Catalyst Bed Dilution for Improving Catalyst Wetting in Laboratory Trickle-Bed Reactors

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The catalyst bed dilution technique has found rather widespread applications as a means of producing reliable and reproducible results for successful scale-up and scale-down when testing commercially used catalyst particle sizes and alternative feedstocks in small-scale laboratory trickle-bed reactors. In such small-diameter laboratory units when the catalyst used in commercial units is employed as the only packing, low liquid velocities lead to incomplete catalyst utilization due to incomplete external catalyst wetting, liquid maldistribution, and wall effects. Diluting the bed with fines is recommended to remedy these shortcomings. The effect of the bed dilution with fines on catalyst wetting efficiency, pressure drop, and liquid holdup are quantified. At atmospheric pressure, fines improve the catalyst wetting efficiency by increasing both the pressure drop and liquid holdup. At high-pressure operation, wetting efficiency improves further, whereas pressure drop increases and liquid holdup decreases. In a highly diluted bed (e.g., 2 or more volume fines/1 volume catalyst) the improvement in catalyst wetting efficiency is about the same as that achieved in a bed packed according to our recommended procedure, which is based on filling the voidage of the original bed with fines.

Introduction

Trickle-bed reactors (Figure 1a) are fixed beds of catalyst particles, contacted by the cocurrent downflow of gas and liquid. The catalyst particles are always porous and usually are in the form of extrudates, spheres, tablets, or granules of diameter ranging from 1 to 3 mm (Duduković and Mills, 1986; Gianetto and Specchia, 1992). Trickle beds are widely used in the petroleum (hydrogenation, hydrocracking, hydrodesulfurization, hydrodenitrogenation, alkylation, etc.), petrochemical (hydrogenation, oxidation, etc.), and chemical industries (hydrogenation of higher aldehydes, reactive ammination, liquid-phase oxidation, syngas conversion, etc.), as well as in waste treatment (oxidation of dilute aqueous and organic solutions, etc.), biochemical processes (using immobilized enzymes or cells, etc.), and electrochemical processing. The vast majority of industrial trickle-bed reactors operate at high pressure, up to about 20–30 MPa (3,000–4,500 psig), in order to improve the solubility of the gaseous reactant, achieve better heat transfer, and to slow down catalyst deactivation. While various flow regimes exist in these reactors, they 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). Trickle-flow regime is of particular industrial interest. In this regime, the catalyst is either partially externally wetted at low liquid mass velocities (external contacting efficiency is less than one, $\eta_{CE} < 1$) or fully externally wetted at high liquid mass velocities ($\eta_{CE} = 1$), as shown schematically in Figure 1b and 1c, respectively.

The design of commercial trickle-bed reactors is based on translation of laboratory (bench-scale) data to large-scale units (i.e., scale-up). In other circumstances, when the commercial process is well established, laboratory studies are aimed to provide information concerning the behavior of new catalyst, alternative feedstocks, and so forth (i.e., scale-down). For both scale-up and scale-down laboratory investigations are essential. Current economic considerations require that the smallest possible laboratory units be used for scale-down and scale-up (Sie, 1991). This poses the following challenges. Since laboratory scale reactors need to match the space velocity of commercial units, the actual velocities in them are

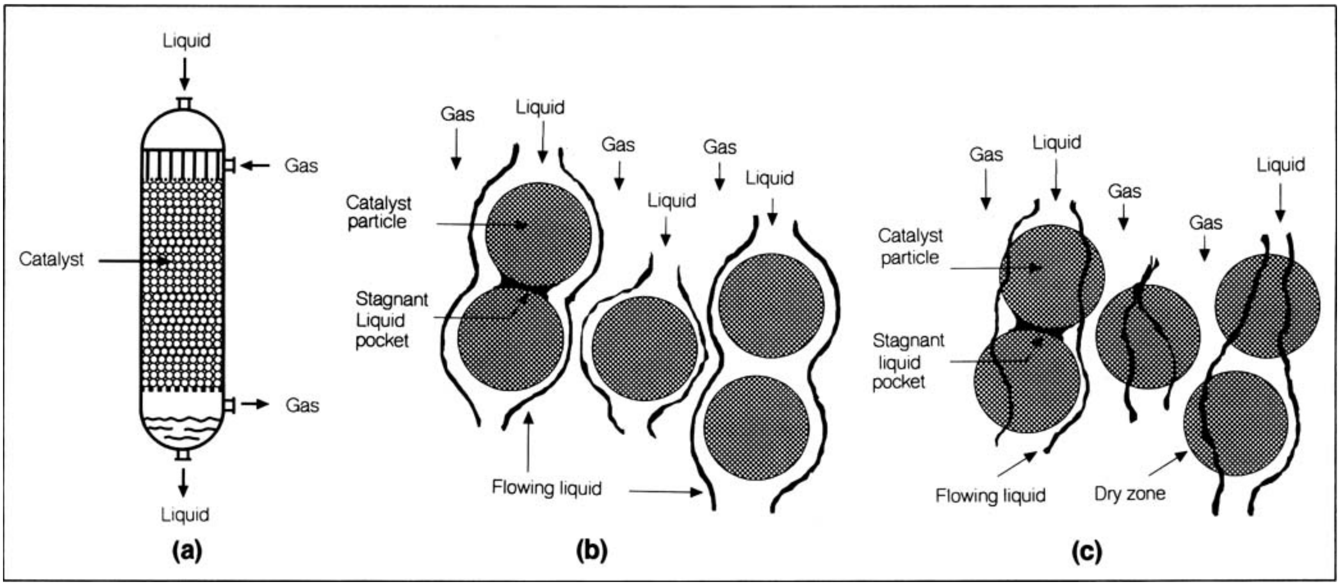


Figure 1. (a) Trickle-bed reactor; (b) externally fully wetted particles in trickle-flow regime; (c) externally partially wetted particles in trickle-flow regime.

much lower, which may lead to incomplete catalyst utilization due to partial external catalyst wetting. It is known that catalyst wetting improves with increased liquid mass velocity (Mills and Duduković, 1982). In commercial trickle-bed reactors, the liquid superficial mass velocity, L, (liquid mass flow rate divided by the cross-sectional area of the empty reactor) can be up to 50 kg/m$^2\cdot$s, while the superficial gas mass velocity, G, reaches up to 25 kg/m$^2\cdot$s. In a laboratory reactor usually $L < 0.1$ kg/m$^2\cdot$s, while $10^{-5} < G < 10^{-2}$ kg/m$^2\cdot$s. It is evident that liquid superficial velocities are changed dramatically with scale-up and scale-down. Table 1 shows typical trickle-flow hydrotreating processes data for different sizes of trickle-bed reactors (Sie, 1991).

Moreover, catalyst particles of the size, type, and shapes employed in the commercial reactor are often used in laboratory reactors of inside diameter between 1 cm to 3 cm (Anderson and Pratt, 1985). Hence, the effect of reactor diameter is more pronounced in a laboratory reactor where the empirical criterion of $d_r/d_p \geq 20$, which assures good and uniform liquid distribution, usually is not met. At low reactor to catalyst particle diameter ratio, d_r/d_p, the bed voidage and specific surface per unit volume near the wall deviates from the mean statistical fluctuation in the interior of the bed. The bed voidage reaches a value of unity very close to the wall, while the specific area approaches zero close to the wall if only particle surface is considered, but may attain a higher value than the average value if the wall surface is also taken into account. This wall effect can contribute to deviation from ideal plug flow of liquid, in which all catalyst is utilized equally and where each particle is surrounded by a flowing film of liquid. Accordingly, low liquid mass velocity and possibly wall effects in laboratory reactors can cause liquid maldistribution, hysteresis effects, and poor utilization of the catalyst bed due to the reduced catalyst wetting efficiency, η_{CE} (Sie, 1991; Van Klinken and Van Dongen, 1980; Duduković and Mills, 1986; Gierman, 1988). It was found that hysteresis effects in laboratory trickle-bed reactors with uniform liquid/gas distributors could be eliminated by prewetting the bed with liquid (soaking the bed at least over night), operating the reactor first in the high interaction regime (i.e., high mass velocities), and then reducing the mass velocities to the desired values (Kan and Greenfield, 1979; Levec et al., 1988). Moreover, such laboratory reactors may not be packed reproducibly, which causes fundamental difficulties in interpretation of kinetic data. The hydrodynamics and reaction kinetics are so closely interlinked in trickle-bed reactors that great caution must be exercised in separating their effects on conversion and selectivity. It is known that contacting efficiency can have a significant effect on the catalyst effectiveness factor for partially wetted catalyst pellets. This can profoundly affect reactor performance. It has been found that incomplete wetting and effectiveness factor are strongly coupled phenomena (Duduković and Mills, 1986; Beaudry et al., 1986, 1987; Zhukova et al., 1990; Duduković, 1977; Herskowitz and Smith, 1983). Therefore the significance of partial wetting on the global rate of reaction depends on intra- and interparticle diffusion and the volatility of the limiting reactants and of the solvent (Herskowitz and Smith, 1983). If the limiting reactant is nonvolatile and Thiele modulus is small, ϕ_T, the effect of the wetting efficiency ($0.6 \leq \eta_{CE} \leq 1.0$) on the effectiveness factor is not large (Herskowitz and Smith, 1983;

Table 1. Typical Hydrotreating Data for Different Sizes of Trickle-Bed Reactors

Specification	Commercial	Pilot Plant	Bench Scale	Microflow
Catalyst vol., L	100,000	10	0.15	0.008
Diameter, cm	250	4	2	1
Length, cm	2,000	800	50	10
Liquid vel., cm/s	1.1	0.4	0.03	0.006
Re_L	55	22	1.4	0.3

LHSV = 21 (L/h); $\nu = 3 \times 10^{-7}$ m^2/s; $d_p = 0.15$ cm.
After Sie, 1991.

