

Determination of Wetting Efficiency in Trickle-Bed Reactors by a Reaction Method

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External wetting efficiencies were determined in a trickle-bed reactor by employing conversion data from the hydrogenation of the anthracene contained in an anthracene oil. Reactions were carried out at 573 K and 9.8 MPa on a sulfided Ni–Mo/ γ -Al₂O₃ catalyst. The results were compared with the total wetted area determined from the correlations based on the tracer method and developed by other authors. The discrepancy between both sets of data was attributed to the existence of a certain surface wetted by stagnant fluid whose fraction, f_s , was estimated from the comparison between tracer and reaction data. The correlations of Ring and Missen (1991) and Al-Dahhan and Dudukovic (1995), developed for high pressure trickle-beds, were employed to estimate f_s . A geometrical model has been employed to relate the static holdup with the fraction of surface covered by stagnant liquid which yielded an estimation of the mean distance between particles. The product of effectiveness factor and intrinsic rate constant were obtained for liquid- and gas-covered surfaces. Individual and overall effectiveness factors were estimated from a liquid phase intrinsic kinetic constant obtained in a previous work, showing that reaction took place preferably on the wetted surface.

Introduction

In trickle-bed reactors operating at low liquid mass velocity, part of the catalyst surface is covered by liquid and part by gas. The liquid phase flows downward through the reactor generally concurrently with a gas phase that partly consists of vaporized compounds introduced with the feed or formed during the reaction. An essential characteristic of a trickle-bed reactor is that the external catalyst surface is not completely wetted except for high liquid flow rates. With respect to the internal surface, however, it has been stated that due to capillarity, the pore filling of catalyst pellets is practically complete even at low liquid flow rates (Schwartz et al., 1976; Colombo et al., 1976; Herskowitz et al., 1979). This should be true at least when a reasonable distribution of the liquid fraction is achieved; most authors agreeing with this assumption (Tan and Smith, 1980; Mills and Dudukovic, 1981, 1982; Goto et al., 1981). Dudukovic (1977) also considered the existence of internal dry zones, but the calculation involved an estimation of the fractional pore fill-up. The limiting reactant may be present only in the liquid phase, and in this case the reaction takes place on the wetted part of the catalyst. On the other hand, when the vapor pressure of the reactant is appreciable in reaction conditions, the limiting reactant may also reach the active centers on the catalyst through the dry surface. In the latter case, it was frequently observed that the reaction rate and the wetting efficiency followed the opposite trend. The reason for this behavior is the additional mass transfer resistance introduced by the liquid phase. Harold and Ng (1987) presented a model combining gas and liquid phase resistance. For the reaction between a volatile and a nonvolatile compound, they found a transition controlled by the depletion of the nonvolatile reactant. For volatile reactants, a contacting efficiency interpreted as external wetting

efficiency should directly relate to the reaction rate (Herskowitz and Smith, 1983).

Two principal methods have been employed for measuring the external wetting efficiency: a tracer method developed from the works of Schwartz et al. (1976) and Colombo et al. (1976) and a reaction method proposed by Morita and Smith (1978). In most cases, an acceptable agreement was found between both sets of data, though some discrepancies have been detected for low liquid Reynolds numbers (Mata and Smith, 1981; El-Hisnawi et al., 1982; Herskowitz and Mosseri, 1983). Comparisons must be handled with care because trickle-bed reactions are normally carried out at high pressure. On the other hand, Lakota and Levec (1990) determined wetting efficiencies by means of solid–liquid mass transfer coefficients obtained from the dissolution of a slightly soluble solid in water following a procedure previously described by Specchia and Baldi (1978). In the present work, wetting reaction data were obtained for the hydrogenation of anthracene, and these data were compared with the predictions of correlations developed by means of pulse-tracer data by other authors.

At high pressure and high gas flow rate, both the increase in gas density and the increase in superficial gas velocity lead to an increase in the pressure gradient. Even for moderate gas flow rates, an elevation of pressure causes an increase in gas density and therefore a higher pressure drop due to the increase in drag forces (Larachi et al., 1991, 1994). Liquid holdup has been reported to decrease as pressure drop increases associated with the higher gas–liquid shear stress (Al-Dahhan et al., 1994). For the same reason the wetting efficiency and the gas–liquid interfacial area significantly increase, especially for higher liquid flow rates (Larachi et al., 1992; Wammes et al., 1991a,b; Al-Dahhan et al., 1995). It has also been shown that at high pressure the transition from trickle-flow regime to pulse flow regime shifts toward higher gas and liquid loads making the trickle flow operating region wider (Wammes and Westerterp, 1990; Wammes et al., 1990, 1991a). Wammes et al. (1991a) and Larachi et al. (1991,

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1994) determined the pressure gradient in the bed by correlating a dimensionless friction factor to the liquid phase Reynolds number. Holub et al. (1992, 1993) developed a phenomenological model for estimating pressure drop based on the Ergun equation. Although Holub et al.'s model was initially stated for atmospheric trickle-beds, Al-Dahhan and Dudukovic (1994) experimentally found that it is also valid for predicting pressure drop at high pressure.

The effect of high pressure on the dynamic holdup has also been investigated by Wammes et al. (1991b) and Larachi et al. (1991). They reported that the liquid holdup decreases when the pressure increases at constant gas and liquid superficial velocities. Recently, Al-Dahhan and Dudukovic (1994, 1995) employed the draining method to determine the liquid holdup in high-pressure trickle-bed operation. Their results were described in the form of several limiting cases according to Holub et al.'s model. The static holdup was measured as residual holdup by van Swaaij et al. (1969) by weighing the liquid that remained in a wet packing after draining for 10 min. They found that the static holdup was not affected by the reactor pressure but depended only on the liquid density included in the Eötvös number and proposed that at a low Eötvös number the residual holdup is limited by a value given by $\epsilon\beta_{\text{res}} = 0.05$, where ϵ is the porosity of the packed bed. This limit has also been accepted by Wammes et al. (1991c). Sáez et al. (1991) also measured the liquid that remained after a draining period and obtained a similar equation for determining the static holdup. They performed experiments at Eötvös numbers as low as $E\ddot{o} = 0.03$ and proposed $\epsilon\beta_{\text{res}} = 0.11$ as the limiting value when gravitational effects become negligible. Al-Dahhan and Dudukovic (1994) have also found that static holdup is not affected by reactor pressure.

The variables employed by Specchia and Baldi (1977) and Wammes et al. (1991a) to calculate dynamic or free-draining holdup were also used by Mills and Dudukovic (1981, 1982) and El-Hisnawi et al. (1982) to correlate the external wetting efficiency in trickle-bed reactors. They employed atmospheric tracer data to evaluate contacting efficiencies by assuming that the latter were directly measured by the square root of the ratio between the effective diffusivity of a tracer in two-phase flow and the same at liquid-full operation. Baldi (1980) and Sicardi et al. (1980) considered that the square root gives a better estimation of the effectively wetted surface than the ratio of the mentioned diffusivities previously employed by Colombo et al. (1976). For trickle beds operating at high pressure, it has been pointed out that the increase in pressure gradient leads to an increased gas-liquid interfacial drag and therefore causes an increase in the catalyst wetting efficiency (Al-Dahhan and Dudukovic, 1995). Ring and Missen (1991) found that the measured wetting efficiency for high-pressure trickle beds lay significantly below the values given by correlations developed from atmospheric data. Ring and Missen (1991) employed tracer data obtained at 10 MPa to correlate wetting efficiency with linear liquid velocity. Al-Dahhan and Dudukovic (1995), also employing tracer techniques, developed a model-based correlation that relates wetting efficiency to liquid phase Reynolds and Galileo numbers and the dimensionless pressure gradient ($\Delta P/\rho_L gZ$). The method based on catalytic liquid-solid chemical reactions has been less frequently employed than the aforementioned pulse-tracer technique to determine wetting efficiencies.

