rate is also achieved in case of gas-limited reaction where gas reactant can access the catalyst pores from the externally dry area. Accordingly, in order to predict trickle-bed reactor performance and model its behavior, it is necessary to know the catalyst wetting efficiency and the effectiveness factor of the resulting partly wetted catalyst (Dudukovic, 1977; Mills, 1980; El-Hisnawi, 1981; Mills and Dudukovic, 1981, 1982a; Dudukovic and Mills, 1986; Zhukova *et al.*, 1990).

Many studies of external liquid–solid contacting efficiency have been reported in the literature (Shulman *et al.*, 1955; Onda *et al.*, 1967; Krauze and Scrwinski, 1971; Puranik and Vogelpohl, 1974; Mills

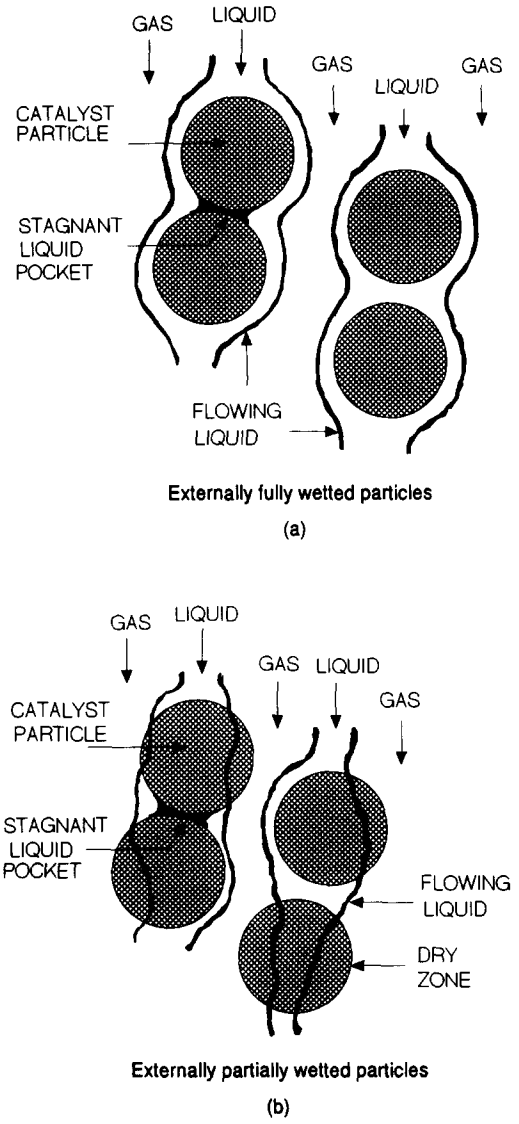


Fig. 1. Schematic of flow patterns in trickle flow regime for externally completely and partially wetted particles.

and Duduković 1981; El-Hisnawi, 1981; Ruecker *et al.*, 1987; Lazzaroni *et al.*, 1987; Ring and Missen, 1991). Some deal with theoretical and experimental methods to evaluate it, while others deal with demonstrating its effect on the performance of trickle-bed reactors. All contacting efficiency correlations reported in the open literature were developed based on atmospheric data. Although Ring and Missen (1991) and Ruecker *et al.* (1987) measured the contacting efficiency also at 10 and 5.2 MPa, respectively, they did not investigate the effect of high pressure. To our knowledge the most extensive experimental study of the contacting efficiency, using nonadsorbable and adsorbable tracers, was performed by Mills (1980). The results, together with the findings from other laboratories in which contacting was inferred from reaction studies, were correlated (Mills and Duduković, 1981). Unfortunately, there were two problems with the resulting correlations: the misprint corrected by the authors was not properly corrected by the publisher as the article went to print, and the actual group of variables that appeared in the correlation was not dimensionless. The errata which was published (Mills and Duduković, 1982b) went unnoticed by many. Since the correlation as printed is off the mark, this caused wide spread skepticism about its usefulness. Later on El-Hisnawi *et al.* (1981, 1982) augmented the data base, still using only atmospheric pressure data, and changed the form of the correlation. One form correlated the collected data for the external contacting efficiency in terms of superficial Reynolds and Galileo numbers, while the other form related it to dynamic liquid saturation. These forms, shown below, are currently the only ones available for predicting contacting efficiency of small porous packing characteristic of trickle-bed reactors.

$$\eta_{CE} = 1.617 Re_L^{0.1461}\, Ga_L^{-0.0711} \tag{1}$$

where

$$Re_L = \frac{L d_P}{\mu_L}, \quad Ga_L = \frac{d_P^3 g \rho_L^2}{\mu_L^2}$$

$$\eta_{CE} = \omega_d^{0.224} \tag{2}$$

where ω_d is dynamic liquid saturation.

The correlation given by eq. (1) does not indicate a dependence on gas flow rate since none was detected at atmospheric conditions. This may not be the case in high pressure operation.

No study appeared in the open literature which investigated directly the effect of high pressure (the operating condition of interest) on the wetting efficiency. Moreover, due to the complex interaction between the flowing phases and the stationary packing no fundamental model or description is available which leads to the better understanding of the incomplete wetting phenomena of the external catalyst surface. While it is speculated that high pressure improves liquid-catalyst contacting, it is unknown to what extent this occurs and whether the correlation developed based on atmospheric data can be utilized for prediction of wetting efficiency at high pressure operation. In this study a phenomenological approach has been developed to describe the effects of high pressure and gas flow rate on the external liquid-catalyst contacting. Experimental investigations have been conducted to demonstrate such effects, and a model has been developed which accounts for the observed effects.

PHENOMENOLOGICAL ANALYSIS

The flow pattern of the flowing liquid and gas in the trickle flow regime (gas continuous flow regime) is visualized approximately as liquid flow in form of films and/or rivulets over the catalyst surface with gas phase flow in the center core. In trickle flow regime, the catalyst can be partially externally wetted at low liquid velocities or completely externally wetted at higher liquid velocities, as illustrated in Fig. 1. Due to

the complexity of the flowing fluid field in trickle-bed reactors, a complete fundamental description of the hydrodynamics on the particle scale has not been accomplished yet. Such description is essential to understand the liquid-catalyst wetting phenomena. Hence, we recognize that Fig. 1 represents a simplification whereby an inherently random process of liquid dribbling along solid particles is represented by rivulets (when dribbling frequency is low) and by a continuous film at high dribbling rate. Accordingly, a phenomenological approach which relies on this simpler physical representation of the phenomena is useful and desirable in the absence of more fundamental approaches. The hydrodynamics of thin liquid films is directly related to processes that determine catalyst wetting (Dudukovic and Mills, 1986). Holub *et al.* (1992, 1993) proposed a phenomenological model based on annular two phase flow in slit as a simple representation of trickle flow regime. In this study, Holub's *et al.* (1992, 1993) model is extended to incorporate the effect of reactor pressure and gas flow rates on the wetting efficiency as well as on pressure drop and liquid holdup.