Zhukova et al., 1990). If the limiting reactant is volatile and/or partially volatile, the effect of η_{CE} depends on the interparticle diffusion. Therefore Thiele modules, ϕ_T, which is the ratio of the maximum reaction rate and the maximum rate of internal diffusion transport, determines whether the catalyst effectiveness factor will be primarily affected by external contacting efficiency, since the catalyst pores in trickle-bed reactor are usually completely filled with liquid, particularly for prewetted bed (Duduković and Mills, 1986). For large moduli ($\phi_T \gg 1$) η_{CE} is the dominant variable, and the utilization of the catalyst is proportional to the fraction of the external area wetted, over which the reactant is supplied to the reaction zone. For small moduli ($\phi_T \ll 1$), when interparticle diffusion can be neglected and the reaction rate is completely kinetically controlled, the effect of η_{CE} on effectiveness factor, and hence on the catalyst, utilization is diminished (Duduković, 1977; Herskowitz and Smith, 1983). Herskowitz and Smith (1983) showed that the effect of partial wetting is very significant at high values of Thiele modules, ϕ_T, and at low liquid superficial flow rate. Moreover, in such case small changes in η_{CE} may cause significant change in the effectiveness factor, and hence in the catalyst utilization. Thus, if the data obtained in a laboratory reactor are not obtained under well-defined hydrodynamic conditions, or conditions duplicating the situation in large units, it can lead to bad commercial design and improper interpretation of catalyst testing or evaluation of an alternative feedstock.

Diluting the laboratory catalyst beds with fines (small, inert, and nonporous particles of about 0.1 catalyst diameter), as shown in Figure 2, has been recommended and utilized to overcome the shortcomings in the hydrodynamics of laboratory scale reactors (Koros, 1976; Van Klinken and Van Dongen, 1980; Sie, 1991). In this technique, inert fines are dispersed among the catalyst particles. More solid-solid contact points and areas over which liquid flows are created, resulting in reduced voidage in the bed, particularly near the reactor wall. This is not the same as reducing the size (0.8 mm–0.2 mm or crushed catalyst) of the uniform catalyst particles in the bed that is often used as another alternative. The latter does not increase the number of contacting points per unit volume as much as the addition of fines does, and also alters the catalyst effectiveness factor due to reduced intraparticle diffusional effects. Hence, the industrial relevance of data obtained is doubtful unless extensive modeling is employed. Accordingly, testing ground catalyst is not suitable for obtaining predictive data for industrial operation. However, small catalyst particles (crushed or fines) are impractical to be used in large-scale packed-bed reactors because they cause excessively high pressure drop. When we add inert fines to the catalyst bed, the hydrodynamics is largely dictated by the fines, whereas the catalytic phenomena are governed by the catalyst particle of the same shape, size, and form as used in the industrial units and, hence, the catalytic performance of the full-size catalyst can be determined properly in small units. This is, in fact, a decoupling of hydrodynamics and kinetics, which means that although the hydrodynamic conditions of diluted laboratory reactor differ from the hydrodynamics of commercial reactor, fines allow the small reactor to approach kinetically the performance of large-scale reactors by improving the plug-flow character of the laboratory reactor. This means that the small-scale reactors with diluted catalyst beds can be representative of an actual trickle-flow reactor in a reaction kinetic sense only, and that it is not a small-scale replica of a commercial reactor in all aspects (Sie, 1991; Van Klinken and Van Dongen, 1980). It was found by many investigators that catalyst utilization is better in a bed diluted with fines due to better liquid distribution (increased liquid holdup as well), reduced wall effects, and minimization of axial dispersion (Sie, 1991; Sedriks and Kenney, 1973; Koros, 1976; Van Klinken and Van Dongen, 1980; Carruthers and DiCamillo, 1988). A qualitative conclusion has been deduced that improving the reactor performance is the result of improving the catalyst wetting efficiency. Unfortunately, no study appeared in the open literature that confirms quantitatively the effect of fines on the catalyst wetting efficiency.

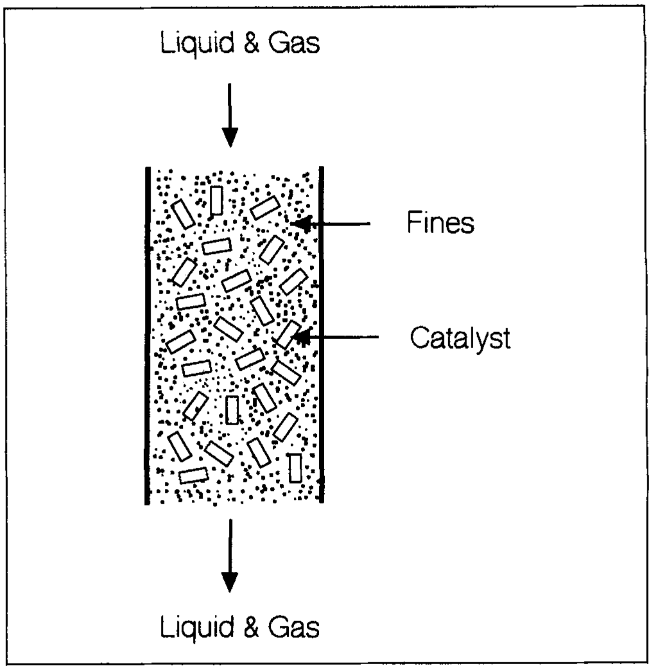


Figure 2. Diluted bed with fines.

The catalyst-bed dilution technique just described has found rather widespread applications as a useful technique for scale-up and scale-down and as means to allow meaningful testing of commercial used catalyst particle sizes and alternative feedstocks in small-scale laboratory reactors. It is noteworthy that the meaningful results of the dilution techniques would be negated if the packing method of mixing the bed of catalyst and fines fails to produce reproducible results. Previous studies in the literature that utilized fines did not report how the diluted bed was packed to ensure reproducibility (Koros, 1976; Gierman, 1988; Carruthers and DiCamillo, 1988; Van Klinken and Van Dongen, 1980). This has been corrected in a recent article by Al-Dahhan et al. (1995).

It should be mentioned that another alternative for scale-up and scale-down of trickle-bed reactor is to operate the unit in the upflow mode (i.e., packed bubble column where the two phases are in upflow). Upflow reactors are often used in laboratory/pilot plant scales studies for testing catalysts and alternative feedstocks for commercial trickle-bed processes, since in them complete catalyst wetting is ensured. Unfortunately, fully wetted catalyst is obtained at the expense of increased liquid holdup, which can alter the relative amount of homogeneous and heterogeneous reactions occurring in more complex systems and should be avoided. In addition, upflow can lead to more dispersion and flow nonidealities than encountered in beds with fines. Finally, holdup and flow regimes in diluted bed are closer to those in trickle-beds than in upflow. However, the use of fines in upflow reactors would mitigate the dispersion effects and eliminate the possibilities of channeling and flow nonideality.

In this study the effect of fines on the catalyst wetting efficiency as well as on pressure drop and liquid holdup in trickle-bed reactors has been investigated by measuring liquid-catalyst contacting via a tracer technique and the improvement in contacting has been confirmed.

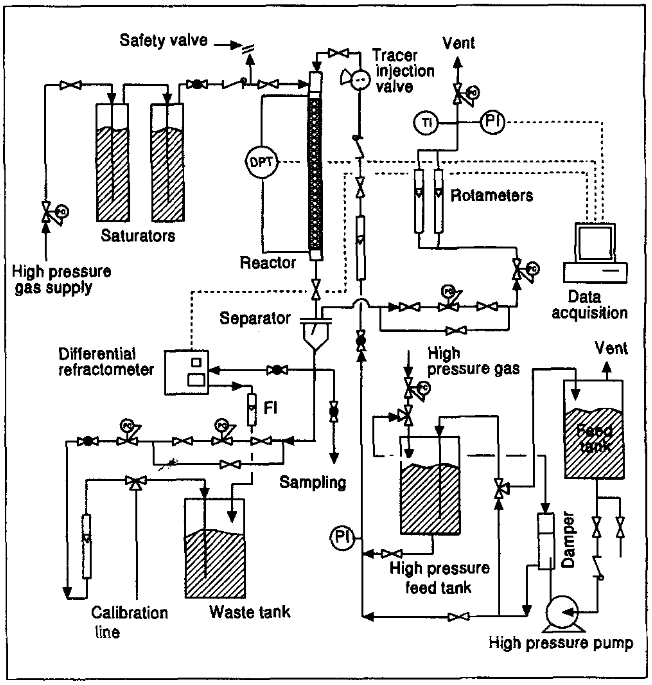


Figure 3. Process and instrumentation diagram (P&ID) of the trickle-bed reactor facility.