However it has been recognized that it has several clear advantages over the tracer method (Herskowitz and Smith, 1983). A proper formulation of this method requires an adequate reactor model, the main difficulty of which lies in axial dispersion. The classical approach to the axial dispersion phenomena in trickle-bed reactors was established by Mears (1971). He proposed a criterion to obtain a conservative estimation of the minimum reactor length above which the deviations from plug flow could be neglected. A much less stringent but very similar criterion was previously proposed by Petersen (1965). The method required an estimation of the Bodenstein number that has often been performed by the correlation of Hochman and Effron (1969). It has been noted that this correlation underestimates the effect of viscosity on the Bodenstein number and unsatisfactorily predicts the influence of particle diameter. These restrictions have been overcome by correlating the Bodenstein number with Re_L/Ga_L , a dimensionless group directly arising from the dimensionless Navier-Stokes equation (Herskowitz and Smith, 1983; Stegeman et al., 1996).

The purpose of this work was to determine the external wetting efficiency in a trickle bed by analyzing conversion data from the hydrogenation of the anthracene contained in a light fraction of anthracene oil. It was assumed that a part of the catalyst surface did not participate in the chemical reaction, most probably the fraction that corresponded to the surface covered by stagnant liquid. Wetting data obtained in this way were compared with those from the correlations based on tracer data. The derivation of the overall effectiveness factor was also discussed. The next section describes in some detail the theoretical background of the method as employed in this work.

Theoretical Considerations on the Reaction Method

Sedriks and Kenney (1973), and thereafter a number of authors, proposed that the reaction rate could be obtained as a function of the fraction of the catalyst surface that is effectively wetted. For a second-order irreversible reaction, the rate expression may be written as follows:

$$r = f(\eta k)_L C_{A,L} C_{B,L} + (1 - f(\eta k)_G C_{A,G} C_{B,G} \quad (1)$$

With substitution of the generic reactants the global reaction rate becomes

$$r = f_c(\eta k)_L C_{\text{ANT},L} C_{\text{HYD},L} + (1 - f_c)(\eta k)_G C_{\text{ANT},G} C_{\text{HYD},G} \quad (2)$$

In this expression, external wetting was represented as f_c to indicate that it was obtained from chemical conversion instead of tracer data (f_{td}). In what follows, axial dispersion for the dynamic liquid phase is neglected, an assumption whose adequacy is discussed below. Also considering that the wetting efficiency remains constant throughout the reactor, a mass balance leads to

$$W = \int_0^{x_{\text{ANT},f}} \frac{N_{\text{ANT},0} dx}{f_c(\eta k)_L C_{\text{ANT},L} C_{\text{HYD},L} + (1 - f_c)(\eta k)_G C_{\text{ANT},G} C_{\text{HYD},G}} \quad (3)$$

Anthracene was the limiting reactant and therefore $N_{\text{ANT}} = N_{\text{ANT},\text{O}}(1 - x)$. If the reaction is performed in the absence of a liquid phase ($f = 0$), the product of the intrinsic rate constant and the effectiveness factor for the gas phase $(\eta k)_G$ may be determined from conversion data as follows:

$$(\eta k)_G = \frac{1}{W} \int_0^{x_{\text{ANT},f}} \frac{N_{\text{ANT},\text{O}} dx}{C_{\text{ANT},G} C_{\text{HYD},G}} \quad (4)$$

On the other hand, if an experiment could be performed so that a complete liquid coverage of the catalyst surface ($f = 1$) is ensured, the following expression may be employed to determine $(\eta k)_L$:

$$(\eta k)_L = \frac{1}{W} \int_0^{x_{\text{ANT},f}} \frac{N_{\text{ANT},\text{O}} dx}{C_{\text{ANT},L} C_{\text{HYD},L}} \quad (5)$$

Ruecker and Akgerman (1987) stated that by taking $(\eta k)_G$ and $(\eta k)_L$ as determined by the preceding equations, wetting efficiencies may be calculated by means of eq 3. This procedure was employed by Huang and Kang (1995) for the hydrogenation of naphthalene and by Ruecker and Akgerman (1987) for the hydrogenation of biphenyl. However, two important assumptions underlie the preceding equations:

1. The entire wetted surface is assumed to be uniform even though a part of the catalyst is wetted by stagnant liquid with low liquid renewal. Effective external wetting is in general different from physical external wetting due to the presence of zones that contribute very little to mass transfer (Sicardi et al., 1980).

2. It has been stated before that internal wetting, defined as the fraction of intraparticle volume filled with liquid, is considered to be complete due to capillarity. A violation of this assumption means that η_G also depends on the fraction of internal volume wetted as noted by Dudukovic (1977).

The concentration of hydrogen in both the liquid and gas phases may be expressed as a function of the inlet molar flow rate of hydrogen, $N_{\text{HYD},\text{O}}$, the vapor to feed molar ratio, λ , the vapor-liquid equilibrium relationship, Π_{HYD} , and the superficial liquid and gas velocities at reaction conditions as indicated thereafter. The number of moles of hydrogen in the gas per mole of hydrogen in the liquid can be obtained from the mentioned variables as $\Pi_{\text{HYD}}\lambda(1 - \lambda)^{-1}$. From this, the quotient between the moles of hydrogen in the gas phase and the total number of moles of hydrogen in the system is $1 + (1 - \lambda)(\Pi_{\text{HYD}}\lambda)^{-1}$. If one multiplies this result by the inlet molar flow rate of hydrogen and divides by the volumetric flow of gas at reaction conditions, the concentration of hydrogen in the gas phase is given by

$$C_{\text{HYD},G} = \frac{4N_{\text{HYD},\text{O}}}{\pi v_G d_T^2 \epsilon} \left[\frac{1 + \lambda(\Pi_{\text{HYD}} - 1)}{\lambda \Pi_{\text{HYD}}} \right] \quad (6)$$

Similarly, the following expression for the concentration of hydrogen in the liquid phase may be obtained:

$$C_{\text{HYD},L} = \frac{4N_{\text{HYD},\text{O}}}{\pi v_L d_T^2 \epsilon} \left[\frac{1 + \lambda}{1 + \lambda(\Pi_{\text{HYD}} - 1)} \right] \quad (7)$$

The concentration of anthracene has been expressed as a function of α_{ANT} . This parameter was defined as the liquid mole fraction of anthracene divided by the total

Table 1. Characteristics of the Catalyst Employed

Chemical Composition (wt %)	
NiO	2.8
MoO ₃	13.5
Na ₂ O	0.04
Physical Characteristics	
surface area, BET, m ² /g	171
pore volume less than 1460 Å, cm ³ /g	0.48
pore volume BJH ads. 17 to 3000 Å, cm ³ /g	0.49
mean pore diameter, Å	110
catalyst particle diameter, μm	360–500
shape approx spherical	

Table 2. Composition of the Anthracene Oil (wt %)

naphthalene	3.2
acenaphthene	5.5
dibenzofuran	3.1
fluorene	6.2
9,10-dihydroanthracene	0.9
phenanthrene	17.7
anthracene	6.0
carbazole	5.5
fluoranthene	11.2
pyrene	9.0

mole fraction of anthracene and is a function of the vapor to feed molar ratio and Π_{ANT} :

$$\alpha_{\text{ANT}} = \frac{1}{1 - \lambda(1 - \Pi_{\text{ANT}})} \quad (8)$$

$$C_{\text{ANT},G} = \frac{4\lambda\Pi_{\text{ANT}}\alpha_{\text{ANT}}N_{\text{ANT},\text{O}}(1 - x_{\text{ANT}})}{\pi v_G d_T^2 \epsilon} \quad (9)$$

$$C_{\text{ANT},L} = \frac{4(1 - \lambda)\alpha_{\text{ANT}}N_{\text{ANT},\text{O}}(1 - x_{\text{ANT}})}{\pi v_L d_T^2 \epsilon} \quad (10)$$

Experimental Section

Catalysts and Reactants. The catalyst was a commercial Shell NiO-MoO₃ on γ -alumina supplied as $1/16$ in. extrudates crushed and sieved to 360–500 μm particles. The characteristics of the catalyst in the oxidized form are given in Table 1. Textural properties were determined by nitrogen adsorption methods employing a Micromeritics ASAP 2000 analyzer and following standard procedures.

