Trickle-Bed Reactors: an Experimental Study of Partial Wetting Effect

The effect of partial external wetting of catalyst particles on conversion for hydrodesulfurization of dibenzothiophene in a white oil was studied in a 25-mm trickle-bed reactor at 10 MPa and 330-370°C with Mo/SiO_2 catalyst. The superficial liquid velocity (L_m) was varied from 0.092 to 0.557 kg · m^{-2} · s^{-1}. Measurements of conversion were augmented by tracer, kinetics and solubility experiments. The objectives were to determine the parameters of a reactor model based on the multizone external wetting (MZEW) model for the overall effectiveness factor, η_o, and to compare the measured and predicted values of η_o. As the wetting efficiency, f, increases, η_o also increases, but, even at the highest L_m, catalyst wetting was not complete and consequently η_o was lower than the value corresponding to $f = 1$. The MZEW model describes the experimental data better than the simpler two-zone model, based on a particular interpretation of f. The difference between the two models can be as high as 200%.

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Introduction

Incomplete wetting of catalyst particles by flowing liquid is an important factor in modeling the performance of short trickle-bed reactors, as used in pilot-plant studies for scale-up to commercial-size reactors. Two factors involved in this are the fractional coverage of the external surface by flowing liquid, and the geometry of the liquid distribution on the surface. We have previously (Ring and Missen, 1986) proposed a multizone model [termed here the multizone external wetting (MZEW) model] to account for the geometry in relating the overall effectiveness factor, η_o, to the fractional coverage or wetting efficiency, f. We presented a comparison of this model with the commonly-used two-zone (wetted and nonwetted regions) model (Sedricks and Kenney, 1973; Duduković, 1977; Duduković and Mills, 1978; Ramachandran and Smith, 1979), both in a simulated sense and in an actual sense with very limited data then available. The comparisons indicated a difference of up to 40% at $f = 0.5$ between an eight-zone model and the two-zone model, and a closer representation of the experimental results by the eight-zone model. The numerical simulation work of Yentekakis and Vayenas (1987) supports the tentative conclusion that a multizone model is superior to a two-zone model.

The purpose of this paper is to present results of experiments leading to a comparison of the predictions of a rigorous solution of the MZEW model, in terms of η_o, with observed behavior in a small trickle-bed reactor. A secondary purpose is to explore approximate models for η_o for use in situations in which the rigorous solution is not feasible, for whatever reason. All this is intended as a contribution towards further understanding of the design and analysis of trickle-bed reactors for commercial processing, particularly for scale-up from small units, from fundamental considerations.

For the comparison of the MZEW model with experimental results, it was considered important to generate results at operating conditions that would be useful for the analysis of commercially-important processes. The chemical system used, however, is a "model" system and is not meant to simulate that in any actual process. Its choice was dictated more by requirements that would facilitate comparison with the predictions of the model: nonvolatile limiting reactant (greater sensitivity to wetting geometry) and carrier liquid, availability of catalyst in spherical shape, and a resulting Thiele modulus (ϕ) close to 3.5, which value is in the region of greatest predicted difference between the MZEW and two-zone models (Ring and Missen, 1986). A literature survey resulted in the choice of hydrodesulfurization of dibenzothiophene (DBT) in a heavy white oil (initial boiling point of 315°C), supplied by Shell Canada Limited. The operating conditions chosen were 330 to 370°C and 10

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MPa, comparable to those used in hydrotreating processes in which trickle-bed reactors are extensively used and conditions for which relatively little published information is available.

To determine independently values of the parameters of the models used and to investigate the performance of a trickle-bed reactor for comparison, the overall program involved four types of experiments: kinetics and phase equilibrium carried out in an autoclave, and stimulus-response (tracer) and integral-conversion of a limiting reactant (performance) carried out simultaneously in the trickle-bed reactor. Only the kinetics and conversion experiments are described in detail here. The phase equilibrium experiments are described by Schofield (1987) and serve to establish that, for the range of conditions investigated, the solubility of H_2 in the liquid used is about 30 times greater than needed to react with all the dissolved DBT and to determine the H_2 flow rate in the system. The DBT is thus the limiting reactant and is essentially nonvolatile, and H_2 is present in excess, so that the reacting system can be investigated for pseudofirst-order behavior. The tracer experiments are also described in detail elsewhere (Ring, 1988), but their results are incorporated here in order to complete the comparison for η_o. These experiments were carried out to determine the wetting efficiency, f, using the method of Colombo et al. (1976).