Experimental Investigation

Facility description

A high-pressure trickle-bed facility has been designed and developed to operate at a pressure up to 7 MPa (~ 1,000 psig) (Al-Dahhan, 1993). Figure 3 shows the process and instrumentation diagram of the facility. The experimental setup consists of a high-pressure trickle-bed reactor setup, liquid and gas delivery systems, tracer technique setup, and the data-acquisition system. Low- and high-pressure experiments can be performed, and liquid holdup and pressure drop can be measured simultaneously 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 a 1-in. (25.4-mm) SS tubing (ID = 2.19 cm). The length of these reactors is 22.5 in. (57.15 cm). The reactor's gas/liquid distributor has been designed similarly to the industrial-type distributor to ensure uniform liquid and gas distribution at the bed inlet. 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 important for the dynamic tracer experiments. A demister of stainless steel mesh is 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 sample collection. The waste stream passes through a back-pressure regulator to the rotameter and then flows to a 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 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 simultaneously shutting off the inlet and outlet streams and draining the reactor. 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.

The tracer setup 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 a 1-mL or a 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 10 to 30 s, and a Gas Chromatograph (column: 20% SP2100/0.1% Carbowax) is utilized to measure the tracer concentration (heptane in hexane). 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).

Packing the bed with a mixture of catalyst and fines

It is important to ensure that the reactor is packed reproducibly with a mixture of catalyst and fines. 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 way the catalyst and fines are packed, which could produce nonreliable data (Gierman, 1988). Ensuring a uniform catalyst/fines distribution along the bed, and reproducing such uniformity, is essential to avoid channeling and segregation.

Packing laboratory trickle-bed reactors with a mixture of catalyst and fines is an ill-defined art. Some claim to use dry methods, others utilize wet methods, and the "word of mouth" recipes for the volumetric ratio of fines to catalyst particles to be used vary from 1 to 1 to 10 to 1. We investigated both the dry and wet methods. In the dry method a predetermined volumetric mixture of fines and catalyst is prepared and poured into the bed with vibration of the reactor tube. In wet methods a slurry of fines, catalyst, and solvent is poured in the reactor with or without pressing the bed. We also studied using exactly the amount of fines that fill all voids of the original catalyst bed. In this case, beds were packed portion by portion as well as whole. The findings were described in a recent manuscript (see Al-Dahhan et al., 1995). We have found that the most reproducible and most uniform distribution of fines was obtained by using a dry method of packing with the fines to catalyst ratio selected in such a way so as to have just enough fines to completely occupy the voids in the bed packed only by catalyst particles. The recommended procedure to achieve this uniform and reproducible packing and its comparison to other methods were reported (Al-Dahhan et al., 1995; Al-Dahhan, 1993). The appendix summarizes the steps for the recommended technique.

Liquid-catalyst contacting efficiency determination

The tracer technique is chosen for determination of external catalyst contacting efficiency because it is the most promising in rapidly producing contacting information, and we have experience with it. 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 (Duduković and Mills, 1986; Van Klinken and Van Dongen, 1980; Sicardi et al., 1980a,b). Schwartz et al. (1976) and Colombo et al. (1976) introduced the tracer-based methods to evaluate both internal and external contacting efficiency. The evaluation of these parameters is based on the method of moments. Mills and Duduković (1981, 1982), El-Hisnawi (1981), El-Hisnawi et al. (1982), and Hanratty and Duduković (1992) confirmed the validity of this method. In tracer-based methods for determination of external contacting efficiency, an impulse of nonadsorbing tracer is injected into the liquid at the inlet of the 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, $E(t)$, are then calculated numerically from the experimental data based on their defining equations. The first moment represents the mean residence time, while the variance represents the measure of the spread of the response peak about the mean: a low value of σ^2 corresponds to a narrow peak, and conversely (Duduković and Felder, 1983).

The calculated values of the first moment, μ_1, and the variance, σ^2, can be utilized to evaluate liquid holdup and effective diffusivity of the tracer, respectively. As shown by Colombo et al. (1976) and Mills and Duduković (1981, 1982), a reliable estimate can be obtained by evaluating from the variance of the impulse response the apparent effective diffusivity for the reactor in a two-phase flow operation, $(De)_{TF}$, and for a liquid-filled reactor (i.e., single-phase flow of liquid in which the bed is fully filled with liquid) operated at the same liquid flow rate, $(De)_{LF}$ (liquid-filled operation). The wetting efficiency for both nondiluted and diluted beds is then given by

$$\eta_{CE} = \sqrt{\frac{(De)_{TF}}{(De)_{LF}}}\,. \qquad (1)$$

Nondiluted Bed (Catalyst Bed Only). The expressions needed to determine the effective diffusivity for two-phase flow and liquid-filled operation modes in nondiluted beds, which are required to evaluate external contacting efficiency, were developed and reported by Mills (1980), El-Hisnawi (1981), Mills and Duduković (1981), and Duduković and Mills (1986). The use of the experimentally measured variance in the expressions for the moments in evaluation of effective diffusivity require liquid–solid mass-transfer coefficient, k_s, and Peclet number for axial dispersion, Pe_L, to be evaluated. In liquid-filled operation, it was found that the effect of k_s on σ^2 vanishes with an increase in liquid flow rate, while the effect of Pe_L is negligible at moderate to high liquid flow rate (El-Hisnawi, 1981). Hence, the effective diffusivity of the tracer in liquid-filled operation, $(De)_{LF}$, can be evaluated at the flow rate of interest without the use of any correlation for k_s and Pe_L. This can be achieved by calculating the dimensionless variance, σ_D^2, at different flow rate. Plotting σ_D^2 vs. volumetric flow rate yields a straight line. By utilizing the expression of the line's slope, $(De)_{LF}$ for a particular bed of particles can be obtained (Mills, 1980).

In two-phase flow El-Hisnawi (1981) found that the effect of k_s and Pe_L is even less pronounced compared to liquid-filled operation and can be neglected. Therefore, the σ_D^2 expression can be simplified further to evaluate the effective diffusivity in two-phase flow experiments, $(De)_{TF}$. Tables 2 and 3 summarize the first moments and variance expressions for cylindrical extrudates (i.e., infinite cylinder extrudate approximation) and spherical porous catalysts, respectively, for nonvolatile and nonadsorbing tracers implemented in this study. El-Hisnawi (1981) has shown that the infinite cylinder approximation can be used for the extrudates' aspect ratio (catalyst length over the diameter) used in this study.

The obtained impulse-response signal, and its moments (μ_1 and σ^2), in both two-phase flow 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). Therefore it is necessary to evaluate the moments of the catalyst bed only. This is achieved by performing liquid-filled and two-phase flow experiments without the catalyst bed (i.e., only system externals) at various liquid flow rates as discussed by Mills and Duduković (1981, 1982). 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 liquid volumetric flow rate, as required by the central volume principle, while the variance is best correlated with the volumetric flow rate in power-law form, $\sigma^2 \propto Q^{-c}$ (Al-Dahhan, 1993; El-Hisnawi, 1981). Hence, μ_1 and σ^2 of the bed externals can be evaluated at the 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 alone can be determined (Duduković and Felder, 1983; Levenspiel, 1986). In the liquid-filled mode of operation, a

Table 2. Expressions for Moments of the Impulse Tracer Response for Cylindrical Catalyst (Infinite Cylinder Approximation) for a Nonvolatile and Nonadsorbing Tracer

Theoretical Expressions

Nondiluted Bed

Two-phase flow operation

$$\mu_1 = \frac{V_r \epsilon_L}{Q_L}\left[1 + \frac{S_{ex} r_p}{2V_p}\left(\frac{1-\epsilon_B}{\epsilon_L}\right)\epsilon_p\right].$$

The dimensionless variance expression:

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

Liquid-filled operation

$$\epsilon_L = \epsilon_B$$

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

The relationship between σ_D^2 and Q_L is linear with slope equal to the following expression:

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

Diluted Bed with Fines

Two-phase flow operation

The dimensionless variance expression is

$$\sigma_D^2 = \frac{\left\{\left(\frac{V_r \epsilon_L}{Q_L}\left[1 + \frac{S_{ex} r_p}{2V_p}\left(\frac{(1-\bar{\epsilon}_B)\epsilon_p}{\epsilon_L}\right)\right]\right) - \frac{V_r \epsilon_L}{Q_L}\right\}\frac{r_p^2 \epsilon_p}{8(De)_{TF}}}{\left(\frac{V_r \epsilon_L}{Q_L}\left[1 + \frac{S_{ex} r_p}{2V_p}\left(\frac{(1-\bar{\epsilon}_B)\epsilon_p}{\epsilon_L}\right)\right]\right)^2}.$$

Liquid-filled operation

In liquid-filled operation, liquid holdup (ϵ_L) is replaced by the actual bed voidage (ϵ_{Bf}). The following is the slope expression of σ_D^2 vs. Q_L:

$$\text{slope} = \frac{\frac{S_{ex} r_p}{2V_p}\left(\frac{1-\bar{\epsilon}_B}{\epsilon_{Bf}}\right)\frac{r_p^2 \epsilon_p^2}{8(De)_{LF}}}{V_r \epsilon_{Bf}\left[1 + \frac{S_{ex} r_p}{2V_p}\left(\frac{(1-\bar{\epsilon}_B)}{\epsilon_{Bf}}\right)\epsilon_p\right]^2}.$$

El-Hisnawi, 1981; Al-Dahhan, 1993.