The liquid feed for the hydrogenation runs consisted of 20 wt % of a light fraction of anthracene oil dissolved in toluene (purity >99.5%). Anthracene oil was supplied by NalonChem (Asturias, Spain), and its major identified components are given in Table 2. Further details are given in a previous paper (Rosal et al., 1992a).

Equipment and Reaction Experiments. The hydrogenation reactions were carried out in a cocurrent downflow high-pressure trickle-bed reactor. The experimental system used in this investigation is shown in Figure 1. The reactor was a stainless steel tube of 9 mm i.d. and 450 mm length placed inside an electrically heated furnace. Five thermocouples measured the temperature at different reactor heights. The temperature of the reaction zone, located in the center of the bed, was kept constant at the desired value. The hydrogen gas flow rate was controlled by a Brooks 5850TR/X-5879E mass flowmeter and controller. The liquid feed was supplied by a Kontron LC T-414 pump. The pressure inside the reactor line was maintained by a Tescom back-pressure regulator. The reactor effluent

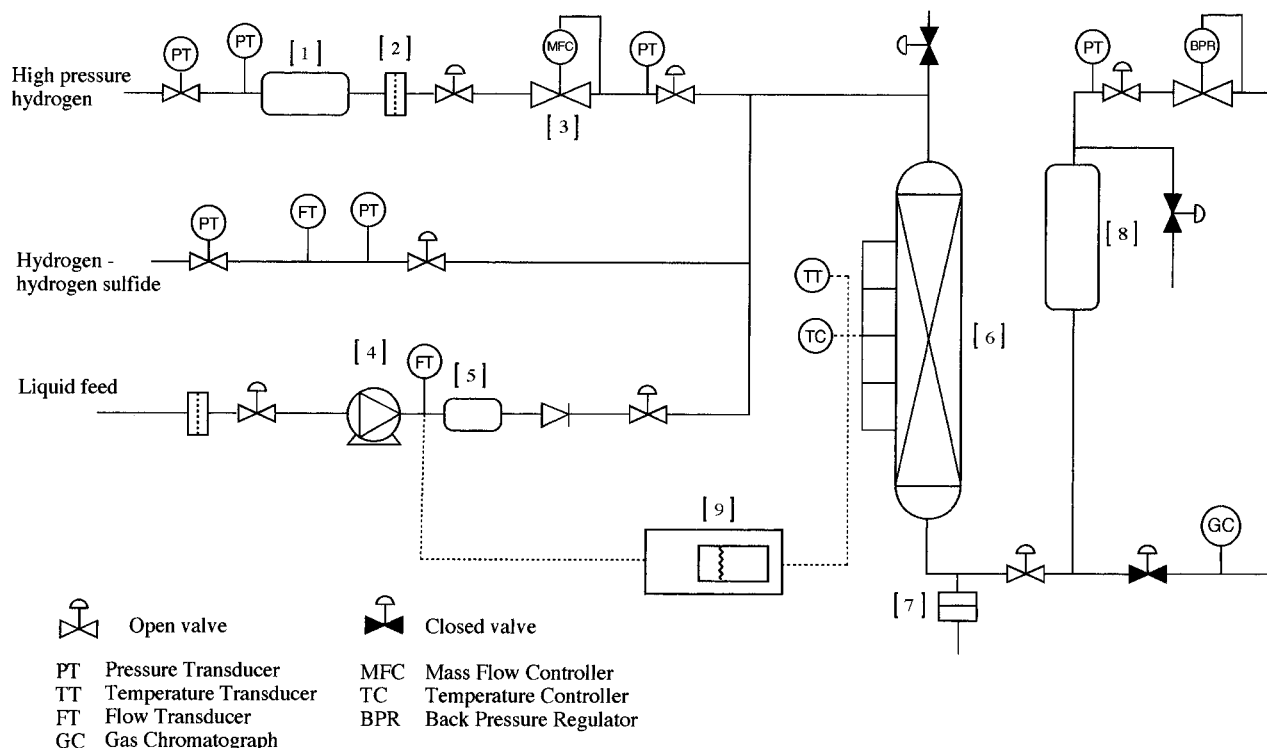


Figure 1. Flow diagram of the trickle-bed hydrogenation unit: (1) hydrogen buffer; (2) filter; (3) mass flowmeter and controller; (4) feed pump; (5) pulse damper; (6) reactor; (7) rupture disk; (8) gas-liquid separator; (9) graphic recorder.

flowed into a 1000 mL stainless steel cylinder acting as a gas liquid separator and a reservoir for liquid reaction product. A two-valve system allowed periodical withdrawal of liquid samples to the analytical equipment. The catalyst was sulfided in situ before use by passing a mixture of 10% of H_2S in H_2 at 673 K over it during 4 h at a flow of $30 \text{ cm}^3(\text{NTP})/\text{min}$. An additional 1 wt % CS_2 was added to the liquid mixture to maintain the catalyst in the sulfided form. A total amount of 2.4 g of catalyst was introduced in the central zone of the reactor diluted with low-area inert alumina (Jansen) of the same granulometry. The reactor was also filled with alumina both above and below the reaction zone, the length of which was 40 mm.

The hydrogenation reactions were carried out at 573 K and a total pressure of 9.8 MPa. The experiments were performed by varying the liquid flow rate and the hydrogen mass flow rate measured under laboratory conditions. The superficial mass velocities of liquid and gas at reaction pressure and temperature were calculated as indicated below and defined an experimental region given by the following limits of superficial mass flow rates: $0.0277 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1} < L < 1.91 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ and $0.0150 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1} < G < 0.819 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$. Figure 2 shows the range of Reynolds numbers experimentally covered in this work. The lines defining the boundaries of hydrodynamic flow regions were taken from the work of Fukushima and Kusaka (1977a,b) and are shown for reference. The Galileo number varied from 4.5×10^2 (low Re_L) $< Ga_L < 1.5 \times 10^4$ (high Re_L).

Analysis. Feed and liquid product samples were analyzed by gas chromatography in a Hewlett-Packard apparatus equipped with a 30 m long, 0.25 mm i.d. fused silica column with a $0.5 \mu\text{m}$ film thickness nonpolar stationary phase (SE-30). Peak assignment was performed by GC-MS in a Hewlett-Packard 5987A apparatus.

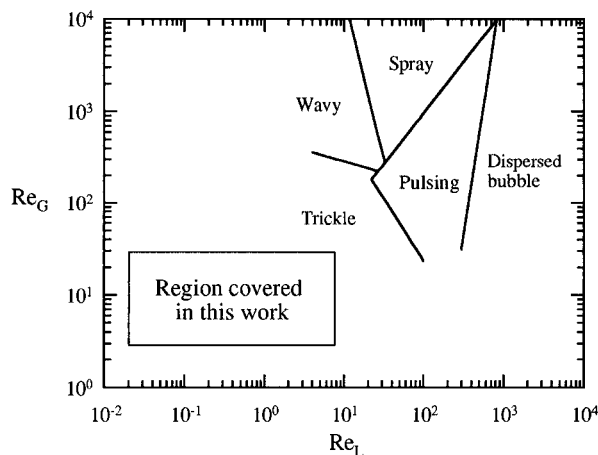


Figure 2. Experimental conditions covered by the data. The lines correspond to the boundaries proposed by Fukushima and Kusaka (1977a,b).