In what follows, we first describe the MZEW model quantitatively for the specific case of a nonvolatile limiting reactant. We then outline the experimental methods used for the kinetics and performance experiments. This is followed by the principal results, and their analysis and interpretation. It is shown that the experimental values of η_o obtained from the trickle-bed reactor, with the aid of the kinetics experiments, conform more closely to the MZEW model than to the simpler two-zone model at all temperatures used, when considered as a function of f, as interpreted by the model of Colombo et al. (1976). It is also shown that the difference between the MZEW and two-zone models can be as much as 200%, reached when $f < 0.5$. It is also indicated how an approximate model for η_o can be developed as a possible (but less desirable) alternative to the rigorous solution of the MZEW model.

Multizone External Wetting Model for η_o of a Nonvolatile Reactant

The multizone external wetting (MZEW) model (Ring and Missen, 1986) has been developed to investigate the effect on the overall effectiveness factor, η_o, of the complexity of the liquid distribution on the external surface of catalyst particle. In this model, it is assumed that the wetted (W) and nonwetted (NW) regions can be divided into a number (N) of alternately grouped zones. This approach might be expected to be more realistic than the two-zone model. The following assumptions are also made:

- The catalyst particle is isothermal.
- There is one chemical reaction which is irreversible and pseudofirst order.
- The particle has pores totally filled with liquid.
- The liquid distribution on the external particle surface in the bed can be idealized as shown previously (Ring and Missen, 1986, Figure 1) for spherical shape.
- The wetted and nonwetted zones have different mass transfer characteristics, as described by the Biot numbers, Bi_L and Bi_g, respectively.

Two cases were identified and discussed separately: case A, in which the limiting reactant originates in, and is confined to, the liquid phase ($Bi_L > 0$ and $Bi_g = 0$); and case B, in which the limiting reactant originates in either fluid phase and is present in both ($Bi_L > 0$ and $Bi_g > 0$).

A single mathematical model, encompassing both cases, was presented. Since only case A is used in the current work, we present the equations describing the model specific to this case as follows:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial c}{\partial \theta}\right) - \phi^2 c = 0 \qquad (1)$$

$$\left(\frac{\partial c}{\partial r}\right)_{r=0} = \left(\frac{\partial c}{\partial \theta}\right)_{\theta=0,\pi} = 0 \qquad (2)$$

$$\left(\frac{\partial c}{\partial r}\right)_{r=1} = Bi_L\left(1 - c\Big|_{r=1}\right), \text{ for } S \in \Omega_W \qquad (3)$$

$$\left(\frac{\partial c}{\partial r}\right)_{r=1} = 0, \text{ for } S \in \Omega_{NW} \qquad (4)$$

where

$$\begin{aligned} &\Omega_W \Longleftrightarrow h_i \le \theta < h_{i+1}, \quad i = 0, 2, \ldots, N \\ &\Omega_{NW} \Longleftrightarrow h_j < \theta \le h_{j+1}, \quad j = 1, 3, \ldots, N-1 \\ &h_0 = 0 \\ &h_N = \pi \end{aligned} \qquad (5)$$

Equation 1 is the steady-state mass balance equation for the limiting reactant (DBT in this case) within a spherical catalyst particle. Two dimensions are considered to account for nonuniformity of external wetting. Here, r is a (dimensionless) radial coordinate, θ is an angular coordinate, c is the (dimensionless) concentration of the reactant, and ϕ is the Thiele modulus. The boundary conditions for solving Eq. 1 are given by Eqs. 2 to 4. Symmetry is taken into account in Eq. 2; as noted previously (Ring and Missen, 1986), the implied symmetry is formally questionable, but has been accepted in practice. The external boundary (particle surface) is described by the alternating arrangement of W and NW zones in Eqs. 3 and 4. These wetted and nonwetted regions consist of N zones, and the borders between them are represented by h_i, as indicated by relations 5. It is assumed that the surface areas of all the wetted zones are equal as well as those for the nonwetted zones. The limiting reactant is supplied to the particle interior through the wetted regions (Eq. 3), but the nonwetted regions are impermeable (Eq. 4).