The effect of high pressure and gas flow rate on the pressure drop of a gas–liquid cocurrent downflow in a packed bed reactor can be described in terms of the energy dissipation. Such dissipation is due to the frictional losses at the packing surface and the driving forces acting on the liquid flow. The driving forces consist of the pressure gradient ($\Delta P/Z$) and the gravitational force ($\rho_L g$). The pressure gradient depends on the velocity and on the density of the flowing fluids. Higher liquid and gas superficial velocity and/or density produce a higher pressure gradient while higher liquid density increases the gravitational force. Since the gas density depends on the gas pressure, increasing the reactor pressure makes the gas more dense. Therefore, the effect of the gas phase on the pressure drop can be separated into the effect of the superficial gas velocity and of the reactor pressure. Accordingly, an increase in the reactor pressure (at constant superficial gas and liquid velocities for a given liquid and a gas phase) results in a higher pressure drop (larger energy dissipation) due to the increase in the gas phase density. Increasing the superficial gas velocity at such high pressure, yields much higher pressure drop due to increased frictional losses.

Based on Holub *et al.*'s (1992, 1993) slit model, the dependence of liquid holdup on pressure drop can be represented by:

$$\varepsilon_L = \varepsilon_B \left(\frac{E_1 Re_L + E_2 Re_L^2}{Ga_L\{1 + [(\Delta P/Z)/\rho_L g]\}} \right)^{1/3} \tag{3}$$

where the term $(\Delta P/Z)/\rho_L g$ is the dimensionless pressure drop that represents the ratio of the pressure drop to the gravitational forces. E_1 and E_2 are the Ergun constants which characterize the bed (i.e. they are only functions of the bed parameters defined by the slit model as $E_1 = 72T^2$ and $E = 6T^3 f_{\text{wall}}$). Therefore, they are determined from single phase flow experiments in the bed (e.g. gas phase flow in dry bed) (Holub, 1990). By assuming uniform porosity and liquid holdup over the packed bed, the same solid surface area per unit solid volume in the slit and in the packed bed, and spherical particles, the mean thickness of the liquid films, δ, can be expressed in terms of the actual trickle-bed parameters as follows:

$$\delta = \left[\frac{\text{total liquid holdup}}{\text{specific external area } (\text{m}^2_{\text{particles}}/m^3_{\text{reactor}})} \right] = \frac{\varepsilon_L}{6(1-\varepsilon_B)/d_P}. \tag{4}$$

Substituting eq. (3) into eq. (4), yields the film thickness dependence on pressure drop and on liquid flow rate through liquid Reynolds number as:

$$\delta = \left(\frac{d_P}{6}\right)\left(\frac{\varepsilon_B}{1-\varepsilon_B}\right)\left(\frac{E_1 Re_L + E_2 Re_L^2}{Ga_L\{1 + [(\Delta P/Z)/\rho_L g]\}}\right)^{1/3}. \tag{5}$$

Both liquid film thickness and liquid spreading determine liquid-catalyst wetting efficiency. Unfortunately, due to the complex geometry of the trickle-bed reactor, no fundamental model is available which quantitatively describes liquid spreading over the external surface of the porous packing in a randomly packed bed. This information is needed to estimate liquid film thickness, film stability and wetting efficiency. However, based on eqs (3) and (5) the following effects can be deduced for a particular bed: "*As the dimensionless pressure drop $(\Delta P/Z)/\rho_L g$ increases at fixed liquid velocity (i.e. fixed Re_L), due to either larger gas velocity or higher reactor pressure, both liquid holdup and liquid film thickness decrease. This increase in dimensionless pressure drop increases the shear stress on the gas–liquid interface and results in an improved spreading of the liquid film over the external packing area making it more wet. This causes the external liquid-catalyst wetting efficiency to increase in spite of the reduction in liquid holdup. As liquid flow rate increases, both liquid holdup and pressure drop increase, which yield a further improvement in the wetting efficiency*". Recently Wammes (1990) and Larachi *et al.* (1992) observed that at high pressure operation gas–liquid interfacial area increases. It becomes even larger as gas velocity increases. This confirms the enhanced spreading of the liquid over the external area of the catalyst which improves the contacting between gas–liquid and liquid–solid at conditions typical of industrial high pressure operations.

Based on the preceding discussion, at fixed liquid flow rate, the contacting efficiency, η_{CE}, is also inversely proportional to some power of Ga_L number (i.e. the larger the particle the lower the wetting and the larger the gravitational to surface forces ratio the lower the wetting) but is directly proportional to the dimensionless pressure drop raised to some power as increased pressure drop spreads the liquid more as argued above. Hence, we assumed

$$\eta_{CE} \propto \left(1 + \frac{\Delta P/Z}{\rho_L g} \right)^m \Big/ Ga_L.$$

The complex dependence on the Reynolds number is assumed of the form Re_L^n to conform to El-Hisnawi *et al.* (1981, 1982) successful low pressure correlation when the dimensionless frictional pressure drop is close to zero [eq. (1)] This yields the form suggested below which describes well our phenomenological reasoning discussed above and also reduces in the limit of low pressure to El-Hisnawi's correlation which has been tested for liquids of different physical properties.

$$\eta_{CE} = c\, Re_L^n \left\{ \frac{1 + [(\Delta P/Z)/\rho_L g]}{Ga_L} \right\}^m. \qquad (6)$$

The required dimensionless pressure drop can be predicted from Holub *et al.*'s (1992) correlation. Five limiting cases can be distinguished for the pressure drop behavior (Al-Dahhan and Duduković, 1995). Hence, eq. (6) indicates the following five limiting cases for the effect of reactor pressure and gas flow rate on the catalyst wetting efficiency for a given bed and a given bed and a given set of physical properties:

Case 1: *No gas flow.* Without gas flow but with stagnant gas present in the system i.e. $U_G = 0$ the ratio $(\Delta P/Z)/(\rho_L g)$ is zero. The gravitational force is the only driving force for liquid flow. Hence, wetting efficiency is minimal while liquid holdup is maximal. Although this case is not of practical interest, it is considered for completeness as a limiting case for low gas flow rates.

Case 2: *Low pressure, low gas superficial velocity.* At atmospheric to low pressure, and at low gas superficial flow rate, the dimensionless pressure drop, $(\Delta P/Z)/\rho_L g$, is very small and liquid holdup is decreased negligibly compared to case 1 of no gas flow. Hence, the wetting efficiency increases very slightly if at all, due to small improvement in liquid spreading over the catalyst particles. As liquid flow rate increases, the contacting efficiency increases due to the increase in both liquid holdup and pressure drop.

Case 3: *Low pressure, high gas superficial velocity.* At atmospheric to low pressure and at high range of gas flow rates, the dimensionless pressure drop is higher and liquid holdup decreases compared to case 2. This improves the wetting efficiency by improving the spreading of the liquid over the catalyst particles. Moreover, the increase in pressure drop and of liquid holdup at higher liquid flow rates further improves liquid-catalyst contacting efficiency.