Results and Discussion

Density, viscosity, and thermal conductivity of both vapor and liquid phases were calculated under reaction conditions by employing a method based on the corresponding states principle. The reference component was methane, for which a state equation is available over a wide range of pressure and temperature. Gas-liquid surface tension was calculated by means of the Macleod-Sugden expression as recommended by Reid et al. (1977). Liquid and gas phase compositions and vapor to feed molar ratio were calculated by assuming that vapor-liquid equilibrium was established for each set of reaction conditions. The liquid-vapor equilibrium relationship (Π_L) was determined by the method of Grayson and Streed (1963), which is based on the correlation of Chao and Seader (1961). The vapor-to-feed molar ratio, λ , was defined as the ratio between the number of moles in the gas phase at equilibrium

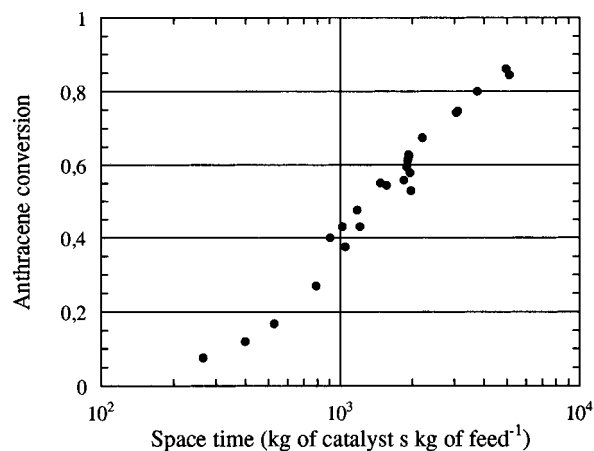
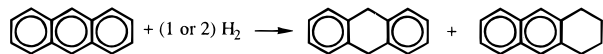
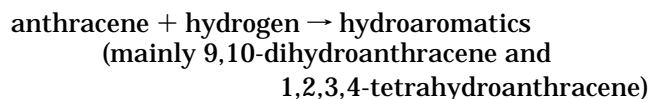


Figure 3. Anthracene conversion plotted vs space time (kg of catalyst · s · kg of feed⁻¹).

and the total number of moles at the reactor inlet. For low liquid velocities, an increase in vapor fraction was observed combined with an elevation of liquid density due to the vaporization of the lighter and more volatile components.

Under the reaction conditions at which the experiments were performed, the only component of the reaction mixture that was hydrogenated to a certain measurable degree was anthracene. It was previously reported that the reaction rate for the hydrogenation of anthracene is at least 1 order of magnitude greater than that of any other component of anthracene oil (Rosal et al., 1992b). Under the reaction conditions employed in this work, the hydrogenation of anthracene was essentially irreversible:



In the same work, Rosal et al. (1992b) determined that second-order kinetics adequately represent the hydrogenation of anthracene so that the global reaction rate may be effectively determined by means of eq 2. Figure 3 plots the conversion of anthracene as a function of space time expressed in kg of catalyst · s · kg of feed (liquid + gas)⁻¹. Anthracene conversion increased for increasing space time and, additionally, it showed a practically linear dependence with G_{A1}/Re_L . The correlation of Spechia and Baldi (1977) and other similar to it, show that dynamic holdup follows the same trend as Re_L/G_{A1} because the exponents of Re_L and G_{A1} are reported to be practically equal in absolute value. Therefore, anthracene conversion decreased following the opposite pattern to dynamic holdup.

Stegeman et al. (1996) showed that the Bodenstein number decreased with Re_L/G_{A1} until a lower limit of $Bo \approx 0.3$ was reached. Considering this lower limit and using Mears' criterion for the most adverse conditions, a minimum length for negligible dispersion was obtained that was very close to the effective length of the bed employed in this work ($L = 40$ mm). Consequently, deviations from plug flow have been neglected. The experimental data available for high vapor-to-feed molar ratio (i.e. at low liquid mass flow rate) were substituted in eqs 6–10, and the resulting concentrations of hydrogen and anthracene in expression 4. An extrapolation

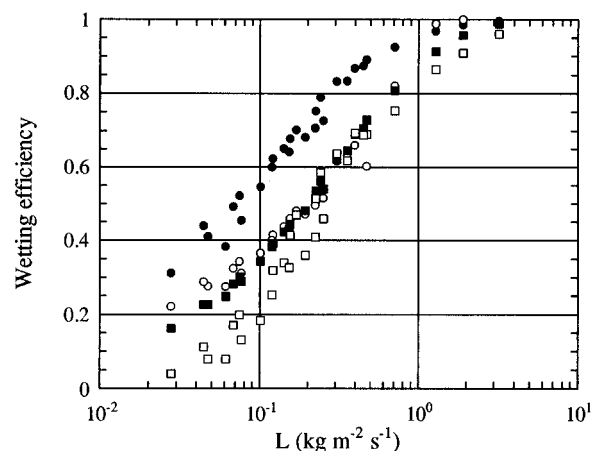


Figure 4. External wetting efficiencies derived from the correlations of Mills and Dudukovic (J), Ring and Missen (E), and Al-Dahhan and Dudukovic (B) and wetting efficiencies obtained in this work (G) by directly employing eq 3.

to $\lambda = 1$ provided a calculated value of $(\eta k)_G = 1.80 \times 10^{-1} \text{ L}^2 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \cdot \text{kg of catalyst}^{-1}$. In a similar manner, using data taken at the low vapor fraction (i.e. high liquid mass flow rate), the extrapolation of expression 5 to $\lambda = 0$ led to $(\eta k)_L = 1.48 \times 10^{-2} \text{ L}^2 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \cdot \text{kg of catalyst}^{-1}$. The substitution of these values in eq 3 with the concentrations given by eqs 6–10 permitted the calculation of f_c from the conversion of anthracene $x_{ANT,F}$. The calculations described above followed the usual pattern found in the literature (Ruecker and Akgerman, 1987; Huang and Kang, 1995). However, comparison with the available information obtained from tracer data revealed some discrepancies. Figure 4 plots the values of the external wetting efficiency obtained in this work from eq 2 and those calculated following the correlations of Mills and Dudukovic (1981), Ring and Missen (1991), and Al-Dahhan and Dudukovic (1995), all of which were obtained with the pulse-tracer method. The correlations of Ring and Missen (1991) and Al-Dahhan and Dudukovic (1995) yielded similar values, whereas that of Mills and Dudukovic (1981), like others developed for atmospheric trickle beds, such as El-Hisnawi et al. (1982), gave wetting efficiencies somewhat in excess. Under the experimental conditions employed in this work, the pressure drop was determined essentially by liquid mass velocity. The gas flow rate was low enough to neglect the effect of its variation on the pressure drop and therefore on wetting efficiency. For this reason, the experimental data, shown in Figure 4 as a function of superficial mass liquid velocity, show no dispersion even though they correspond to different gas flow rates. This behavior is in good agreement with theoretical predictions and has been observed before (Holub et al., 1992; Al-Dahhan and Dudukovic, 1994, 1995). The observed differences for low liquid flow were consistent with the findings of other authors who employed the reaction method (Mata and Smith, 1981; Herskowitz and Mosseri, 1983). A possible explanation for this may come from the assumption that the part of the catalyst surface wetted by stagnant liquid may be excluded from participating in the chemical reaction but is revealed as wetted in the tracer technique. Sicardi et al. (1980) showed that the values of the wetting efficiency obtained from the square root of the ratio of the effective diffusivities reveal the total wetted fraction of the packing area. Colombo et al. (1976) also pointed out that tracer-derived wetting efficiencies decreased with

increasing the molecular diffusivity of the tracer. The overall mass-transfer rate must be calculated considering the contribution of the rate through the static and the dynamic area. In general, mass transfer takes place in parallel between solid and stagnant or dynamic liquid and also between stagnant and dynamic liquid. Whereas for slow reactions the existence of stagnant liquid affect the global rate very little, for relatively high reaction rates, a considerable difference in reactant concentration should exist between the static and dynamic liquid phases. In such circumstances one might assume that the effective liquid–solid contacting area would be lower than the total wetted surface reflecting the fact that only the wetted surface covered by non stagnant fluid contributes to conversion. In fact, for relatively rapid reactions the contacting area could be identified with the surface wetted by the dynamic holdup. The total wetting efficiency, represented by f_{td} , and the unit fraction of effectively wetted surface introduced in eqs 1 and 2 and denoted by f_c , are related to f_s by means of the following expression:

$$f_{td} = f_c(1 - f_s) + f_s \quad (11)$$

Figure 5 plots the wetting efficiency f_{td} derived from the correlations proposed by Ring and Missen (1991) and Al-Dahhan and Dudukovic (1995) and from the conversion data obtained in this work and recalculated by means of eq 11 under the assumptions stated above. The value of f_s was calculated by minimizing the quadratic deviations between the wetting efficiencies obtained from anthracene conversion and those given by the indicated correlations: $\sum [f_c(1 - f_s) + f_s - f_{td(\text{calcd})}]^2$. The value obtained employing both Ring and Missen's and Al-Dahhan and Dudukovic's expressions was practically the same and their arithmetic mean, $f_s = 0.16$, was considered a good estimation of the unit fraction of surface that did not participate in the chemical reaction.