Two limiting and asymptotic solutions for η_o were derived. For a spherical particle, these are:

$$\eta_{o+} = \frac{3}{\phi^2}\left(\frac{1}{\dfrac{1}{fBi_L} + \dfrac{1}{\phi\coth\phi - 1}}\right), \qquad (6)$$

$$\eta_{o-} = \frac{3}{\phi^2}\left(\frac{f}{\dfrac{1}{Bi_L} + \dfrac{1}{\phi\coth\phi - 1}}\right). \qquad (7)$$

η_{o+} is the upper limiting solution and η_{o-} is the lower limiting solution. When liquid-solid mass transfer resistance is negligible, η_{o+} becomes identical with the catalyst effectiveness factor, η, in the case of complete wetting, and η_{o-} corresponds to the approximate model of Mears (1974). For η_{o+}, it is assumed (for large N) that the intraparticle concentration profile of the limiting reactant is nearly symmetric, and only external mass transfer is affected by incomplete wetting. For η_{o-}, it is assumed that the most severe assymmetry of the profile (for $N = 2$) is where there is no diffusional transport in the direction normal to external mass transfer.

Based on numerical simulation, it was concluded that the effect of N on η_o depends on the difference between Bi_L and Bi_g. It is most pronounced when one of the Biot numbers is practically infinite while the other is zero (extreme of case A when $Bi_L = \infty$ and $Bi_g = 0$) and in the range of the Thiele modulus from 1 to 10 with the maximum at 3.5. Such conditions occur, for example, for hydrodesulfurization of petroleum fractions. It is usually carried out at 350 to 400°C at 5 to 10 MPa with Co-Mo/γ-Al_2O_3 catalysts. Intraparticle diffusion effects are often significant. Effectiveness factors have been estimated by different authors (as reviewed by Goto et al., 1977) at : 0.5 to 0.8 for 3 by 3 mm pellets, 0.36 for 3.6-mm particles, and 0.7 to 0.9 for 0.5 to 0.8-mm particles. Therefore, the effect may be important in industrial practice.

The general trends indicated by the MZEW model include: 1) for a given wetting efficiency f, the greater N the more uniform the supply of reactant to the particle interior, and consequently the smaller the effect of incomplete wetting on η_o; 2) if a catalytic process is limited severely by (intrinsic) kinetics or by (external and intraparticle) mass transport, the effect of liquid distribution on the exterior particle surface becomes insignificant (on η_o). For case A and spherical particles (of interest here), it was calculated that, e.g., for $Bi_L = 150$ and $f = 0.5$, the difference between the MZEW model with $N = 8$ and the two-zone model, in terms of η_o, becomes as much as 40% for a Thiele modulus of about 3.5.

Both the MZEW and two-zone models are used in this work to interpret experimental results in a trickle-bed reactor. Both these models for the particular case considered here contain three parameters: ϕ, Bi_L and f; in addition, the MZEW model contains the parameter N. In this paper we describe measurements of k and D_{EA}, the effective diffusivity of reactant A (DBT), for the purpose of determining ϕ. We also show that $Bi_L \rightarrow \infty$. Wetting efficiency, f, can be obtained from stimulus-response (tracer) experiments. Although the results of such experiments are used here, the details of the experiments are not given here, but are described by Ring (1988). f can be calculated in one of the following two ways (from tracer experiments): $f = D_{ETa}/D_{ET}$ (Colombo et al., 1976) or $f = (D_{ETa}/D_{ET})^{1/2}$ (Sicardi et al., 1980); D_{ET} is the true effective intraparticle diffusivity of tracer (T) in a totally-wetted catalyst particle, and D_{ETa} is the apparent effective diffusivity in a partially-wetted catalyst particle. We explore the use of both these methods of determining f in the dependence of η_o on f.

Experimental Methods

Kinetics of hydrodesulfurization

The kinetics of hydrodesulfurization of dibenzothiophene (DBT) in a white oil was investigated in a batch reactor at 330 to 371°C and 10 MPa, to confirm the first-order behavior and to measure the (intrinsic) rate constant k, together with the Arrhenius parameters, and the effective diffusivity of DBT in the catalyst, D_{EA}.