Case 4: *High pressure, low gas superficial velocity.* At high pressure, the gas density increases which causes an increase in pressure drop and a decrease in liquid holdup compared to case 2. Since the effect of gas velocity on pressure drop is greater than that of gas density (Ergun, 1952), elevated reactor pressure at low gas velocity causes a smaller increase in pressure drop and decrease in liquid holdup than that of case 3 at both low and high liquid flow rates. Therefore, the wetting efficiency improves more than in case 2 but less than in case 3 due to the improvement in liquid spreading over the catalyst particles in spite of reduced holdup. At higher liquid flow rates in this regime the wetting efficiency is enhanced by both increased liquid holdup and elevated pressure drop.

Case 5: *High pressure, high gas superficial velocity.* At elevated pressure and high gas superficial velocity, the pressure drop increases significantly and liquid holdup decreases considerably compared to all previous cases (due to the effect of both gas density and velocity). The wetting of the particles improves noticeably because of further improvement in liquid spreading over the catalyst particles. This effect becomes significantly greater at high liquid flow rates when the dimensionless pressure drop increases considerably as well as liquid holdup.

According to the above analysis eq. (6) should be capable of predicting external liquid-catalyst contacting efficiency, η_{CE}, once the constants c, m and n are evaluated by fitting a sufficient number of experimental data. The effect of bed characteristics and physical properties are accounted for by the dimensionless pressure drop, Reynolds and Galileo numbers.

It is instructive to note that a form of eq. (6) without the $[1 + (\Delta P/Z)/\rho_L g]$ term, and with Reynolds and Galileo numbers that did not include the bed voidage, was suggested at atmospheric pressure by El-Hisnawi (1981) and El-Hisnawi *et al.* (1982). The other form of El-Hisnawi *et al.*'s (1981, 1982) correlation [eq. (2)] which expresses contacting efficiency in terms of dynamic liquid saturation is not compatible with the phenomenological analysis discussed above and may only be used at atmospheric pressure.

EXPERIMENTAL INVESTIGATION

Experimental facility

High pressure trickle-bed facility has been designed and developed to operate at a pressure up to 7 MPa (~1000 psig) (Al-Dahhan, 1993). Figure 2 shows the process and instrumentation diagram of the facility. The facility consists of a high pressure trickle-bed reactor set-up, liquid and gas delivery systems, tracer technique set-up, and data acquisition system. This facility allows both low and high pressure experiments with simultaneous measurements of liquid holdup and pressure drop over a broad range of operating conditions. Two reactors have been designed and constructed. One contains a thick optically clear acrylic window (ID = 2.2 cm) to observe the two phase flow at least near the wall while the other is made of 1″ S.S. tubing (ID = 2.19 cm). The length of each reactor is 57.15 cm (22.5 in). The reactors gas–liquid distributor has been designed similar to the industrial type distributor to ensure uniform liquid and gas distribution at the bed inlet (Al-Dahhan, 1993). The bottom of the reactor is connected to the gas–liquid separator. The separator is constructed from a thick optically clear acrylic to monitor the liquid level. Its bottom was designed like a funnel in order to minimize the liquid volume in the bottom part of the separator which is needed for the dynamic tracer experiments when the volume of the externals to the packed bed need to be minimized. A demister of stainless steel mesh is

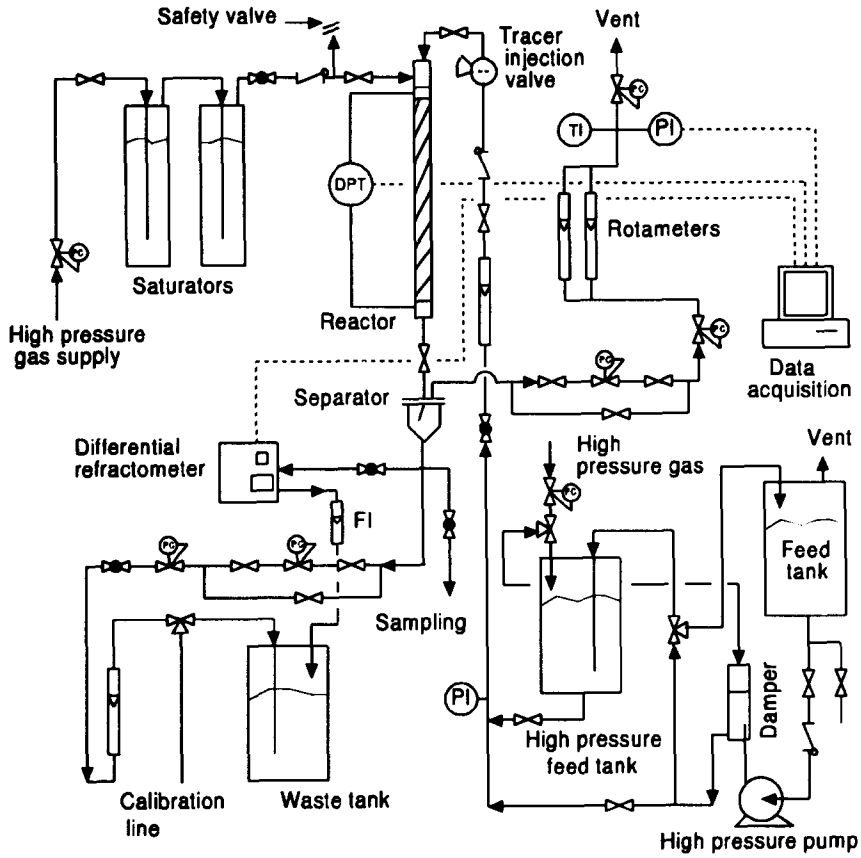


Fig. 2. Process and instrumentation diagram (P& ID) of the trickle-bed reactor facility.

mounted in the upper part of the separator to trap the liquid mist from the gas effluent stream. Liquid phase is delivered to the reactor by either a high pressure feed tank or a high pressure metering pump. The exit liquid stream from the gas–liquid separator is split into the sampling and waste stream. The sampling stream goes to either an on-line differential refractometer or to a needle valve for manual samples collection. The waste stream passes through the back-pressure regulator to the rotameter and then to the waste tank. The gas phase is delivered to the reactor from high pressure gas cylinders. The gas is allowed to pass through two high pressure saturators (bubblers) to be saturated with liquid in order to prevent evaporation in the reactor catalyst bed. The gas outlet stream from the gas–liquid separator passes through two back pressure regulators. Upon leaving the regulators, the gas flows to high and low range rotameters and then to the vent. A high pressure differential pressure transducer, which is used to measure the pressure drop across the catalyst bed, is connected to the top and bottom of the reactor bed. Liquid holdup is measured by the draining method in which the inlet and outlet streams are simultaneously shut off and the liquid drained from the reactor is measured. The remaining holdup in the bed is measured by weighing the reactor after being drained and subtracting the weight of the dry reactor. This holdup consists of external to the catalyst and capillary (inside the pore) holdups.