The chemical wetting involved in eqs 2 and 3 was calculated without considering the part of the catalyst surface wetted by stagnant liquid. For this reason, the expressions leading to the product of effectiveness factor and intrinsic rate constant for wetted and dry surfaces must be recalculated for them to have their usual meaning:

$$(\eta k)_L = \frac{1}{W(1 - f_s)} \int_0^{x_{A,f}} \frac{N_{AO} dx}{C_{A,L} C_{B,L}} \quad (12)$$

$$(\eta k)_G = \frac{1}{W(1 - f_s)} \int_0^{x_{A,f}} \frac{N_{AO} dx}{C_{A,G} C_{B,G}} \quad (13)$$

In accordance with these arguments, the following values were calculated by means of the preceding eqs: $(\eta k)_L = 1.8 \times 10^{-2} \text{ L}^2 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \cdot \text{kg of catalyst}^{-1}$ and $(\eta k)_G = 2.1 \times 10^{-1} \text{ L}^2 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \cdot \text{kg of catalyst}^{-1}$. The difference with the values obtained previously revealed the importance of carefully determining the chemically active surface so as to obtain reliable kinetic measurements from trickle-bed data. Only a fraction of the outer surface is covered by liquid, and therefore unsymmetrical concentration profiles exist inside the particle (Morita and Smith, 1978). It has been stated that if the limiting reactant is present in both phases, the reaction rate on the gas-covered surface should be greater than that on the wetted surface (Ring and Missen, 1986). The reason is that the mass transfer resistance between the gas and the liquid existing inside

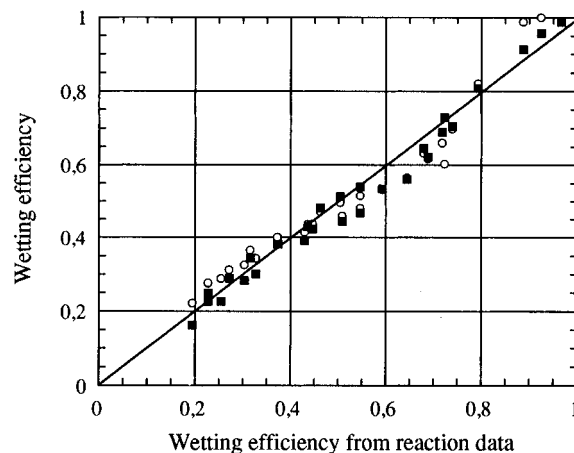


Figure 5. External wetting efficiencies obtained from Ring and Missen (J) and Al-Dahhan and Dudukovic (E) compared with those obtained in this work and recalculated with eq 11 ($f_s = 0.16$ as indicated in the text).

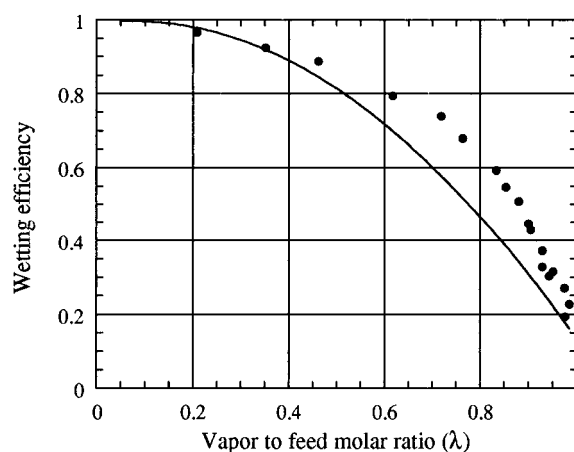


Figure 6. Wetting efficiencies calculated from anthracene reaction data and eq 12 as a function of vapor to feed molar ratio (λ). The solid line corresponds to the values obtained from the correlation proposed by Ruecker and Akgerman (1987): $0.24 \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1} < L < 1.91 \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, $0.25 \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1} < G < 0.62 \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, and $15 < \Delta P / \rho_L g L < 50$.

the pores of the catalyst is lower than that between bulk and pore liquid. If so, the effectiveness factor for the gas-covered surface should be greater than that for the wetted part of the catalyst. Ramachandran and Smith (1979) proposed an expression for the effectiveness factor in partially wetted particles assuming complete internal wetting:

$$\eta_{TB} = f\eta_L + (1 - f)\eta_G \quad (14)$$

In the present work, it has been assumed that even for experiments performed at the lowest liquid coverage, a stagnant holdup existed that resulted in a constant fraction of unreactive surface. In the case of runs performed at high vapor fractions, it could have been assumed that no stagnant liquid holdup existed, in which case eq 4 would yield overestimated values for the gas side rate constant. The wetting efficiency (f_{td}) was clearly related to the vapor fraction under reaction conditions. Wetting increased sharply as the vapor fraction decreased and a practically total wetting was attained for values of λ lower than 0.2. Figure 6 plots the results obtained in this work for $8 < \text{Re}_G < 20$. The same figure also plots the wetting efficiency calculated from the correlation of Ruecker and Akgerman (1987)

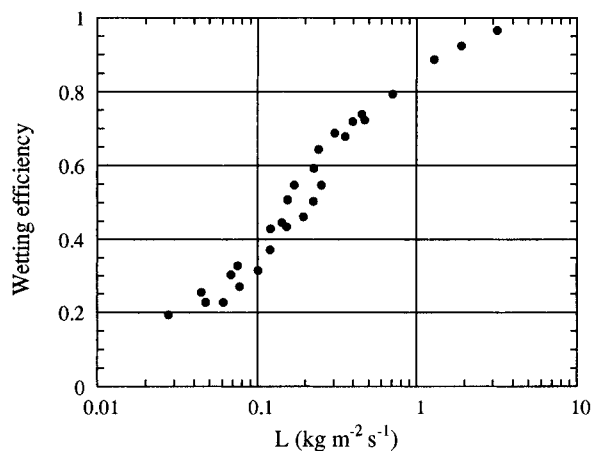


Figure 7. Wetting efficiencies calculated from anthracene reaction data as a function of superficial liquid mass flow rate L : $0.015 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1} < G < 0.819 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ and $1.5 < \Delta P/\rho_L gL < 90$.

modified by the assumption that a surface fraction of $f_s = 0.16$ was not reactive. The comparison shows that for increasing liquid superficial velocity, a sharper increase in wetting efficiency was obtained in this work with regard to the conditions tested by Ruecker and Akgerman (1991). Though no information is given on pressure drop in the work of Ruecker and Akgerman (1991), the reason for the difference could be attributed to the higher values of the dimensionless pressure gradient, in the range of $15 < (\Delta P/\rho_L gL) < 50$ in the present work, excluding some extreme values. The results presented here showed that total wetting of the 0.43 mm particles was achieved for a superficial liquid mass velocity slightly above $1 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$. This result is in good agreement with those reported by other authors. Mills and Dudukovic (1981, 1982) and Al-Dahhan and Dudukovic (1995) also found that superficial liquid mass velocities in the range of $1\text{--}10 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ were necessary to completely wet catalyst particles of similar sizes. Figure 7 plots the total external wetting efficiency (f_{td}) based on anthracene conversion for the different superficial liquid mass velocities employed in this work.