Table 3. Expressions for the Impulse Tracer Response for Spherical Particles for a Nonvolatile and Nonadsorbing Tracer

Theoretical Expressions

Nondiluted Bed

Two-phase flow operation

The dimensionless variance expression is

$$\sigma_D^2 = \frac{Q_L}{V_r \epsilon_L}\frac{\frac{(1-\epsilon_B)\epsilon_p}{\epsilon_L}\left(\frac{r_p^2 \epsilon_p}{15(De)_{TF}}\right)}{\left[1 + \frac{(1-\epsilon_B)\epsilon_p}{\epsilon_L}\right]^2}.$$

Liquid-filled operation

The relationship between σ_D^2 and Q_L is linear with a slope equal to the following expression:

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

Diluted Bed with Fines

Two-phase flow operation

The dimensionless variance expression is

$$\sigma_D^2 = \frac{Q_L}{V_r \epsilon_L}\frac{\frac{(1-\bar{\epsilon}_B)\epsilon_p}{\epsilon_L}\left(\frac{r_p^2 \epsilon_p}{15(De)_{TF}}\right)}{\left[1 + \left(\frac{(1-\bar{\epsilon}_B)\epsilon_p}{\epsilon_L}\right)\right]^2}.$$

Liquid-filled operation

In liquid-filled operation, liquid holdup (ϵ_L) is replaced by the actual bed voidage (ϵ_{Bf}). The following is the slope expression of σ_D^2 vs. Q_L:

$$\text{slope} = \frac{\frac{(1-\bar{\epsilon}_B)\epsilon_p^2}{\epsilon_{Bf}}\frac{r_p^2}{15(De)_{LF}}}{V_r \epsilon_{Bf}\left[1 + \frac{(1-\bar{\epsilon}_B)\epsilon_p}{\epsilon_{Bf}}\right]^2}.$$

Mills and Duduković, 1981; Al-Dahhan, 1993.

smaller volume of the reactor head (i.e., liquid-phase distributor) than that used in two-phase flow is utilized. This was found in this work, as well as by El-Hisnawi (1981), to produce a better response signal. One should note that Mills and Duduković (1988, 1989) analyzed the tracer response data by convolution and deconvolution methods where they compared experimental RTDs and the fit of the predicted curve with the model used. The differences were within the accuracy of the experimental tracer response measurements.

Diluted Bed (Mixture of Catalyst and Fines). For a diluted bed packed with a mixture of catalyst and fines, the expressions needed to calculate the effective diffusivities in both liquid-filled and two-phase flow operations can be obtained by modifying the expressions for nondiluted bed (Tables 2 and 3—nondiluted bed) as follows (Al-Dahhan, 1993):

1. The catalyst particle radius, r_p, is used as in the case of the nondiluted bed, since the tracer diffusion occurs only into the pores of the catalyst particles (because the fines are nonporous silicon carbide particles).

2. In the expressions for two-phase flow (Tables 2 and 3—nondiluted bed), the voidage of the nondiluted bed, ϵ_B, which is (total bed volume−catalyst volume)/total bed volume, is replaced in the expressions for the diluted bed by $\bar{\epsilon}_B$ defined as the volume fraction of the reactor not occupied by catalyst particles:

$$\bar{\epsilon}_B = \frac{(\text{total bed vol.} - \text{cat. vol.})}{\text{total bed vol.}} \tag{2}$$

Hence, $\bar{\epsilon}_B$ for a diluted bed that is packed according to the recommended procedure (fines just fill its voidage) is the same as the voidage of the original undiluted bed, ϵ_B. However, for a bed that is not packed based on the recommended proce-

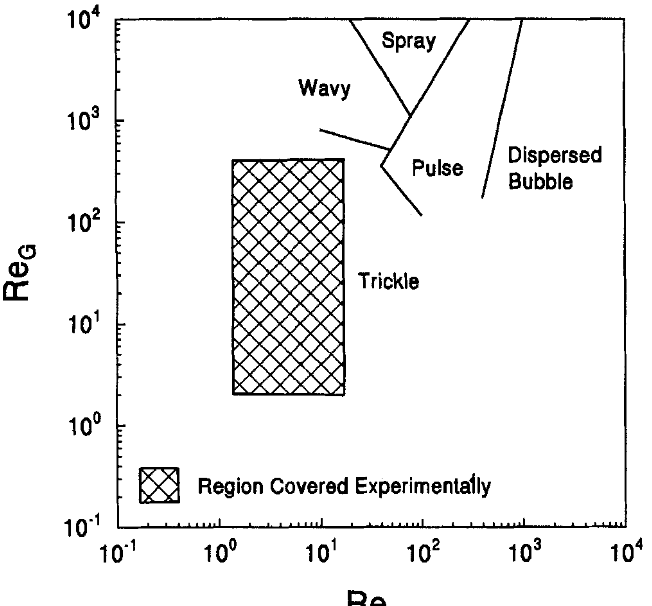


Figure 4. Experimentally covered trickle-flow regime based on flow map of Fukushima and Kusaka (1977a,b).

dure (e.g., for highly diluted bed such as 2 volume fines/1 volume catalyst) $\bar{\epsilon}_B$ is larger than ϵ_B. The bed tracer mass balance equation in the interstitial liquid is (Mills, 1980; El-Hisnawi, 1981)

$$D_L \frac{\partial^2 C}{\partial Z^2} - U_L \frac{\partial C}{\partial Z} - a_{LS} N_{LS} = \epsilon_L \frac{\partial C}{\partial t}. \tag{3}$$

The term $a_{LS}N_{LS}$ is the rate of tracer loss to particles by liquid–solid mass transfer to liquid-filled pores, where a_{LS} is the effective (i.e., wetted) liquid–solid area through which mass transfer of tracer may occur from liquid bulk to the catalyst particle surface per unit volume of the reactor. Thus, the only difference between the a_{LS} expression for the undiluted catalyst bed and that of the diluted bed occurs in the definition for the bed voidage mentioned earlier. Hence, a_{LS} in the nondiluted, and in the diluted bed is defined as follows:

Catalyst bed only

$$a_{LS} = \frac{S_{ex}}{V_p} \eta_{CE} (1 - \epsilon_B)$$

where

$$(1 - \epsilon_B) = \frac{\text{cat. vol.}}{\text{total bed vol.}}$$

Diluted bed (catalyst and fines)

$$a_{LS} = \frac{S_{ex}}{V_p} \eta_{CE} (1 - \bar{\epsilon}_B)$$

where

$$(1 - \bar{\epsilon}_B) = \frac{\text{cat. vol.}}{\text{total bed vol.}}$$

Table 4. Range of Covered Operating Conditions

Condition	Covered Range
Reactor pres., MPa	$0.31 \le P \le 1.82$
(Psig)	$(30 \le P \le 250)$
Gas superficial velocity, cm/s	$1 \le U_G \le 8.5$
Gas superficial mass velocity, kg/m^2·s	$6.64 \times 10^{-3} \le G \le 4.0$
Liquid superficial flow rate, mL/min	$15 \le Q_L \le 70$
Liquid superficial mass flow rate, kg/m^2·s	$0.42 \le L \le 2.1$
Temperature, K	≈ 298

3. In the expressions for the liquid-filled operation, the liquid holdup, ϵ_L, and the bed voidage, ϵ_B, in two-phase flow expressions (Tables 2 and 3—nondiluted bed) are replaced by the actual voidage of the diluted bed, ϵ_{Bf} (i.e., the volume fraction of the reactor unoccupied by either catalyst or fines) and $\bar{\epsilon}_B$ previously discussed in (2), respectively. ϵ_{Bf} of the diluted bed is defined as follows:

$$\epsilon_{Bf} = \frac{(\text{total bed vol.} - \text{cat. vol.} - \text{fines vol.})}{\text{total bed volume}}. \tag{4}$$

Accordingly, the expressions for a diluted bed with fines required to evaluate the effective diffusivities in both liquid-filled and two-phase flow operations are reported in Tables 2 and 3 for extrudate and spherical particles, respectively (Al-Dahhan, 1993).

Operating conditions investigated

The flow conditions covered in this study are within the trickle-flow regime based on the available flow maps (Charpentier and Favier, 1975; Talmor, 1977; Fukushima and Kusaka, 1977a,b). For illustration, Figure 4 shows the range of the investigated operating conditions superimposed on the flow map of Fukushima and Kusaka (1977a,b). All the data are in the trickle-flow regime in agreement with other flow maps, also. Visual observation through the acrylic window and stable pressure-drop measurements also confirm that the flow regime is trickle flow. The selection of the physical system used in this study is based on earlier studies by Schwartz et al. (1976), Mills (1980), Mills and Duduković (1981), and Hanratty and Duduković (1992). Thus the hydrocarbon solvent is selected to be hexane. 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. The range of reactor pressure, liquid, and gas superficial velocities covered are listed in Table 4.