A tracer technique has been chosen to evaluate the external liquid-catalyst wetting efficiency. The tracer set-up consists of an injection valve, sampling and analytical equipment. The tracer is introduced in the liquid stream through a high pressure multiport valco valve located close to the reactor and equipped with either 1 or 3 ml loop. Differential refractometer is used to analyze the outlet stream in liquid-filled operation. In two phase flow operation, differential refractometer fails to operate properly at high pressure due to continuous release of bubbles inside its sampling cell. Therefore, samples are collected manually each 5–30 s and a Gas Chromatograph is utilized to measure the tracer concentration. The facility is connected to a portable, flexible and user friendly data acquisition and computation system. Detailed discussion about the design and the facility development can be found in Al-Dahhan (1993).

External liquid-catalyst wetting efficiency determination

The tracer technique developed in our laboratory (Mills and Duduković, 1981) was chosen for evaluation of contacting efficiency because it produced contacting information rapidly. It is also the only technique that allows the determination of contacting

efficiency in actual beds under operating conditions using catalyst packing and liquid of interests (Van Klinken and Van Dongen, 1980; Sicardi *et al.*, 1980; Dudukovic and Mills, 1986). Schwartz *et al.* (1976) and Colombo *et al.* (1976) introduced the tracer-based methods to evaluate both internal and external (total) contacting efficiency, respectively. The evaluation of these parameters is based on the method of moments. Mills and Dudukovic (1981, 1982b) and El-Hisnawi *et al.* (1981, 1982) confirmed the validity of this method. In the tracer-based method for evaluation of external contacting an impulse of nonadsorbing tracer is injected into the liquid at the inlet of trickle-bed reactor and the impulse response is monitored at the outlet. The first moment, μ_1, and the variance, σ^2, of the normalized bed impulse response, $E(t)$, defined by eq. (7), are then calculated numerically from the experimental data based on their defining equations.

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)\,dt} = \frac{R(t)}{\int_0^\infty R(t)\,dt}. \tag{7}$$

Here $C(t)$ is the tracer concentration in the effluent at time t, while $R(t)$ is a measured response linearly proportional to concentration at time t.

Table 1. Expressions for the moments of the impulse tracer response for an infinite cylinder catalyst for a nonvolatile and nonadsorbing tracer (El-Hisnawi, 1981)

Theoretical expressions

$$\sigma_D^2 = \frac{\sigma^2}{\mu_1^2}$$

For porous catalyst,

$\varepsilon_L = \varepsilon_{Lt} - \varepsilon_{Li}$; $\varepsilon_{Li} = f_i(1 - \varepsilon_B)\varepsilon_p$, where $f_i = 1$ due to capillary effect;

$\varepsilon_L = \varepsilon_{Ls} + \varepsilon_{Ld}$

I-Liquid-filled operation

$\varepsilon_L = \varepsilon_B$

$$\mu_1 = \frac{V_r\varepsilon_B}{Q_L}\left[1 + \frac{S_{ex}r_p}{2V_p}\left(\frac{1-\varepsilon_B}{\varepsilon_B}\right)\varepsilon_p\right]$$

$$\sigma^2 = \frac{\mu_1^2\delta_0}{2} + \frac{V_r}{Q_L}\varepsilon_P\frac{S_{ex}r_p}{2V_p}(1-\varepsilon_B)\frac{r_p^2\varepsilon_p}{8}\left[\frac{1}{(De)_{LF}} + \frac{4}{k_{Ls}r_p}\right]$$

where $\delta_0 = 2\left[\frac{1}{Pe_L} - \frac{1}{Pe_L^2}(1 - e^{-Pe_L})\right]$

Substitution of μ_1 into the expression for σ_D^2 results in a linear relationship between σ_D^2 and Q_L with slope equal to the following expression (k_{Ls} and Pe_L terms appear in the expression for the intercept):

$$\text{slope} = \frac{\frac{S_{ex}r_p}{2V_p}\left(\frac{1-\varepsilon_B}{\varepsilon_B}\right)\frac{r_p^2\varepsilon_p^2}{8(De)_{LF}}}{V_r\varepsilon_B\left[1 + \frac{S_{ex}r_p}{2V_p}\left(\frac{1-\varepsilon_B}{\varepsilon_B}\right)\varepsilon_p\right]^2}$$

II-Two phase flow operation

$$\mu_1 = \frac{V_r}{Q_L}\varepsilon_L$$

$$\mu_1 = \frac{V_r\varepsilon_L}{Q_L}\left[1 + \frac{S_{ex}r_p}{2V_p}\left(\frac{1-\varepsilon_B}{\varepsilon_L}\right)\varepsilon_p\right]$$

$$\sigma^2 = \mu_1^2\delta_0 + \frac{V_r}{Q_L}\varepsilon_P\frac{S_{ex}r_p}{2V_p}(1-\varepsilon_B)\frac{r_p^2\varepsilon_p}{4}\left[\frac{1}{(De)_{TF}} + \frac{4}{k_{Ls}r_p}\right]$$

$$\sigma_D^2 = \frac{\delta_0}{2} + \frac{\left(\mu_1 - \frac{V_r\varepsilon_L}{Q_L}\right)\frac{r_p^2\varepsilon_p}{8}\left[\frac{1}{(De)_{TF}} + \frac{4}{k_{Ls}r_p}\right]}{\mu_1^2}$$

By neglecting k_{Ls} and Pe_L, and substituting for μ_1 the dimensionless variance expression becomes:

$$\sigma_D^2 = \frac{\left(\left(\frac{V_r\varepsilon_L}{Q_L}\left\{1 + \frac{S_{ex}r_p}{2V_p}\left[\frac{(1-\varepsilon_B)\varepsilon_p}{\varepsilon_L}\right]\right\}\right) - \frac{V_r\varepsilon_L}{Q_L}\right)\frac{r_p^2\varepsilon_p}{8(De)_{TF}}}{\left(\frac{V_r\varepsilon_L}{Q_L}\left\{1 + \frac{S_{ex}r_p}{2V_p}\left[\frac{(1-\varepsilon_B)\varepsilon_p}{\varepsilon_L}\right]\right\}\right)}$$

The calculated values of the first moment and the variance can be utilized to evaluate liquid holdup and effective diffusivity of the tracer, respectively. Total liquid holdup, external plus internal, is obtained due to the central volume principle directly from the first moment of the normalized impulse response, $E(t)$. A comparison between the liquid holdup measured by draining and tracer methods reveals acceptable agreement between these methods (Al-Dahhan, 1993) and such comparison is similar to the comparison reported by Tukac and Hanika (1992). Evaluation of the contacting efficiency is model dependent. As shown by Colombo *et al.* (1976) and Mills and Duduković (1981) a reliable estimate can be obtained by evaluating from the variance of the impulse response, the apparent effective diffusivity for the reactor in two phase flow operation, $(De)_{TF}$, and for a liquid full reactor run at the same liquid flow rate, $(De)_{LF}$. Contacting efficiency is then given by

$$\eta_{CE} = \sqrt{\frac{(De)_{TF}}{(De)_{LF}}}. \tag{8}$$

The pertinent information regarding the expressions for the first moment and the variance for the impulse response of a nonvolatile, nonadsorbing tracer in beds of spherical and cylindrical (i.e. infinite cylinder approximation) catalysts is summarized in Tables 1 and 2, respectively. It is evident that the variance of the curve (i.e. spread around the mean) depends on the liquid–solid mass transfer coefficient, k_s, and via bed Peclet number for dispersion, Pe_L, on the axial dispersion coefficient, i.e. on the flow nonideality. El-Hisnawi (1981) showed that the effect of liquid–solid mass transfer coefficient is negligible compared to internal diffusion in liquid-full operation. Plotting the data for the dimensionless variance, σ_D^2, vs volumetric liquid flow rate yields a straight line from the slope of which the effective diffusivity for the liquid-full operation, $(De)_{LF}$, can be calculated. In two phase flow the effective diffusivity thus completely dominates the expression for the variance (El-Hisnawi, 1981) and results in the expressions given in Tables 1 and 2. By using the experimentally determined values of the dimensionless variance in these expressions allows us to determine the effective diffusivity for two phase flow operation.