In order to employ eq 14 to calculate the overall effectiveness factor values for the intrinsic rate constant must first be obtained. A liquid phase kinetic study performed by Rosal et al. (1992b) with the same feed and a very similar nickel–molybdenum catalyst might yield an estimation of k_L . These authors hydrogenated anthracene oil in a batch liquid phase reactor with experimental conditions in the range 563–623 K and 9.4–13.6 MPa, which included those employed in this work. The reaction rate for 573 K and 9.8 MPa was $k_L = 0.052 \text{ L}^2\cdot\text{mol}^{-1}\cdot\text{s}^{-1}\cdot\text{kg}$ of catalyst $^{-1}$. The kinetic constant k_G may be rewritten by introducing Henry's law constants to give $k_L = k_G H_{\text{ANT}} H_{\text{HYD}}$. Henry's law constants can be calculated from equilibrium data as mentioned above. Figure 8 shows the calculated overall effectiveness factor as a function of external wetting efficiency (f_{td}). The effectiveness factor increased with liquid coverage as expected if the reaction took place only or preferably in the liquid phase (Sakornwimon and Sylvester, 1982). The value of $\eta_{\text{TB}} = 0.3$ is in good agreement with those encountered by several authors in hydrodesulfurization reactions (Yentekakis and Vayenas, 1987; Ring and Missen, 1989). The effectiveness factors for the gas covered surface were in the range $0.05 < \eta_G < 0.21$. For relatively high wetting efficiencies, the reaction behaved as if anthracene was non-

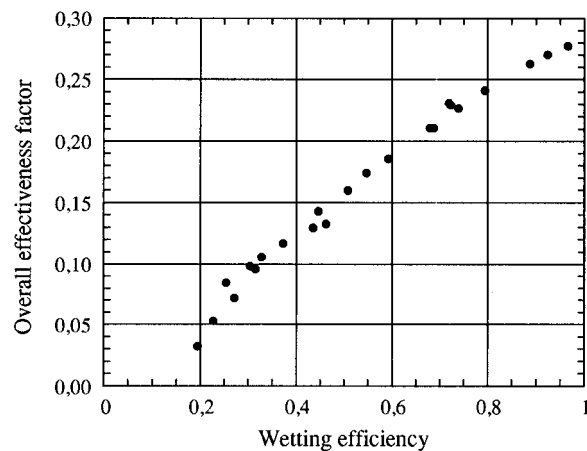


Figure 8. Dependence of the overall effectiveness factor (η_{TB}) on wetting efficiency.

volatile and was confined to the liquid phase. However, for high gas flow rates, the amount of anthracene that reacted on the part of the catalyst externally covered by gas was not negligible.

Sicardi et al. (1980) presented a geometrical model to calculate the fraction of surface wetted by static holdup, f_s . The packing was considered to be adequately represented by a regular array of equal spheres with a number n of contact points where stagnant liquid accumulates. It was assumed that still liquid is encountered wherever two spheres are physically in contact and that stagnant zones do not overlap. This model, in the light of the values of static holdup obtained by Sáez et al. (1991) at low Eötvös numbers, yield very high values for f_s . A more realistic approach may be that of considering that the bed can be represented by a random packing of equal spheres in which a given particle is characterized by a mean number of total contacts, n_t , and a number, n_c , of close contacts, the difference, $n_t - n_c$, being near contacts (Bernal and Mason, 1960). If the meniscus curvature is neglected, these ideas may be integrated to determine a relationship between the static holdup, β_s , the unit fraction of surface wetted by stagnant liquid, f_s , the total number of contacts, n_t , and the mean distance between particle centers, denoted as d_{pc} :

$$\beta_s = \frac{n_t(1 - \epsilon)}{\epsilon} \left[\frac{3f_s^2}{n_t^2} - \frac{4f_s^3}{n_t^3} + 6 \left(\frac{d_{\text{pc}}}{d_p} - 1 \right) \left(\frac{f_s}{n_t} - \frac{f_s^2}{n_t^2} \right) \right] \quad (15)$$

Haughey and Beveridge (1966) evaluated the total number of contacts as $n_t = 7.1$ for random packings of equal (or narrow size distributed) spheres. In this case, d_{pc} is determined only by bed characteristics. Therefore, the stagnant holdup would cover a surface whose limit for a low Eötvös number should be constant irrespective of other variables. In the present work, the experiments were performed at Eötvös numbers in the range $0.14 < \text{Eö} < 0.50$, low enough to assume that static holdup reached its maximum value. All the particles surrounding a given one would be connected by stagnant liquid. From eq 11, employing the limit for stagnant holdup proposed by Sáez et al. (1991), a value of $d_{\text{pc}} = 1.14d_p$ was obtained. With this value, some additional information about bed structure may be obtained. If the bed is homogeneous and the particles are randomly distributed, the mean space between particles is usually transformed so as to be expressed as a packing parameter ζ defined as

$$\zeta = \sqrt{1 - \epsilon} \left(1 - \frac{d_{pc} - d_p}{d_p} \right) \quad (16)$$

This parameter represents the space available for flow and can be related to the pressure drop across the bed. From this work, an estimation of $\zeta = 0.96$ was obtained upon substitution in eq 16. Pressure drop measurements in fixed beds also permitted an accurate determination of the bed structure that led to the value of $\zeta = 0.95$ (Molerus, 1993).

Conclusions

The partial external wetting of the catalyst particles in a trickle bed was studied by employing the chemical reaction method. The external surface was considered to consist of a dynamic and a static or stagnant area. The latter has been viewed as a consequence of the accumulation of a part of the liquid at the points of contact between bed particles. A geometrical model has been proposed on the basis of the work of Sicardi et al. (1980), to reconcile the observed discrepancies between wetting efficiencies from the chemical reaction method and from pulse-tracer data. For low Eötvös numbers, the stagnant holdup reached a constant value determined by bed characteristics. Assuming that the accumulation of liquid takes place only at the contact points between bed particles, a simple relationship has been established between β_s and f_s by means of a parameter d_{pc} that represents the mean distance between particles. In this work, a value of $d_{pc} = 1.14d_p$ was obtained in good agreement with measurements of packing geometry from pressure drop data in beds of equal spheres. Irrespective of the complex phenomena involved in high-pressure trickle-bed operation, wetting efficiency determined from tracer data, chemical reaction data and basic knowledge about the structure of random beds yielded a consistent picture.

Some correlations were obtained during recent years for high-pressure trickle beds under conditions not very different from those used in this work. They permitted the calculation of the total external wetting efficiency as a function of operating condition parameters provided that the pressure drop can be measured or predicted. The activity of the surface covered by nonrenewable liquid should considerably decrease, and therefore the chemical wetting should be lower than that calculated from the mentioned correlations. The system studied in this work behaved as if a fraction of the external surface, $f_s = 0.16$, was not available for chemical reaction. With this assumption, a good agreement between the data presented here and the correlations of Ring and Missen (1991) and Al-Dahhan and Dudukovic (1995) was achieved. The consistency of this result suggests that a combination of pulse-tracer correlations and some insight into bed structure may allow a reasonable prediction of conversions in trickle-bed reactors.

The part of the surface excluded from chemical conversion must be taken into account to allow the calculated values of $(\eta k)_{L/G}$ to have their common meaning. This introduced an additional factor in the derivation of the product of effectiveness factor and kinetic constant not considered in other works that have employed the chemical reaction method. Anthracene and hydrogen distribute between liquid- and gas-covered regions of the catalyst in a way that could be calculated by means of their equilibrium relationships.

Experimental values for $(\eta k)_L$ and $(\eta k)_G$ have been proposed based on the assumption that vapor-liquid equilibrium relationships, Π_s , and the value of wetting efficiency remained constant throughout the reactor. The conversion data obtained in this work indicated that the hydrogenation of anthracene took place preferably on the wetted surface. Though intrinsic kinetic constants were not determined, an estimation has been adopted from a previously published work that allowed the effectiveness factors to be calculated. The overall effectiveness factor increased with liquid coverage up to a value of $\eta_{TB} = 0.29$ for f_{id} near unity. The low values obtained for η_G were most probably due to the low volatility of anthracene ($\Pi_{ANT} < 0.05$). However, they might also be explained by incomplete internal liquid pore filling associated with a negligible gas-solid reaction. Finally, interface temperature differences were determined as indicated by Herskowitz and Smith (1983). Even for the highest conversion obtained, the temperature increase was less than 1.5 K, and an additional vaporization of the liquid in contact with catalyst surface could be excluded.