Different bed characteristics and degrees of bed dilution, shown in Table 5, have been used to investigate the effect of fines on catalyst contacting efficiency, pressure drop, and liquid holdup. In Table 5 the evaluated liquid-filled effective diffusivities are listed as well. The somewhat higher effective diffusivity obtained in a liquid-full highly diluted bed (2 volumes fines/1 volume catalyst), compared to the one determined for the bed of undiluted extrudates and for the bed of extrudates diluted with fines by the recommended procedure

Table 5. Packed-Bed Characteristics

Reactor/Packing	Bed Characteristics	Liquid-filled Effective Diffusivity	Packing Procedure
Nondiluted Bed			
0.5% Pd on alumina-stainless steel reactor	$d_r = 2.19$ cm, length = 51.61 cm; cat. type: porous extrudate; size = 0.157 cm × 0.43 cm; $(d_p)_{eq} = 0.199$ cm; $\epsilon_p = 0.599$; $\rho_{\text{bulkcat}} = 1.189$ g/cm^3; $d_r/d_p = 11$; $\epsilon_B = 0.36$	17.49×10^{-6} cm^2/s	Portion by portion with tapping
Silica shell-stainless steel reactor	$d_r = 2.19$ cm, length = 51.63 cm; cat. type: porous sphere; $d_p = 0.152$ cm; $\epsilon_p = 0.697$; $\rho_{\text{bulkcat.}} = 0.697$ g/cm^3; $d_r/d_p = 14.6$; $\epsilon_B = 0.41$	14.82×10^{-6} cm^2/s	Portion by portion with tapping
Diluted Bed with Fines			
Fines	Type: nonporous silicon carbide $d_p = 0.021$ cm; $\rho_{\text{bulk}} = 1.51$ g/cm^3; $\rho_{\text{material}} = 3.21$ g/cm^3		
0.5% Pd on alumina/fines (fines just fill the bed voidage) —stainless steel reactor	$d_r = 2.19$ cm, length = 53.81 cm; vol. fines/vol. cat. = 0.54; $\epsilon_{Bf} = 0.22$; $\bar{\epsilon}_B = 0.38$;	17.98×10^{-6} cm^2/s	Packing dry a portion of catalyst then a portion of fines with tapping according to the recommened procedure (Al-Dahhan et al., 1995)
0.5% Pd on alumina/fines (2:1, fines/cat.)—stainless steel reactor	$d_r = 2.19$ cm, length = 51.51 cm; vol. fines/vol. cat. = 2; $\epsilon_{Bf} = 0.35$; $\bar{\epsilon}_B = 0.77$;	18.95×10^{-6} cm^2/s	Mixing a portion of 2 vol. of fines and 1 vol. of catalyst in the presence of a solvent until the mixture becomes as uniform as possible, then introducing the mixture part by part with pressing each part inside the bed (Al-Dahhan et al., 1995)
Silica shell/fines (bed voidage is partially filled with fines) —stainless steel reactor	$d_r = 2.19$ cm, length = 53.51 cm; vol. fines/vol. cat. = 0.4; $\epsilon_{Bf} = 0.31$; $\bar{\epsilon}_B = 0.42$; Note: according to the recommended procedure, the ratio of fines/cat. is 0.7	14.3×10^{-6} cm^2/s	Recommended procedure as previously mentioned

(e.g., so as to contain only the fines needed to fill the original bed voidage), is apparently due to increased accessibility of the catalyst to the tracer in highly diluted beds, which is reflected in the calculated somewhat larger diffusivity. The maximum difference, however, is not large (5.4%). This can be phenomenologically explained as follows. At high dilution with fines each catalyst particle is far removed from another catalyst particle and receives the tracer without interaction with other catalyst particles. In other diluted beds (e.g., packed according to the recommended procedure), the catalyst particles touch and together act as an effectively larger particle. Since the mathematical model is always based on the actual catalyst diameter, the former bed will yield slightly higher computed diffusivity.

Prior to each two-phase flow experiment, the catalyst bed, after being extensively prewetted by soaking the bed and leaving it overnight soaked, is operated first in the high interaction regime (pulse and/or bubble-flow regime) at high liquid mass velocities. The mass velocities are then 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). Upon the previously described startup procedure, the operation is assumed to be stable when the reactor pressure, pressure drop, and the gas and liquid throughout do not change for at least 10 minutes. 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, the first moment, variance, and dimensionless variance, of the impulse responses for the beds can be found in Al-Dahhan (1993). The first moment, variance, and dimensionless variance are reproducible within ±5%. As an example, Figure 5 shows a comparison of the E-curves at closest available liquid mass velocities for the nondiluted extrudate catalyst bed and the diluted bed packed with a mixture of extrudate catalyst and fines according to the recommended procedure. The same trend (with broader spread of the response peak about the mean) has been reported by Van Klinken and Van Dongen (1980) for a system of different physical properties and for liquid mass flow rate an order of magnitude smaller than that of the data presented in Figure 5.

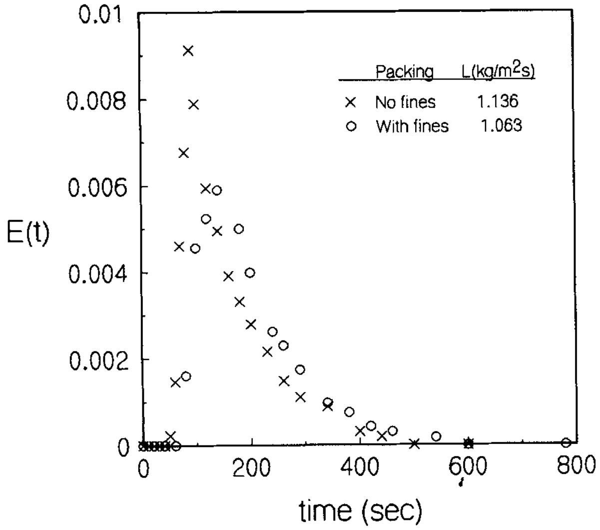


Figure 5. Normalized tracer impulse-response for nondiluted vs. diluted beds packed by the recommended procedure.

System: hexane/nitrogen; tracer: n-heptane; catalyst: porous 0.5% Pd extrudate ($(d_p)_{eq} = 0.199$ cm); vol. fines/vol. cat. = 0.54 (packed by the recommended procedure), $\epsilon_{Bf} = 0.22$; pressure = 0.31 MPa (30 psig); $U_G = 1.0$ cm/s; without fines; $\mu_1 = 129$ s, $\sigma_D^2 = 0.212$; with fines: $\mu_1 = 161$ s, $\sigma_D^2 = 0.153$ (the bed characteristics are in Table 5).

Results and Discussion

The effects of fines on catalyst wetting efficiency, pressure drop, and liquid holdup are interlinked. Figure 6b and 6c demonstrate the influence of fines on pressure drop and liquid holdup in a diluted bed packed by the recommended procedure (i.e., fines only fill the voids). At 0.31 MPa and 1.02 cm/s, superficial gas velocity, pressure drop, and liquid holdup are larger in the diluted bed compared to those in the undiluted bed at the same mass velocities. Pressure drop increases in the diluted bed because bed voidage of the diluted bed ($\epsilon_{Bf} = 0.22$) is less than that of the nondiluted bed ($\epsilon_{Bf} = 0.36$), and in the former bed the flow is retarded further causing more energy dissipating, and hence higher pressure drop. Liquid holdup is larger in the diluted bed than in the undiluted bed because solid-to-solid contact points over which liquid flows are more numerous in the diluted bed. Hence, at fixed operating conditions, total external liquid holdup increases in a diluted bed as indicated by a residence time distribution that shifts to longer time. The same effect is obtained in a diluted bed of spheres packed with less fines than determined by the recommended procedure (i.e., the spheres' bed voidage is partially filled with fines), as shown in Figure 7b and 7c. However, the smaller amount of fines produces a smaller pressure drop and less holdup in this particular catalyst bed compared to those in diluted bed with fines that fill completely its bed voidage (i.e., packed according to the recommended procedure).

The effect of the reactor pressure and gas flow rate on pressure drop and liquid holdup obtained in a diluted bed of extrudates is shown in Figure 8a and 8b, respectively. It is obvious that at fixed liquid mass velocity, as the reactor pressure and gas flow rate increase, pressure drop increases sig-

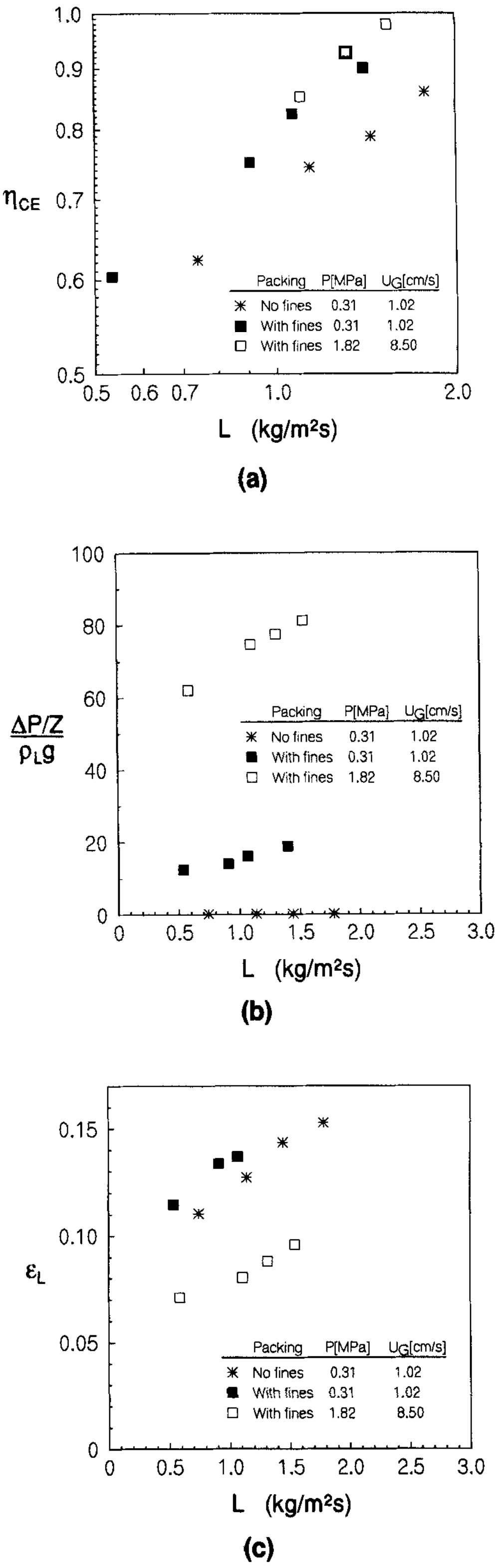


Figure 6. Effect of fines on catalyst wetting efficiency (a), pressure drop (b), and liquid holdup (c) in a diluted bed of extrudates.