It should be noted that the experimentally obtained impulse response signal and the moments (μ_1 and σ^2) in both two phase and liquid-filled experiments represent both the catalyst bed and the system externals to the bed (e.g. tubes, fittings, reactor head and bottom, connectors, valves, etc.). Therefore it is necessary to evaluate the moments of the catalyst bed only to which the expressions in Tables 1 and 2 pertain. This is achieved by performing liquid-filled and two phase flow experiments without the catalyst bed (i.e. only with system externals) at various liquid flow rates. It was found that gas velocity and density (reactor pressure) has a negligible effect on the moments of the externals. The first moment, μ_1, is a linear function of the inverse of the liquid volumetric flow rate, based on central volume principle, while the variance is best correlated with the volumetric flow rate in power law form, $\sigma^2 \propto Q^{-c}$ (El-Hisnawi, 1981; Al-Dahhan, 1993). Hence, μ_1 and σ^2 of externals can be evaluated at the

Table 2. Expressions for the impulse tracer response for spherical particles for a nonvolatile and nonadsorbing tracer (Mills and Duduković, 1981)

Theoretical expressions

$$\sigma_D^2 = \frac{\sigma^2}{\mu_1^2}$$

For porous catalyst,

$\varepsilon_L = \varepsilon_{Le} - \varepsilon_{Li}$; $\varepsilon_{Li} = f_i(1 - \varepsilon_B)\varepsilon_p$, where $f_i = 1$ due to capillary effect;

$$\varepsilon_L = \varepsilon_{Ls} + \varepsilon_{Ld}$$

I-Liquid-filled operation

$$\varepsilon_L = \varepsilon_B$$

$$\sigma_D^2 = \frac{1}{Pe_L} + \frac{Q_L}{V_r \varepsilon_B} \frac{\delta_1}{(1+\delta_2)^2}$$

where $\delta_1 = \delta_i + \delta_e$

$$\delta_i = \frac{(1-\varepsilon_B)\varepsilon_p}{\varepsilon_B} \frac{r_p^2 \varepsilon_p}{15(De)_{LF}}$$

$$\delta_e = \frac{(1-\varepsilon_B)\varepsilon_p}{\varepsilon_B} \frac{r_p^2 \varepsilon_p}{15} \frac{5}{k_{Ls} r_p}$$

$$\delta_2 = \frac{(1-\varepsilon_B)\varepsilon_p}{\varepsilon_B}$$

Plotting σ_D^2 vs Q_L yields a straight line with a slope equal to the following expression (k_{Ls} and Pe_L terms appear in the expression for the intercept):

$$\text{slope} = \frac{\dfrac{(1-\varepsilon_B)\varepsilon_p^2}{\varepsilon_B} \dfrac{r_p^2}{15(De)_{LF}}}{V_r \varepsilon_B \left[1 + \dfrac{(1-\varepsilon_B)\varepsilon_p}{\varepsilon_B}\right]^2}$$

II-Two phase flow operation

$$\mu_1 = \frac{V_r}{Q_L} \varepsilon_L$$

$$\sigma_D^2 = \frac{1}{Pe_L} + \frac{Q_L}{V_r \varepsilon_L} \frac{\delta_1}{(1+\delta_2)^2}$$

where, $\delta_1 = \delta_i + \delta_e$

$$\delta_i = \frac{(1-\varepsilon_B)\varepsilon_p}{\varepsilon_L} \frac{r_p^2 \varepsilon_p}{15(De)_{TF}}$$

$$\delta_e = \frac{(1-\varepsilon_B)\varepsilon_p}{\varepsilon_L} \frac{r_p^2 \varepsilon_p}{15} \frac{5}{k_{Ls} r_p}$$

$$\delta_2 = \frac{(1-\varepsilon_B)\varepsilon_p}{\varepsilon_L}$$

By neglecting k_{Ls} and Pe_L, dimensionless variance expression becomes:

$$\sigma_D^2 = \frac{Q_L}{V_r \varepsilon_L} \frac{\dfrac{(1-\varepsilon_B)\varepsilon_p}{\varepsilon_L}\left[\dfrac{r_p^2 \varepsilon_p}{15(De)_{TF}}\right]}{\left[1 + \dfrac{(1-\varepsilon_B)\varepsilon_p}{\varepsilon_L}\right]^2}$$

same liquid flow rates at which overall system experiments (bed and externals) are conducted. By subtracting the values of the moments of the externals from those of the overall system, the moments of the catalyst bed can be determined (Duduković and Felder, 1983; Levenspiel, 1986). In liquid-filled mode a smaller volume of the reactor head than that of two phase flow is utilized. This was found in this work, as well as by El-Hisnawi (1981), to produce a better response signal. It is noteworthy to mention that Mills and Duduković (1988, 1989) analyzed the tracer response data by convolution and deconvolution methods and compared between an experimental RTD's and the fit of the predicted curve with the model used. They found that the differences are within the accuracy of the experimental tracer response measurements.

Operating conditions investigated

The region of the experimental investigation is within the trickle flow regime shown in Fig. 3 on the flow map of Fukushima and Kusaka (1977a, b). Visual observation through acrylic window and stable pressure drop measurements also confirm that the flow regime is trickle flow.

The selection of the system to be used is based on earlier studies by Schwartz *et al.* (1976), Mills (1980), El-Hisnawi (1981), Mills and Duduković (1981), Hanratty (1988) and Hanratty and Duduković (1992). Thus, the hydrocarbon solvent is selected to be hexane. In order to remove traces of water, sulfur and other strongly adsorbing compounds, commercial grade hexane is passed over activated bed F-1 porous alumina. The alumina is activated at 140°C in presence of dry nitrogen by using high temperature stainless steel packed bed reactor set-up. The selected tracer compound which gives the desired nonvolatile and nonadsorbing characteristics is high purity *n*-heptane. Nitrogen is used as the gas phase since it has low solubility in liquid hydrocarbons and is more dense where the effect of pressure is more pronounced. The range of reactor pressure, liquid and gas superficial velocities covered in this investigation are listed in Table 3, while the packing bed characteristics utilized are shown in Table 4.