Acknowledgment

This work was supported by the Foundation for the Support of Research in Applied Science and Technology (FICYT), the Science and Technology Division of the Ministry of Education of Spain (CICYT), and Industrial Química del Nalón (NalonChem), Asturias, Spain. The authors also wish to thank Dr. Rufino García for his help in this research.

Nomenclature

- $C_{A,G}$ = gas phase concentration of reactant A, mol·L⁻¹
- $C_{A,L}$ = liquid phase concentration of reactant A, mol·L⁻¹
- d_p = particle diameter, m
- d_{pc} = mean distance between particles, m
- d_r = reactor diameter, m
- $Eö = \rho_L g d_p^2 / \sigma_L$, Eötvös number
- f = wetting efficiency, dimensionless
- f_c = wetting efficiency obtained from conversion data, dimensionless
- f_s = unit fraction of surface covered by stagnant fluid, dimensionless
- f_{id} = wetting efficiency obtained from tracer data, dimensionless
- g = acceleration of gravity, m·s⁻²
- G = superficial gaseous mass flow rate, kg·m⁻²·s⁻¹
- $Ga_L = \rho_L^2 g d_p^3 / \mu_L^2$, Galileo number of the liquid phase
- H_A = Henry's law constant for species A, dimensionless
- k_L, k_G = kinetic rate constant for a catalyst which external surface is covered by liquid and gas, L²·mol⁻¹·s⁻¹·kg of catalyst⁻¹
- L = superficial liquid mass flow rate, kg·m⁻²·s⁻¹
- n = number of contact points between particles in the packing
- n_t, n_c = number of total and close contacts between particles in the packing
- N_A = molar flow rate of reactant A, mol·s⁻¹
- $N_{A,o}$ = inlet molar flow rate of reactant A, mol·s⁻¹
- $P, \Delta P$ = pressure and pressure gradient, Pa
- r = reaction rate, mol·s⁻¹·kg of catalyst⁻¹
- $Re_L = \rho_L v_L d_p / \mu_L$, Reynolds number of the liquid phase
- $Re_G = \rho_G v_G d_p / \mu_G$, Reynolds number of the gas phase
- v_L = liquid phase superficial velocity (based on the empty cross section of the reactor), m·s⁻¹
- v_G = gas phase superficial velocity (based on the empty cross section of the reactor), m·s⁻¹
- W = weight of catalyst, kg

x, x_f = conversion and conversion at the reactor outlet, dimensionless

Z = length of the packed bed, m

Greek Letters

α_A = liquid mole fraction of A divided by the total mole fraction of A, dimensionless

β_{res} = residual liquid holdup unit fraction of the empty space, m^3 of liquid $\cdot m^{-3}$ of void

ζ = packing parameter defined in eq 16

ϵ = overall porosity of the packed bed, m^3 of free space $\cdot m^{-3}$ of reactor

η_L, η_G = effectiveness factor for the liquid- and gas-covered external surface of the catalyst

λ = vapor to feed molar ratio, dimensionless

μ_L, μ_G = dynamic viscosity of liquid and gas phase, $kg \cdot m^{-1} \cdot s^{-1}$