System: hexane/nitrogen; tracer: n-heptane; catalyst: porous 0.5% Pd extrudate ($(d_p)_{eq} = 0.199$ cm); vol. fines/vol. cat. = 0.54 (packed by the recommended procedure); $\epsilon_{Bf} = 0.22$ (the bed characteristics are in Table 5).

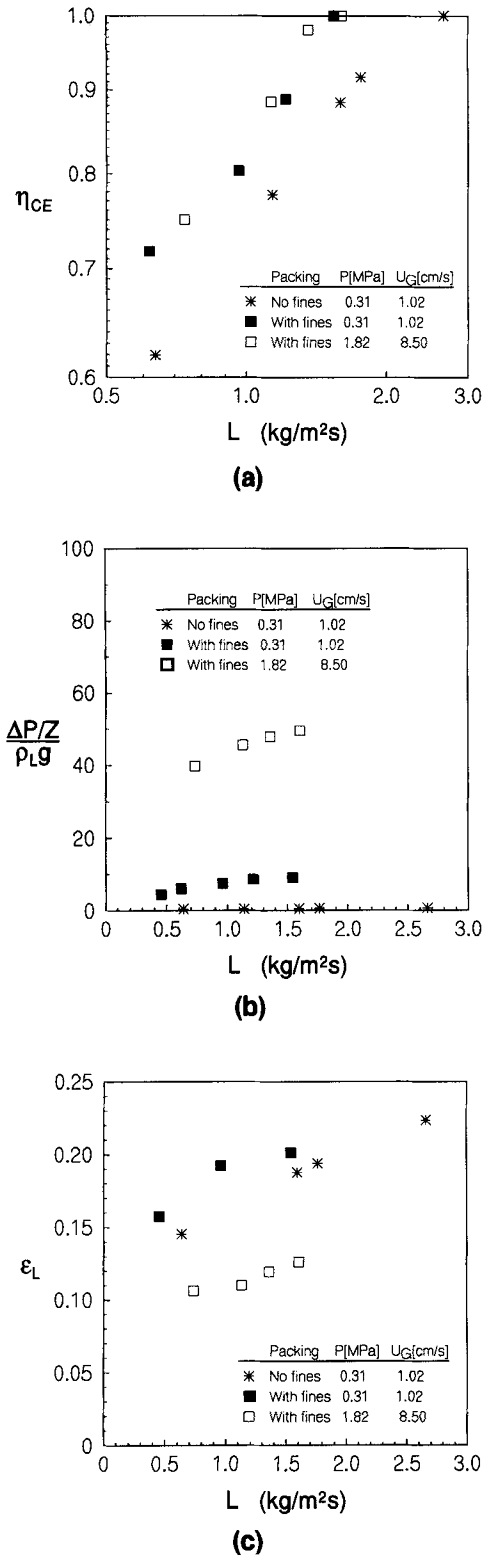


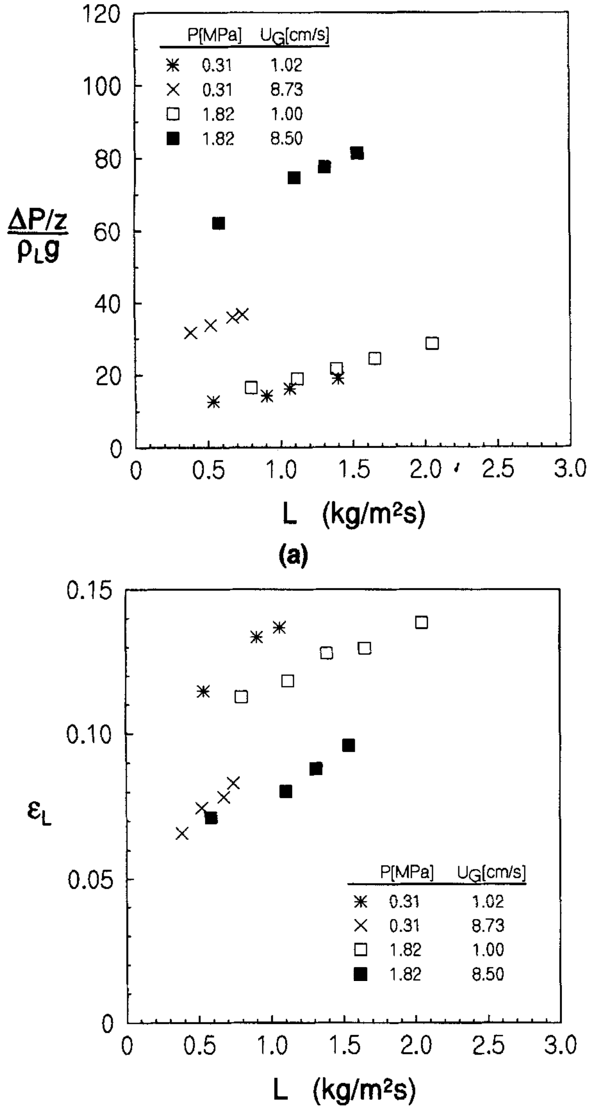
Figure 7. Effect of fines on catalyst wetting efficiency (a), pressure drop (b), and liquid holdup (c) in a diluted bed of spheres with less fines than that required by the recommended procedure.

System: hexane/nitrogen; tracer: n-heptane; catalyst: porous spherical silica shell ($d_p = 0.152$ cm); vol. fines/vol. cat. = 0.4; $\epsilon_{Bf} = 0.305$ (the recommended procedure required vol. fines/vol. cat. = 0.7) (the bed characteristics are in Table 5).

nificantly while liquid holdup decreases noticeably, which is similar to what was found in a nondiluted bed (Al-Dahhan and Duduković, 1994; Al-Dahhan, 1993; Wammes, 1990). A comparison of pressure drop and liquid holdup obtained in a nondiluted bed, diluted bed packed according to the recommended procedure, and diluted bed with a ratio of 2 volumes of fines to 1 volume of extrudates packed by the wet method (mixing portion of catalyst with required portion of fines in the presence of a solvent until the mixture becomes as uniform as possible and then introducing the mixture part by part by pressing each part inside the reactor) is illustrated in Figure 9b and 9c. The data reveal that the pressure drop in the diluted packed bed with 2 volumes of fines to 1 volume of catalyst is less than that of the bed packed by the recommended procedure. This is because the voidage in the first bed (2:1 fines/catalyst; $\epsilon_{Bf} = 0.35$) is larger than that of the second bed (fines just fill the voidage, $\epsilon_{Bf} = 0.22$). However, liquid holdup is higher in the bed of 2 volumes of fines to 1 volume of extrudates due to more available void space for the liquid around a larger number of solid-to-solid contacting points over which liquid flows. It is evident that such effects affect wetting efficiency in the diluted bed, since at high-pressure operation, both pressure drop and liquid holdup were found to affect catalyst wetting due to better spreading of liquid over the catalyst bed as described phenomenologically by Al-Dahhan and Duduković (1995).

As shown in Figures 6a, 7a and 9a, the results of this study quantitatively confirm that diluting the bed with fines improves the catalyst wetting efficiency. Figure 6a compares the contacting efficiency in an undiluted bed of extrudates with that of a diluted bed packed according to the recommended procedure. It shows that liquid–solid contacting efficiency, η_{CE}, increases as a result of dilution with fines. As reactor pressure and gas flow rate increase, pressure drop increases and contacting efficiency increases due to the better spreading of the flowing liquid. The increase in reactor pressure (gas density) and/or gas flow rate increases the pressure gradient, which increases the driving force acting on liquid flow. This causes a decrease in liquid holdup, but the remaining liquid film spreads better around the catalyst. A decrease in the liquid film thickness, and an increase in the shear stress on the gas–liquid interface, due to larger pressure drop caused by either higher gas velocity or pressure (gas density), result in an improved spreading of the liquid film over the external packing area, making them more wet. As the liquid flow rate increases, both liquid holdup and pressure drop increase, which yields further improvement in the wetting efficiency (Al-Dahhan and Duduković, 1995; Al-Dahhan, 1993).