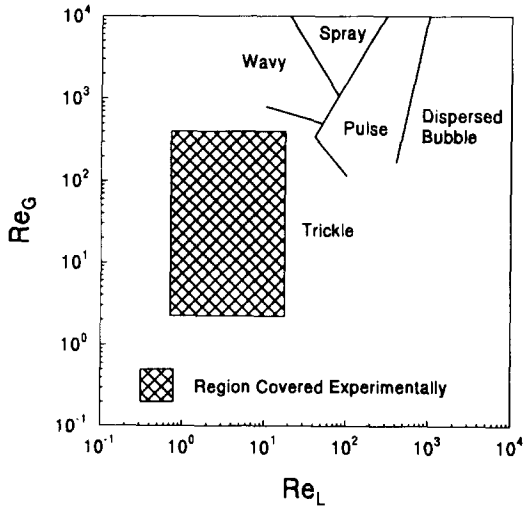


Fig. 3. Region of trickle flow regime covered experimentally in this study [flow map based on Fukushima and Kusaka (1977a, b)].

Prior to each two phase flow experiment, the catalyst bed, after being extensively prewetted by soaking the bed and leaving it over night soaked, is operated first in the high interaction regime (pulse and/or bubble flow regime) at high liquid mass velocities and then the mass velocities are reduced to the desired level at which wetting efficiency, pressure drop and liquid holdup are measured. This procedure, in addition to the uniform liquid–gas distribution at the bed entrance, minimizes liquid maldistribution and prevents hysteresis effects in measured pressure drop (Kan and Greenfield, 1979; Levec *et al.*, 1988). The operation is assumed to be stable when the reactor pressure, pressure drop and the gas and liquid throughput do not change for at least 5 min. At this stage the tracer is injected into the liquid stream. The experimental data of the typical differential refractometer and Gas Chromatograph output, $E(t)$ curves, beds' first moment, variance, and dimensionless variance, can be found in Al-Dahhan (1993). They are reproducible within $\pm$ 5%.

RESULTS AND DATA ANALYSIS

The effect of high pressure and gas flow rate on wetting efficiency

The experimental observations of the effects of reactor pressure and gas flow rate on catalyst wetting efficiency, pressure drop and liquid holdup are consistent with the deductions from the phenomenological analysis discussed earlier. Examination of the results for contacting efficiency, liquid holdup and dimensionless pressure drop presented in Figs 4 and

Table 3. Range of operating conditions covered in this study

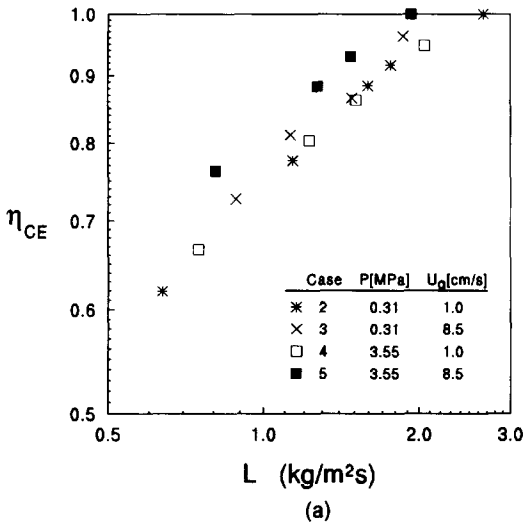
Condition	Covered range
Reactor pressure, MPa	$0.31 \leqslant P \leqslant 5.0$
Psig	$30 \leqslant P \leqslant 700$
Gas superficial velocity, cm/s	$1 \leqslant U_G \leqslant 8.75$
Gas superficial mass velocity, kg/m^2 s	$6.64 \times 10^{-3} \leqslant G \leqslant 4.03$
Liquid superficial flow rate, ml/min	$15 \leqslant Q_L \leqslant 93$
Liquid superficial mass flow rate, kg/m^2 s	$0.42 \leqslant L \leqslant 2.7$
Temperature, K	≈ 298

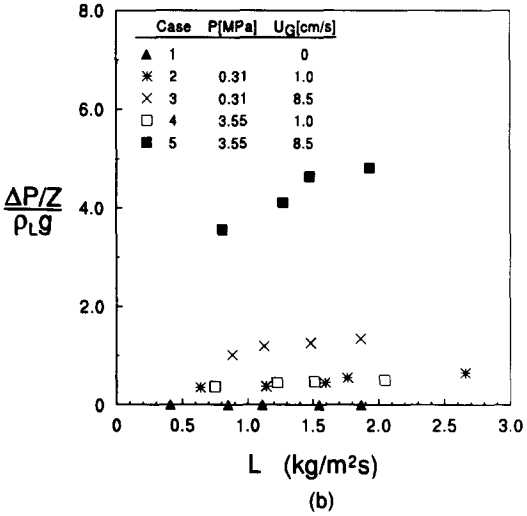
Table 4. Packed bed characteristics

Reactor/packing	Characteristics
Reactor	
Acrylic window reactor	d_r = 2.22 cm; length = 57.23 cm
Stainless steel reactor	d_r = 2.19 cm; length = 57.31 cm
Packing	
0.5% Pd on alumina—stainless steel reactor	Type: Porous extrudate; size = 0.157 cm × 0.43 cm; $(d_p)_{eq}$ = 0.199 cm; d_r/d_p = 11; Bed length (Z) = 51.61 cm; ε_B = 0.355; ε_p = 0.599; ρ_p = 1.189 g/cm^3
Silica Shell—acrylic window reactor	Type: Porous sphere; d_p = 0.152 cm; d_r/d_p = 14.6; Bed length (Z) = 51.63 cm; ε_B = 0.412; ε_p = 0.697; ρ_p = 0.697 g/cm^3

5 for spherical and extrudate (cylindrical) catalyst, respectively, confirms this. Small dimensionless pressure drop encountered at low reactor pressure and at low gas velocity (case 2, *) has a negligible effect on liquid holdup and contacting efficiency compared to the situation of no gas flow (case 1, ▲) at fixed liquid mass velocity. Liquid holdup is the highest in this case and contacting efficiency is low at all liquid mass velocities. At constant liquid mass velocity, when the gas velocity is high at still low reactor pressure (about atmospheric) (case 3, ×), pressure drop is increased, liquid holdup somewhat decreased and contacting efficiency is improved due to increased spreading of the liquid over catalyst particles as illustrated in Figs 4 and 5. As liquid mass velocity increases, both pressure drop and liquid holdup increase which results in further improvement in the catalyst wetting efficiency.