The reactor was a 4-L stainless-steel vessel supplied by Autoclave Engineers. It was equipped with a variable speed Magnedrive stirrer, a jacket heater, an internal cooling coil, a pressure gauge, a thermocouple connected to a digital indicator for temperature measurement to ±0.1°C, and a proportional temperature controller, which, in conjunction with the heater and cooler, maintained T within ±0.5°C. Gas (H_2 for reaction and N_2 for purging) was supplied from cylinders. At the beginning of a series of experiments, the oil was added to the reactor, which was then purged with N_2, and presulfided Mo/SiO_2 catalyst (supplied by Shell Canada Limited) was added (catalyst loading usually 0.03 to 0.05 g/g oil). Provision was made for the injection of dimethyldisulfide (DMDS) (to provide H_2S to stabilize catalyst activity during an experiment) and of DBT in a concentrated solution in the oil and for the withdrawal of liquid samples for analysis. The samples were analyzed for sulfur (after being degassed with N_2 to remove dissolved H_2S) with a System 701 sulfur analyzer (Xertex, Dohrmann). Details of the equipment and operating and analytical procedures are given by Ring (1988).

Trickle-bed reactor performance

The fractional conversion of DBT, reacting with H_2, was investigated in a trickle-bed reactor at 330, 350 and 370°C and 10 MPa to provide experimental values of η_o under conditions of incomplete external wetting of catalyst particles.

The reactor was a vertical stainless-steel tube about 0.025 m in inside diameter and 1-m-long, containing a packed bed as described below. In the center of the reactor, a thermowell with 12 thermocouples spaced vertically allowed measurement of T to ±0.1°C. Other instrumentation allowed control of T in the bed to ±0.5°C, P within ±1.5%, liquid flow rate within ±3%, and gas flow rate within ±0.5%. Provision was made for the liquid (oil containing dissolved DBT) and gas (H_2) to be fed continuously at the top or bottom of the reactor. The effluent, gas and liquid, passed through a phase separator to allow batch sampling of the liquid for sulfur analysis.

The superficial liquid velocity, L_m, was varied from 0.092 to 0.557 $kg \cdot m^{-2} \cdot s^{-1}$. The flow rate of H_2 was adjusted to give a volumetric rate equal to that of the oil at the operating conditions, after allowing for the dissolution of H_2 in the oil. This was to ensure that all experiments were carried out in the trickle-flow regime.

The packed bed consisted of four layers. At the top was an 11-cm layer of fine particles of SiC to act as a liquid distributor; underneath that was a 15-cm layer of inert catalyst base (silica), with particles of the same size and porosity as the catalyst particles; next was a 50-cm layer of catalyst and below that another 15-cm layer of the base. The layers were separated by stainless-steel screens. The catalyst was sulfided *in situ*. At the beginning of each series of experiments, the bed was prewetted at the operating T with liquid flowing upward for several hours. The liquid samples were analyzed for sulfur as described for the kinetics experiments.

Details of the equipment and experimental procedures are given by Ring (1988). All the experiments using the trickle-bed reactor were carried out at the Oakville Research Centre of Shell Canada Limited, using the facilities provided there.

Results and Discussion

Kinetics of hydrodesulfurization

The kinetics experiments (a total of 32) were carried out in four series with two batches of catalyst. Only the results from the last two series using the second batch (the same batch used in the trickle-bed reactor) are reported in detail here. These results are given in Table 1, which shows values of k_a for spherical catalyst particles with a mean diameter, d_p (after screening) of 2.17×10^{-3} m, for $T = 331$ to 371°C, and for $C^0_{DMDS} = 0.02$ and $0.005\ \mathrm{cm}^3 \cdot g^{-1}$. The latter value of C^0_{DMDS} corresponded to the concentration of H_2S used in the trickle-bed reactor experiments to stabilize the catalyst. (It turned out not to be feasible to use DMDS for this purpose in the trickle-bed reactor.)

The first two series of experiments were used: to establish stirrer speed to eliminate liquid-solid mass transfer limitations (20 to 25 Hz); to establish that the reaction is pseudofirst-order (from linearity of the ln c_s vs. t relation); to establish the precision of determining k_a from this relation (about 3%); to investigate the effects of catalyst age and of particle size. These last two are discussed further briefly in turn.

The kinetics experiments in the autoclave indicated some decline in catalyst activity over extended periods of time (up to 50 h of operation at $T > 300$°C), both by the values of k_a obtained and by the dark color of the catalyst particles and oil (liquid samples). In the trickle-bed reactor experiments (next section), however, the activity remained unchanged for the entire period of the experiments (about 500 h of operation), and the catalyst particles and liquid samples were "clear." It was concluded that deactivation in the autoclave was caused by the accumulation of "coke" from cracking of the oil. The effect can be ignored in the final analysis, because it did not occur in the trickle-bed reactor (relatively short oil residence time), and only the results from "young" catalyst particles (in the sense of catalyst-oil contact times) were used to determine kinetic parameters from the autoclave experiments.