The increase in η_{CE} in a more diluted bed (2 volumes of fines/1 volume of catalyst) was found to be comparable to that of the diluted bed with just enough fines to fill its voidage (the recommended procedure) as illustrated in Figure 9a. This is related to finding that the pressure drop in the diluted packed bed with 2 volumes of fines to 1 volume of catalyst is less than that of the recommended procedure, while liquid holdup is higher. Hence, the effect of lower pressure drop and higher liquid holdup in a diluted bed with more voidage on the contacting efficiency compensate each other in producing the same contacting efficiency at a given liquid flow rate as in the bed of less voidage and of higher pressure drop and lower liquid holdup. It is noteworthy that while fines do



(a)

(b)

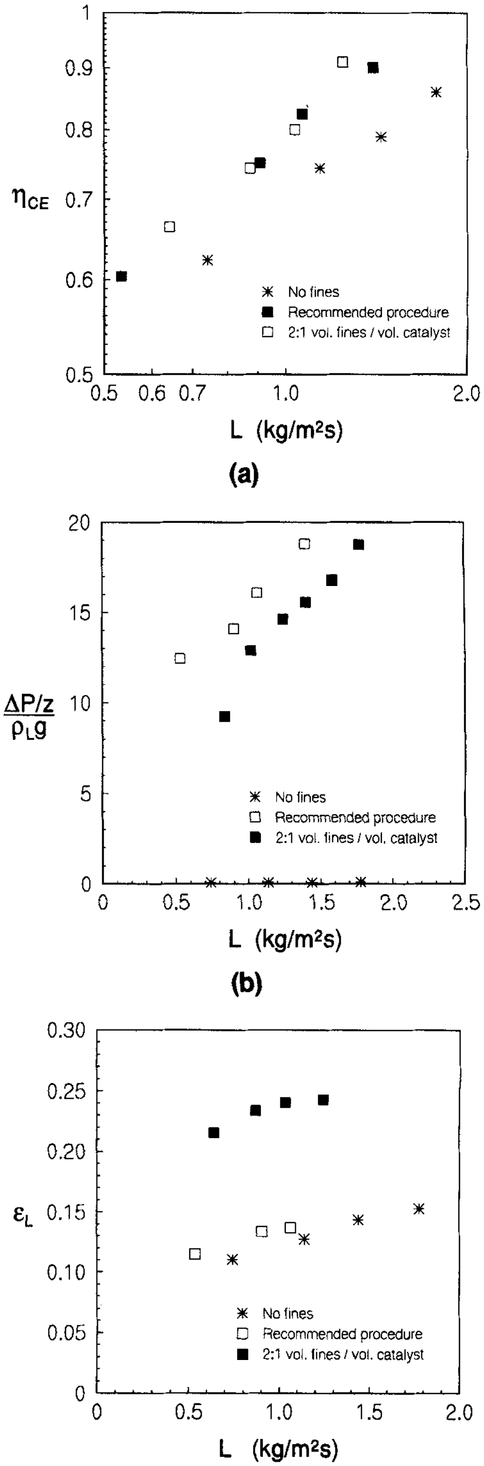
Figure 8. Effect of reactor pressure and gas flow rate on pressure drop (a) and liquid holdup (b) in a diluted bed of extrudates.

System: hexane/nitrogen; catalyst: porous 0.5% Pd extrudate ($(d_p)_{eq} = 0.199$ cm); vol. fines/vol. cat. = 0.54 (recommended procedure); $\epsilon_{Bf} = 0.22$ (the bed characteristics are in Table 5).

improve the contacting efficiency at all liquid mass velocities, contacting efficiency is not unity (as sometimes assumed) and still remains a function of the liquid velocity.

Conclusions

Catalyst wetting efficiency is improved in a diluted bed containing the mixture of catalyst and fines, and liquid holdup and pressure drop in such a bed increase as well. A reproducible procedure summarized in the Appendix to pack the diluted bed is recommended (Al-Dahhan et al., 1995). This procedure is based on filling the voidage of the original dry bed with dry fines. In a highly diluted bed (packed by the wet method with pressing) pressure drop was found to be smaller due to more voidage, while liquid holdup is larger due to the larger number of solid-to-solid contact points compared to those of a bed packed according to the developed procedure. The improvement of catalyst wetting efficiency in a highly



(a)

(b)

(c)

Figure 9. Comparison of catalyst wetting efficiency (a), pressure drop (b), and liquid holdup (c).

Obtained in a nondiluted bed of extrudates, diluted bed with vol. fines/vol. cat. = 0.54 (recommended procedure), and diluted bed with vol. fines/vol. cat. = 2 packed by wet method, pressure: 0.31 MPa (30 psig); $U_G = 1.0$ cm/s (the bed characteristics are listed in Table 5).

diluted bed is approximately similar to that obtained in the bed packed by the developed procedure. This would indicate that the effect of a smaller pressure drop and larger liquid holdup in a highly diluted bed compensate each other and produce contacting obtainable in the bed packed by the recommended procedure, which has higher pressure drop and less liquid holdup. Therefore, packing the bed with a mixture of catalyst and fines by the recommended procedure (fines just fill the voidage) is the only method that ensures not only improved catalyst contacting but also a uniform catalyst and fines distribution and reproducibility of such distribution. These are not obtainable by other packing methods (Al-Dahhan et al., 1995).

The quantitative improvement of the contacting efficiency in the diluted bed, as shown in Figures 6a, 7a and 9a, are consistent with Koros's (1976) findings, which were based on studies of hydrogen peroxide decomposition in evaluating the effect of fines (sand) on the catalyst utilization efficiency. Thus, the improvement of liquid-catalyst contacting efficiency in a diluted bed improves the performance of laboratory reactor as discussed earlier. However, the extent of improvement would depend on the type of reaction.

Our purpose in this work is to demonstrate that the assertion that fines improve contacting has a basis in fact, and that this is achieved at the expense of increased pressure drop and lower liquid holdup. Further work is recommended for gathering an extensive database (different solvent, particle sizes, and shapes, etc.) to develop a model that predicts the percentage change in the catalyst wetting in the diluted bed.

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Notation

C = tracer concentration, mol/m^3
D_L = axial dispersion coefficient, m^2/s
g = gravitational acceleration, m/s^2
Ga_L = liquid Galileo number, $d_p^3 \rho_L^2 g \epsilon_B^3/\mu_L^2(1-\epsilon_B)^3$, dimensionless
Ga_G = gas Galileo number, $d_p^3 \rho_G^2 g \epsilon_B^3/\mu_G^2(1-\epsilon_B)^3$, dimensionless
$\Delta P/Z$ = pressure drop per unit bed length, N/m^3
Q_L = liquid volumetric flow rate, m^3/s
Re_L = liquid Reynolds number, $U_L \rho_L d_P/\mu_L(1-\epsilon_B)$, dimensionless
Re_G = gas Reynolds number, $U_G \rho_G d_P/\mu_G(1-\epsilon_B)$, dimensionless
S_{ex} = external area of catalyst pellet, m^2
t = time, s
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
$1-\bar{\epsilon}_B$ = volume of catalyst per reactor volume
ϵ_{Ld} = dynamic liquid holdup per reactor bed volume
ϵ_{Ls} = static liquid holdup per reactor bed volume
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 $(\epsilon_L + \epsilon_{Li})$
ϵ_p = particle porosity
μ_1 = first moment, s, $\mu_1 = \int_0^\infty tE(t)dt$
μ_2 = second moment, s^2, $\mu_2 = \int_0^\infty t^2 E(t)\,dt$
μ_L = liquid viscosity, N·s/m^2
μ_G = gas viscosity, N·s/m^2
ρ_L = liquid density, kg/m^3
ρ_G = gas density, kg/m^3
σ^2 = variance or second central moment, s^2

$$\sigma^2 = \frac{\int_0^\infty (t-\mu_1)^2 E(t)\,dt}{\int_0^\infty E(t)\,dt} = \mu_2 - \mu_1^2$$

σ_D^2 = dimensionless variance, $\sigma_D^2 = \sigma^2/\mu_1^2$

Literature Cited

Al-Dahhan, M., "Effects of High Pressure and Fines on the Hydrodynamics of Trickle-Bed Reactors," DSc Thesis, Washington Univ., St. Louis, MO (1993).

Al-Dahhan, M., and M. P. Duduković, "Pressure Drop and Liquid Holdup in High Pressure Trickle-Bed Reactors," *Chem. Eng. Sci.*, **49**(24B), 5681 (1994).

Al-Dahhan, M., and M. P. Duduković, "Catalyst Wetting Efficiency in Trickle-Bed Reactors at High Pressure," *Chem. Eng. Sci.*, **50**(15), 2377 (1995).

Al-Dahhan, M., Y. Wu, and M. P. Duduković, "Reproducible Technique for Packing Laboratory Scale Trickle-Bed Reactors with a Mixture of Catalyst and Fines," *Ind. Eng. Chem. Res.*, **34**, 741 (1995).

Anderson, J. R., and K. C. Pratt, *Introduction to Characterization and Testing of Catalyst*, Academic Press, New York (1985).

Beaudry, E. G., P. L. Mills, and M. P. Duduković, "Gas-Liquid Downflow, Upflow, and Countercurrent Flow in Packed Beds-Reactor Performance for Gas Limiting Reaction," *World Congress III of Chemical Engineering*, Tokyo, Japan, p. IV-173 (Sept., 1986).

Beaudry, E. G., M. P. Duduković, and P. L. Mills, "Trickle Bed Reactors: Liquid Diffusional Effects in a Gas Limited Reaction," *AIChE J.*, **33**(9), 1435 (1987).

Carruthers, D. J., and D. J. DiCamillo, "Pilot Plant Testing of Hydrotreating Catalyst Influence of Catalyst Condition, Bed Loading and Dilution," *Appl. Catal.*, **43**, (1988).

Charpentier, J. C., and M. Favier, "Some Liquid Holdup Experimental Data in Trickle-Bed Reactors for Foaming and Nonfoaming Hydrocarbons," *AIChE J.*, **21**, 1213 (1975).

Colombo, A. J., G. Baldi, and S. Sicardi, "Solid-Liquid Contacting Effectiveness in Trickle-Bed Reactors," *Chem. Eng. Sci.*, **31**, 1101 (1976).