At elevated reactor pressure and at low gas flow rate (case 4, □), the pressure drop increases and liquid holdup decreases only slightly compared to case 2 (*), and this increase in pressure drop is much less than that of case 3 (×) at constant liquid mass velocity. As a result, the wetting efficiency increases only a little compared to case 2 (*) and is much less improved than





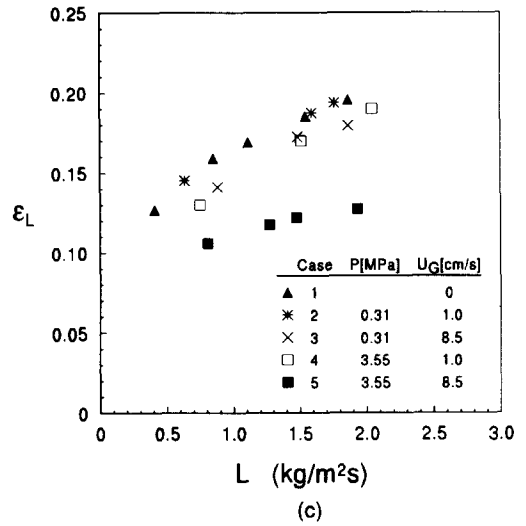
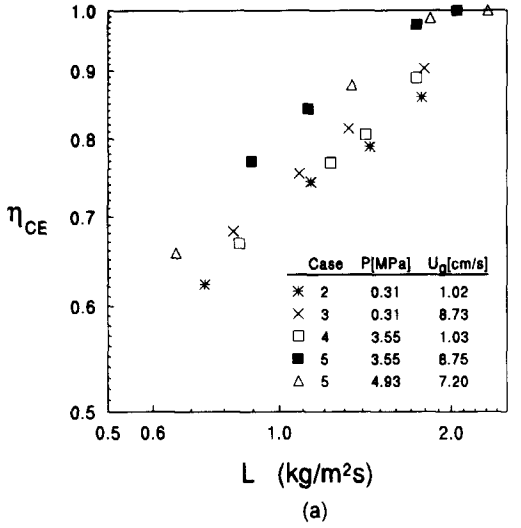
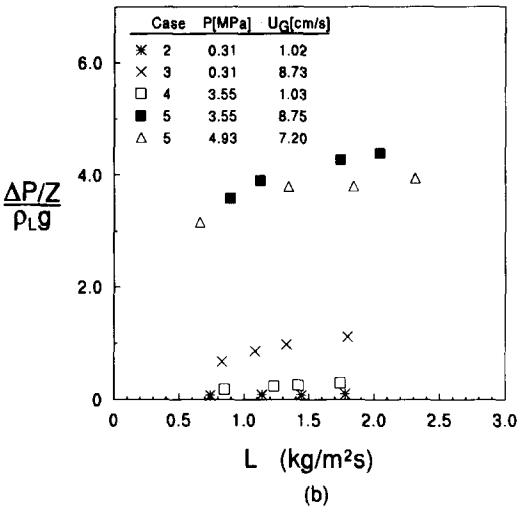


Fig. 4. Effect of high pressure and gas flow rate on liquid–solid contacting efficiency (a), pressure drop (b) and liquid holdup (c) in a bed of spheres. Solvent: hexane; tracer: heptane; gas: nitrogen; (d_p) (sphere) = 0.152 cm.

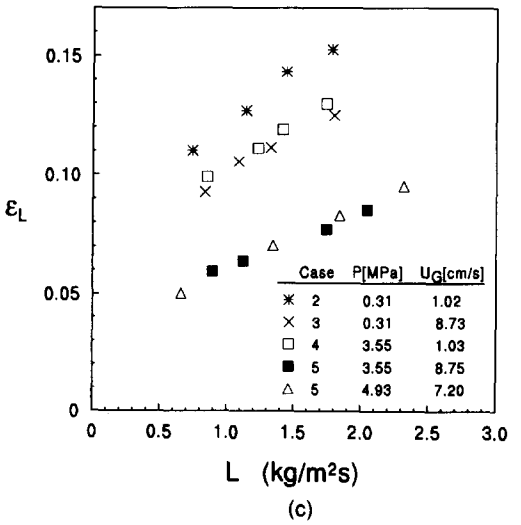
in case 3 (×) if improved at all. At higher liquid mass velocity in this region the wetting efficiency is enhanced by both the increase in pressure drop and in liquid holdup. At high pressure and high gas flow rate



(a)



(b)



(c)

Fig. 5. Effect of high pressure and gas flow rate on liquid–solid containing efficiency (a), pressure drop (b) and liquid holdup (c) in a bed of extrudates. Solvent: hexane; tracer: heptane; gas: nitrogen; $(d_p)_{eq}$ (extrudate) = 0.199 cm.

(case, 5, ■, △) contacting efficiency increases noticeably due to further improvement of liquid spreading on the catalyst surface whereas pressure drop increases significantly and liquid holdup decreases considerably. Such improvement is even more noticeable at higher liquid mass velocity due to increase in both pressure drop and liquid holdup. The effect of gas superficial velocity is more pronounced on the contacting efficiency, pressure drop and liquid holdup at high pressure. For example, as shown in Figs 4 and 5, the change in contacting efficiency, pressure drop and holdup is much larger when the gas superficial velocity is increased from 1.02 to 8.75 cm/s at 3.55 MPa than when the same increase in gas superficial velocity occurs at 0.31 MPa. The improvement in the contacting efficiency at high pressure and high gas flow rate (case 5) compared to low pressure and gas flow rate (case 2) is larger than the experimental error which is below 5% [e.g. about 20% improvement in the extrudate bed (Fig. 5) and about 10% improvement in the bed of spheres (Fig. 4)]. The lesser improvement observed in the bed of spheres compared to the extrudate bed is due to spherical particles being smaller than the extrudates and the fact that contacting efficiency increases as the particle diameter decreases (El-Hisnawi *et al.*, 1981, 1982; Duduković and Mills, 1986).

As shown above, the data of this study support the phenomenological analysis which indicates that high pressure operation and higher gas flow rates improve catalyst wetting efficiency. Although liquid holdup decreases at high pressure operation, contacting efficiency improves due to the improved spreading of the liquid film over more external particle surface. As liquid flow rate increases, both liquid holdup and pressure drop increase, thereby resulting in further increase in contacting efficiency.

The developed model

The catalyst wetting efficiency data obtained in this study are used to evaluate the parameters of the model proposed by eq. (6) and the following relationship is obtained:

$$\eta_{CE} = 1.104\, Re_L^{1/3} \left\{ \frac{1 + [(\Delta P/Z)/\rho_L g]}{Ga_L} \right\}^{1/9} \quad (9)$$

where

$$Re_L = \frac{U_L \rho_L d_p}{\mu_L (1 - \varepsilon_B)}, \quad Ga_L = \frac{d_p^3 \rho_L^2 g \varepsilon_B^3}{\mu_L^2 (1 - \varepsilon_B)^3}.$$

The mean relative error is 3.7%. A comparison between experimental and predicted liquid-catalyst contacting efficiency is presented in Fig. 6. The data are bounded by ± 10%. Moreover, the developed model predicts properly the trend of the effect of reactor pressure and gas flow rate on the contacting efficiency as illustrated in Fig. 7.