$\Pi_A = y_A/x_A$, vapor-liquid equilibrium relationship for compound A

ρ_L, ρ_G = liquid and gas density, $kg \cdot m^{-3}$

σ_L = gas-liquid surface tension, $N \cdot m^{-1}$

Subscripts and Superscripts

A, B = reactants

ANT = anthracene

HYD = hydrogen

TB = trickle bed

Literature Cited

- Al-Dahhan, M.; Dudukovic, M. P. Pressure Drop and Liquid Holdup in High Pressure Trickle-Bed Reactors. *Chem. Eng. Sci.* **1994**, *49*, 5681.
- Al-Dahhan, M.; Dudukovic, M. P. Catalyst Wetting Efficiency in Trickle-Bed Reactors at High Pressure. *Chem. Eng. Sci.* **1995**, *50*, 2377.
- Baldi, G. Design and Scale-up of Trickle-Bed Reactors. Solid-Liquid Contacting Effectiveness. In *Multiphase Chemical Reactors. Vol. II: Design Methods* Rodrigues, A. E., Calo, J. M., and Sweed, N. M., Eds.; NATO Advanced Study Institute Series E52; Sijthoff and Noordhoff: Alphen aan den Rijn, The Netherlands, 1980; pp 323-341.
- Bernal, J. D.; Mason, J. Coordination of Randomly Packed Spheres. *Nature*, **1960**, *188*, 910.
- Chao, K. C.; Seader, J. D. A General Correlation of Vapor-Liquid Equilibria in Hydrocarbon Mixtures. *AIChE J.* **1961**, *7*, 598.
- Colombo, A. J.; Baldi, G.; Sicardi, S. Solid-Liquid Contacting Effectiveness in Trickle-Bed Reactors. *Chem. Eng. Sci.* **1976**, *31*, 1101.
- Dudukovic, M. P. Catalyst Effectiveness Factor and contacting Efficiency in Trickle-Bed Reactors. *AIChE J.* **1977**, *23*, 940.
- El-Hisnavi, A. A.; Dudukovic, M. P.; Mills, P. L. Trickle-Bed Reactors: Dynamic Tracer Tests, Reaction Studies and Modelling of Reactor Performance. *ACS Symp. Ser.* **1982**, *No. 196*, 431.
- Fukushima, S.; Kusaka, K. Interfacial Area and Boundary of Hydrodynamic Flow Region in Packed Column with Cocurrent Downward Flow. *J. Chem. Eng. Jpn.* **1977**, *10*, 461.
- Fukushima, S.; Kusaka, K. Liquid-Phase Volumetric and Mass-Transfer Coefficient, and Boundary of Hydrodynamic Flow Region in Packed Column with Cocurrent Downward Flow. *J. Chem. Eng. Jpn.* **1977**, *10*, 468.
- Goto, S.; Lakota, A.; Levec, J. Effectiveness Factors of n^{th} Order Kinetics in Trickle-Bed Reactors. *Chem. Eng. Sci.* **1981**, *36*, 157.
- Grayson, H. G.; Streed, C. W. Vapor-Liquid Equilibria for High Temperature, High Pressure Hydrogen-Hydrocarbon Systems. *Proceedings of the Sixth World Petroleum Congress*, Frankfurt am Main, Germany, June 19-26, 1963; Paper 20, Section VII, p 233.
- Harold, M. P.; Ng, K. M. Effectiveness Enhancement and Reactant Depletion in a Partially Wetted Catalyst. *AIChE J.* **1987**, *33*, 1448.
- Haughey, D. P.; Beveridge, G. S. G. Local Voidage Variation in a Randomly Packed-Bed of Equal Sized Spheres. *Chem. Eng. Sci.* **1966**, *21*, 905.
- Herskowitz, M.; Mosseri, S. Global Rates of Reaction in Trickle-Bed Reactors: Effect of Gas and Liquid Flow Rates. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 4.
- Herskowitz, M.; Smith, J. M. Trickle-Bed Reactors: a Review. *AIChE J.* **1983**, *29*, 1.
- Herskowitz, M.; Carbonell, R. G.; Smith, J. M. Effectiveness Factors and Mass Transfer in Trickle-Bed Reactors. *AIChE J.* **1979**, *25*, 272.
- Hochman, J. M.; Effron, E. Two-Phase Cocurrent Downflow in Packed Beds. *Ind. Eng. Chem. Fundam.* **1969**, *8*, 63.
- Holub, R. A.; Dudukovic, M. P.; Ramachandran, P. A. A Phenomenological Model for Pressure Drop, Liquid Holdup and Flow Regime Transition in Gas-Liquid Trickle-Flow. *Chem. Eng. Sci.* **1992**, *47*, 2343.
- Holub, R. A.; Dudukovic, M. P.; Ramachandran, P. A. Pressure Drop, Liquid Holdup and Flow Regime Transition in Trickle-Flow. *AIChE J.* **1993**, *39*, 302.
- Huang, T. C.; Kang, B. C. Naphthalene Hydrogenation over Pt/Al₂O₃ Catalyst in a Trickle Bed Reactor. *Ind. Eng. Chem. Res.* **1995**, *34*, 2349.
- Lakota, A.; Levec, J. Solid-Liquid Mass Transfer in Packed Beds with Cocurrent Downward Two-Phase Flow. *AIChE J.* **1990**, *36*, 1444.
- Larachi, F.; Laurent, A.; Midoux, N.; Wild, G. Experimental Study of a Trickle-Bed Reactor Operating at High Pressure: Two-Phase Pressure Drop and Liquid Saturation. *Chem. Eng. Sci.* **1991**, *46*, 1233.
- Larachi, F.; Laurent, A.; Wild, G. E.; Midoux, N. Pressure Effects on Gas-Liquid Interfacial Areas in Cocurrent Trickle-Flow Reactors. *Chem. Eng. Sci.* **1992**, *47*, 2325.
- Larachi, F.; Wild, G.; Laurent, A.; Midoux, N. Influence of Gas Density on the Hydrodynamics of Cocurrent Gas-Liquid Upflow Fixed Bed Reactors. *Ind. Eng. Chem. Res.* **1994**, *33*, 519.
- Mata, A. R.; Smith, J. M. Oxidation of Sulfur Dioxide in a Trickle-Bed Reactor. *Chem. Eng. J.* **1981**, *22*, 229.
- Mears, D. E. The Role of Axial Dispersion in Trickle-Flow Laboratory Reactors. *Chem. Eng. Sci.* **1971**, *26*, 1361.
- Mills, P. L.; Dudukovic, M. P. Evaluation of Liquid-Solid Contacting in Trickle-Bed Reactors by Tracer Methods. *AIChE J.* **1981**, *27*, 893. Erratum. *AIChE J.* **1982**, *28*, 526.
- Molerus, O. *Principles of Flow in Disperse Systems*; Chapman & Hall: London, 1993; p 27.
- Morita, S.; Smith, J. M. Mass Transfer and Contacting Efficiency in a Trickle-Bed Reactor. *Ind. Eng. Chem. Fundam.* **1978**, *17*, 113.
- Petersen, E. E. *Chemical Reactor Analysis*; Prentice-Hall: Englewood Cliffs, NJ, 1965.
- Ramachandran, P. A.; Smith, J. M. Effectiveness Factors in Trickle-Bed Reactors. *AIChE J.* **1979**, *25*, 538.
- Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*; McGraw-Hill: New York, 1977.
- Ring, Z. E.; Missen, R. W. Trickle-Bed Reactors: Effect of Wetting Geometry on Overall Effectiveness Factor. *Can. J. Chem. Eng.* **1986**, *64*, 117.
- Ring, Z. E.; Missen, R. W. Trickle-Bed Reactors: an Experimental Study of Partial Wetting Effect. *AIChE J.* **1989**, *35*, 1821.
- Ring, Z. E.; Missen, R. W. Trickle-Bed Reactors: Tracer Study of Liquid Holdup and Wetting Efficiency at High Temperature and Pressure. *Can. J. Chem. Eng.* **1991**, *69*, 1016.
- Rosal, R.; Díez, F. V.; Sastre, H. Estimation of the Concentration of Hydroaromatic Compounds in a Hydrogenated Anthracene Oil. *Fuel* **1992a**, *71*, 761.
- Rosal, R.; Díez, F. V.; Sastre, H. Catalytic Hydrogenation of Multiring Aromatic Hydrocarbons in a Coal Tar Fraction. *Ind. Eng. Chem. Res.* **1992b**, *31*, 1007.
- Ruecker, C. M.; Akgerman, A. Determination of Wetting Efficiencies for a Trickle-Bed Reactor at High Temperatures and Pressures. *Ind. Eng. Chem.* **1987**, *26*, 164.
- Sáez, A. E.; Yépez, M. M.; Cabrera, C.; Soria, E. M. Static Liquid Holdup in Packed beds of Spherical Particles. *AIChE J.* **1991**, *37*, 1733.
- Sakornwimon, W.; Sylvester, D. Effectiveness Factors for Partially Wetted Catalysts in Trickle-Bed Reactors. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 16.
- Schwartz, J. G.; Weger, E.; Ducukovic, M. P. A New Tracer Method for Determination of Liquid-Solid Contacting Efficiency in Trickle-Bed Reactors. *AIChE J.* **1976**, *22*, 894.
- Sedriks, W.; Kenney, C. N. Partial Wetting in Trickle-Bed Reactors. The Reduction of Crotonaldehyde over a Palladium Catalyst. *Chem. Eng. Sci.* **1973**, *28*, 559.
- Sicardi, S.; Baldi, G.; Gianetto, A.; Specchia, V. Catalyst Areas Wetted by Flowing and Semistagnant Liquid in Trickle-Bed Reactors. *Chem. Eng. Sci.* **1980**, *35*, 67.

- Specchia, V.; Baldi, G. Pressure Drop and Liquid Holdup for Two-Phase Cocurrent Flow in Packed Beds. *Chem. Eng. Sci.* **1977**, *32*, 515.
- Specchia, V.; Baldi, G. Solid-Liquid Mass Transfer in Cocurrent Two-Phase Flow through Packed Beds. *Ind. Eng. Chem. Process Des. Dev.* **1978**, *17*, 362.
- Stegeman, D.; van Rooijen, F. E.; Kamperman, A. A.; Weijer, S.; Westerterp, K. R. Residence Time Distribution in the Liquid Phase in a Cocurrent Gas-Liquid Trickle-Bed Reactor. *Ind. Eng. Chem. Res.* **1996**, *35*, 378.
- Tan, C. S.; Smith, J. M. Catalyst Particle Effectiveness with Unsymmetrical Boundary Conditions. *Chem. Eng. Sci.* **1980**, *35*, 1601.
- van Swaaij, W. P. M.; Charpentier, J. C.; Villermaux, J. Residence Time Distribution in the Liquid Phase of Trickle Flow in Packed Columns. *Chem. Eng. Sci.* **1969**, *24*, 1083.
- Wammes, W. J. A.; Westerterp, K. R. The Influence of the Reactor Pressure on the Hydrodynamics in a Cocurrent Gas-Liquid Trickle-Bed Reactor. *Chem. Eng. Sci.* **1990**, *8*, 2247.
- Wammes, W. J. A.; Mechielsen, S. J.; Westerterp, K. R. The Transition between Flow and Pulse Flow in a Cocurrent Gas-Liquid Trickle-Bed at Elevated Pressures. *Chem. Eng. Sci.* **1990**, *45*, 3149.
- Wammes, W. J. A.; Middelkamp, J.; Huisman, W. J.; de Baas, C. M.; Westerterp, K. R. Hydrodynamics in a Cocurrent Gas-Liquid Trickle-Bed at Elevated Pressures, Part 2: Liquid Holdup, Pressure Drop, Flow Regimes. *AIChE J.* **1991a**, *37*, 1855.
- Wammes, W. J. A.; Middelkamp, J.; Huisman, W. J.; de Baas, C. M.; Westerterp, K. R. Hydrodynamics in a Cocurrent Gas-Liquid Trickle-Bed at Elevated Pressures, Part 1: Gas-Liquid Interfacial Areas. *AIChE J.* **1991b**, *37*, 1849.
- Wammes, W. J. A.; Mechielsen, S. J.; Westerterp, K. R. The Influence of Pressure on the Liquid Hold-up in a Cocurrent Gas-Liquid Trickle-Bed Reactor Operating at Low Gas Velocities. *Chem. Eng. Sci.* **1991c**, *46*, 409.
- Yentakakis, I. V.; Vayenas, C. G. Effectiveness Factors for Reactions Between Volatile and non-Volatile Components in Partially Wetted Catalysts. *Chem. Eng. Sci.* **1987**, *42*, 1323.

Received for review July 24, 1996

Revised manuscript received April 25, 1997

Accepted April 29, 1997[®]

IE960435O

[®] Abstract published in *Advance ACS Abstracts*, June 1, 1997.