Duduković, M. P., and P. L. Mills, "Contacting and Hydrodynamics in Trickle-Bed Reactors," *Encyclopedia of Fluid Mechanics*, N. P. Cheremisinoff, ed., Chap. 32, Gulf Pub., Houston, p. 969 (1986).

Duduković, M. P., "Catalyst Effectiveness Factor and Contacting Efficiency in Trickle-Bed Reactors," *AIChE J.*, **23**, 6 (1977).

Duduković, M. P., and R. M. Felder, "Mixing Effects in Chemical Reactors—III Dispersion Model," *AIChE Modular Instruction*, Ser. E, Vol. 4, *Reactor Stability, Sensitivity and Mixing Effects* (Module E4.7), AIChE (1983).

El-Hisnawi, A. A., "Tracer and Reaction Studies in Trickle Bed Reactors," DSc Thesis, Washington Univ., St. Louis, MO (1981).

El-Hisnawi, A. A., M. P. Duduković, and P. L. Mills, "Trickle-Bed Reactors: Dynamic Tracer Tests, Reaction Studies, and Modeling of Reactor Performance," *ACS Symp. Ser.*, **196**, 431 (1982).

Fukushima, S., and K. Kusaka, "Interfacial Area and Boundary of Hydrodynamic Flow Region in Packed Column with Cocurrent Downward Flow," *J. Chem. Eng. Japan*, **10**(6), 461 (1977a).

Fukushima, S., and K. Kusaka, "Liquid Phase Volumetric and Mass Transfer Coefficient, and Boundary of Hydrodynamic Flow Region in Packed Volume with Cocurrent Downward Flow," *J. Chem. Eng. Japan*, **10**(6), 468 (1977b).

Gianetto, A., and V. Specchia, "Trickle-Bed Reactors: State of Art and Perspectives," *Chem. Eng. Sci.*, **47**(13/14), 3197 (1992).

Gierman, H., "Design of Laboratory Hydrotreating Reactors Scaling Down of Trickle-Flow Reactors," *Appl. Catal.*, **43**, 285 (1988).

Hanratty, P. J., and M. P. Duduković, "Detection of Flow Maldistribution in Trickle-Bed Reactors via Tracers," *Chem. Eng. Sci.*, **47**(12), 3003 (1992).

Herskowitz, M., and J. M. Smith, "Trickle-Bed Reactors: A Review," *AIChE J.*, **29**(1), 1 (1983).

Kan, K., and P. E. Greenfield, "Pressure Drop and Holdup in Two-

Phase Cocurrent Trickle Flows Through Beds of Small Packings," *Ind. Eng. Chem. Process Des. Dev.*, **18**, 740 (1979).

Koros, R. M., "Catalyst Utilization in Mixed-Phase Fixed Bed Reactors," *European Symp. on Chemical Reaction Engineering*, Heidelberg, Germany (1976).

Levec, J., K. Grosser, and R. G. Carbonell, "The Hysteretic Behavior of Pressure Drop and Liquid Holdup in Trickle Bed Reactor," *AIChE J.*, **34**, 1027 (1988).

Levenspiel, O., *The Chemical Reactor OmniBook+*, Oregon State University, Book Store, Corvallis (1986).

Mills, P. L., "Catalyst Effectiveness and Solid-Liquid Contacting in Trickle-Bed Reactors," DSc Thesis, Washington Univ., St. Louis, MO (1980).

Mills, P. L., and M. P. Duduković, "Evaluation of Liquid-Solid Contacting in Trickle by Tracer Methods," *AIChE J.*, **27**, 893 (1981).

Mills, P. L., and M. P. Duduković, "Evaluation of Liquid-Solid Contacting in Trickle Bed Reactors by Tracer Methods," *AIChE J.*, **28**, 52 (1982).

Mills, P. L., and M. P. Duduković, "Deconvolution of Noisy Tracer Response Data by a Linear Filtering Method," *AIChE J.*, **34**, 1752 (1988).

Mills, P. L., and M. P. Duduković, "Convolution and Deconvolution of Nonideal Tracer Response Data with Application to Three-Phase Packed-Beds," *Comput. Chem. Eng.*, **31**, 881 (1989).

Schwartz, J. G., E. Weger, and M. P. Duduković, "A New Tracer Method for Determination of Liquid-Solid Contacting Efficiency in Trickle-Bed Reactors," *AIChE J.*, **22**, 5 (1976).

Sedriks, W., and N. Kenney, "Partial Wetting in Trickle-Bed Reactors: The Reduction of Crotonaldehyde Over a Palladium Catalyst," *Chem. Eng. Sci.*, **38**, 559 (1973).

Sicardi, S., G. Baldi, A. Gianetto, and V. Specchia, "Catalyst Areas Wetted by Flowing and Semistagnant Liquid in Trickle-Bed Reactors," *Chem. Eng. Sci.*, **35**, 67 (1980).

Sicardi, S., G. Baldi, V. Specchia, I. Mazzarino, and A. Geianetto, "Packing Wetting in Trickle Bed Reactors: Influence of the Gas Flow Rate," *Chem. Eng. Sci.*, **36**, 226 (1980).

Sie, S. T., "Scale Effects in Laboratory and Pilot-Plant Reactors for Trickle-Flow Processes," *Rev. Inst. Fr. Pet.*, **46**, 4 (1991).

Talmor, E., "Two-Phase Downflow Through Catalyst Beds: I. Flow Maps," *AIChE J.*, **23**, 868 (1977).

Van Klinken, J., and R. H. Van Dongen, "Catalyst Dilution for Improved Performance of Laboratory Trickle-Flow Reactors," *Chem. Eng. Sci.*, **35**, 59 (1980).

Wammes, W. J. A., "Hydrodynamics in Cocurrent Gas-Liquid Trickle-Bed Reactor at Elevated Pressure," PhD Thesis, University of Twente, Enschede, The Netherlands (1990).

Zhukova, T., B. V. Pisarenko, and V. V. Kafarov, "Modeling and Design of Industrial Reactors with a Stationary Bed of Catalyst and Two-Phase Gas-Liquid Flow—A Review," *Int. Chem. Eng.*, **30**(1), 57 (1990).

Appendix: Recommended Technique to Pack a Diluted Bed Reproducibly

The following is the step-by-step procedure developed and recommended by Al-Dahhan et al. (1995) to pack the diluted bed reproducibly.

Portion of catalyst by portion of fines packing procedure

1. Use dry catalyst and fines.

2. Load the reactor with the known amount of catalyst to be utilized and determine the bed height.

3. Calculate the catalyst bed void volume based on the catalyst amount in step 2.

4. Discharge the catalyst.

5. Calculate the amount of fines that is required to just fill all the bed voidage volume as:

$$\text{weight of fines required} = \text{bed void volume} * \text{fines bulk density}$$

6. Divide the amount of catalyst and fines into portions. The number of portions (i.e., amount of each portion) was found not to be critical. The user can choose a number of portions based on convenience (e.g., 5 to 10 cm catalyst bed length is packed at a time).

7. Load a portion of the catalyst to the reactor. Gently tap or vibrate the reactor until the catalyst bed settles. The duration of the vibrating or tapping period was found not to be critical. A few minutes is adequate.

8. Load a portion of fines to the reactor. Vibrate or tap the bed gently, which qualitatively means maintaining the original bed of catalyst as stable as possible while the fines migrate to fill its voids. Tapping/vibrating is continued until the top layer of the catalyst becomes visible. It is critical to detect this since when the tapping/vibrating period exceeded the time of the appearance of the catalyst layer at the top, segregation occurred. Therefore in case of a stainless steel tube that is frequently used in practice, a light source and/or optical fiber can be utilized to observe the bed surface.

9. Repeat steps 7 and 8 until the total amount of catalyst and fines are packed. It should be noted that tapping/vibrating of the next portion of catalyst and/or fines does not lead to segregation of the previously loaded portions (if tapping/vibrating is kept as qualitatively described in step 8). This is because the new portion of fines migrates to fill the voidage above the previous loaded mixture.

Note: The expansion in the bed height due to the addition of fines and tapping was found to be within 2%.

Whole-bed packing procedure

In a long stainless steel reactor with small inside diameter it is very difficult to observe the top surface of a short bed at the bottom with the help of a light source. Moreover, an optical fiber is not always available for this purpose. Therefore, another procedure of packing the whole bed is tested and recommended by Al-Dahhan et al. (1995). This seemed promising based on the finding of step 6 that the number of portions used are not critical. Such procedure overcomes the difficulties associated with monitoring the catalyst surface at the reactor bottom. In contrast, the catalyst surface at the upper part of the reactor can be easily observed. The step-by-step procedure is as follows:

1. Follow steps 1 to 5 of the procedure just outlined.

2. Load the amount of catalyst required portion by portion with associated tapping/vibrating. This is recommended to make the bed stable and reproducible.

3. Load all fines into the reactor. If there is not enough room to hold the total calculated amount of fines, load it portion by portion. Tap/vibrate until all the fines migrate into the bed and the top catalyst layer becomes visible.

Note: (1) On the basis of whether there is adequate room to accommodate fines at the top of the reactor, the catalyst bed can be loaded in two portions. The first portion is the major one that gives a suitable volume to load the fines into it and helps in observing easily the top of the catalyst surface. (2) The expansion in the bed height due to the addition of fines and tapping was found to be even less than that of the first procedure, but in both of the procedures, the expansion is within 2% (for example, in a 50-cm bed, the expansion obtained with the first procedure is about 1 cm while with the second procedure is about 0.7 cm).

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