Comparison of data for contacting efficiency obtained in this study at low pressure with the data obtained by El-Hisnawi (1981) at atmospheric pres-

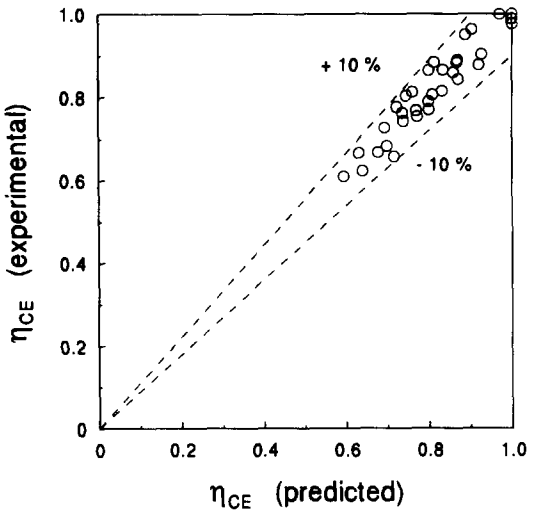


Fig. 6. Comparison of the developed model prediction and data for liquid-catalyst contacting efficiency.

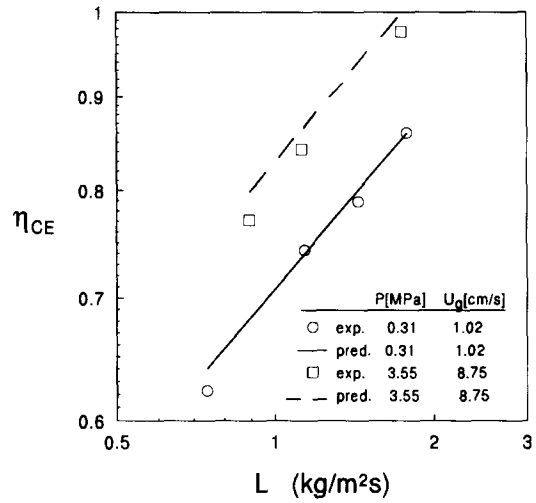


Fig. 7. The trend in model predictions of the effect of high pressure and gas flow rate on the contacting efficiency in the bed of extrudates [$(d_p)_{eq} = 0.199$ cm].

sure and with the predictions of his correlation, reveals that the two data sets for about the same equivalent particles diameter and the same solvent are quite close (within $\pm 4\%$ relative difference). However, both his and our low pressure data seem to have somewhat higher slope with respect to the Reynolds number than indicated by El-Hisnawi's correlation [eq. (1) mentioned earlier] which predicts higher contacting values than both sets of data but within the error margin of the correlation ($\pm$ 10%). The mean relative error of the developed model for El-Hisnawi's (1981) data is 20%. In calculating this error the dimensionless pressure drop term of the developed model is neglected, since El-Hisnawi did not measure the pressure drop across the bed. If pressure drop is incorporated into eq. (6) based on the interpolation of the current data obtained in a bed close to that of El-Hisnawi's work (1981), the mean relative error of the developed model becomes 13%. In contrast, El-Hisnawi's correlation (1981) [eq. (1)], fails to predict the effect of reactor pressure and gas flow rate since it does not include the $[1 + (\Delta P/Z)/\rho_L g]$ term and its Reynolds and Galileo numbers do not involve the bed voidage parameter. The fact that our correlation matches so well the data of El-Hisnawi (1981) which is based on data containing a broad variation in liquid physical properties justifies the use of dimensionless groups in our correlation and the exponents that are evaluated here.

The other form of El-Hisnawi's correlation which relates contacting to holdup [eq. (2)] predicts the opposite trend of the effect of pressure on the contacting efficiency (Al-Dahhan, 1993) and, hence, is not suitable for general use.

4. CONCLUSION

A phenomenological analysis describes properly the experimental observations for the effect of elevated pressure and gas flow rate on the wetting efficiency, pressure drop and liquid holdup. Contacting efficiency is linked to both pressure drop and liquid holdup. For a fixed liquid mass velocity, at high pressure and high gas flow rate, wetting efficiency improves noticeably whereas pressure drop increases significantly and liquid holdup decreases considerably. As liquid flow rate increases, wetting efficiency improves further due to an increase in both pressure drop and liquid holdup. The effect of gas flow rate on the wetting efficiency, pressure drop and liquid holdup is more pronounced at elevated pressure. The improvement in wetting efficiency is due to the improved spreading of the liquid holdup over the external packing area as a result of the increase in the shear stress on the gas–liquid interface by means of higher gas velocity or pressure (gas density).

The results of this study indicate that other design, scaleup and operating parameters of trickle-bed reactors such as flow regime transition, liquid distribution, volumetric mass and heat transfer coefficients, etc., need to be re-evaluated at high pressure operation before implementing models or correlations developed based on investigations at atmospheric pressure.

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NOTATION

C	tracer concentration, mol/m^3
d_p	particle diameter, m
d_r	reactor diameter, m
$(De)_{LF}$	effective diffusivity in liquid-filled operation, m^2/s
$(De)_{TF}$	effective diffusivity in two phase flow operation, m^2/s

$E(t)$ normalized tracer response curve
f_{wall} catalyst wall friction factor
g gravitational acceleration, m/s^2
G superficial gas mass velocity, kg/m^2 s
Ga_L dimensionless liquid Galileo number $[= d_p^3\rho_L^2 g\varepsilon_B^3/\mu_L^2\,(1-\varepsilon_B)^3]$
L superficial liquid mass velocity, kg/m^2 s
$\Delta P/Z$ pressure drop per unit bed length, N/m^3
Pe_L dimensionless Peclet number, $(= U_L d_p/De_L)$
Q_L liquid volumetric flow rate, m^3/s
r_p particle radius, m
Re_L dimensionless liquid Reynolds number $[= U_L\rho_L d_P/\mu_L(1-\varepsilon_B)]$
Re_G dimensionless gas Reynolds number $[= U_G\rho_G d_P/\mu_G(1-\varepsilon_B)]$
S_{ex} external area of catalyst pellet, m^2
t time, s
T tortuosity
U_L superficial liquid velocity, m/s
U_G superficial gas velocity, m/s
V_p particle volume, m^3
V_r reactor bed volume, m^3
Z packed-bed length, m

Greek letters

ω_d dynamic liquid saturation (liquid volume per void volume)
δ liquid mean film thickness, m
ε_B packed-bed void per reactor volume (bed porosity)
ε_{Ld} dynamic liquid holdup per reactor bed volume
ε_{Ls} static liquid holdup per reactor bed volume
ε_L external liquid holdup per reactor bed volume $(\varepsilon_{Ld} + \varepsilon_{Ls})$
ε_{Li} internal liquid holdup per reactor bed volume (inside the pores) for porous particles
ε_{Lt} total liquid holdup (external and internal) per reactor bed volume $(\varepsilon_L + \varepsilon_{Li})$
ε_p particle porosity
η_{CE} external liquid–solid contacting efficiency
μ_1 first moment, s
μ_2 second moment, s^2
μ_L liquid viscosity, Ns/m^2
ρ_L liquid density, kg/m^3
σ^2 variance or second central moment, s^2
σ_D^2 dimensionless variance
ψ_L liquid dimensionless pressure drop $\{= [(\Delta P/Z)/(\rho_L g) + 1]\}$
ψ_G Gas dimensionless pressure drop $\{= [(\Delta P/Z)/(\rho_G g) + 1]\}$

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