A portion of the first batch was crushed to obtain particles of smaller size (0.23, 0.27 and 0.38 mm). Although k_a was found to depend on particle size, analysis of the results showed that, in the usual method of obtaining the intrinsic rate constant, k, by reducing d_p, it was not possible to separate intraparticle diffusion resistance (indicated by an Arrhenius plot) from external mass transfer resistance (indicated by increase in k_a with increase in d_p for the three sizes of crushed catalyst).

Table 1. Summary of Kinetics Experiments*

T/°C	$C^0_{DMDS}/\mathrm{cm}^3 \cdot \mathrm{g}^{-1}$	$10^3\,k_a/\mathrm{kg_{oil}} \cdot \mathrm{kg_{cat}} \cdot {}^{-1}\,\mathrm{s}^{-1}$
331	0.02**	0.92
340		1.49
350		2.15
365		2.85
371		2.70
330	0.005†	1.63
331		1.83
340		2.20
351		2.82
361		3.18
371		3.50
371		3.83

*Second batch of catalyst; $d_p = 2.17 \times 10^{-3}$ m (spherical).

**Used with fresh catalyst from second batch.

†Used with spent catalyst from second batch after 500-h operation in trickle-bed reactor.

Parameter estimation, to obtain values of the Arrhenius parameters (A and E_A for k) and of D_{EA} simultaneously, was hence achieved by nonlinear regression using the values of k_a, the Arrhenius equation, the definition of η, the particle effectiveness factor, and the expression for η in terms of ϕ. Gas-liquid mass transfer effects could be neglected because of an initially large excess of H_2 in the liquid phase, as confirmed by solubility measurements (Schofield, 1987). Only the results given in Table 1 were used in this analysis, which was implemented by a computer program (Ring, 1988). The results of the two series were treated separately. They resulted in essentially the same value of D_{EA}, but in different values for A and E_A, the latter difference because of the different values of C^0_{DMDS} used. Since the value of $C^0_{DMDS} = 0.005\ \mathrm{cm}^3 \cdot \mathrm{g}^{-1}$ corresponded to the concentration used in the trickle-bed reactor experiments, only the results for this C^0_{DMDS} were used eventually, as follows:

$$k = 5.28 \times 10^4 \exp(-10{,}170/T), \tag{8}$$

where k is in $\mathrm{kg_{oil}} \cdot \mathrm{kg_{cat}^{-1}} \cdot \mathrm{s}^{-1}$ and T is in K, and

$$D_{EA} = 7.0 \times 10^{-10}\mathrm{m}^2 \cdot \mathrm{s}^{-1}, \tag{9}$$

based on void cross section and essentially independent of T over the range used. From Eq. 8, the activation energy is $E_A = 84{,}600\ \mathrm{J} \cdot \mathrm{mol}^{-1}$.

Sensitivity analysis performed using the parameter estimation program indicated that for the range of ϕ used, A, E_A, and D_{EA} can be estimated simultaneously from k_a vs. T data (for spherical catalyst). This procedure required that D_{EA} be assumed constant, which is reasonable, since the variation over the range of T used is estimated to be about 1.5%. Furthermore, the final estimates did not depend on the initial estimates of the parameter values, and D_{EA} values obtained for the two series of experiments differed by less than 10%.

The results also reveal that $\phi = 3.69$ at 350°C, which was close to the desired value of 3.5 (and influenced choice of conditions).

Trickle-bed reactor performance

The 15 performance experiments were carried out in three series, at 330, 350 and 370°C, respectively, to determine the dependence of η_o on T and L_m, the mass superficial liquid velocity. The results are summarized in Table 2, which gives values of η_o calculated both for plug flow (*PF*) and dispersed plug flow (*DPF*), the latter based on an estimate of the Peclet number (*Pe*) using the correlation of Furzer and Michell (1970). Each value of the measured fractional conversion of DBT (α_A) is based on two to four analyses of sulfur concentration in the liquid effluent from the reactor. The calculation of η_o (DPF) was done as follows: an apparent rate constant ($k\eta_o$) was first obtained from α_A and Pe using the Danckwerts (1953) solution of the dispersion model; η_o was then calculated using values of k from the kinetics experiments. Values of bed and catalyst particle characteristics used in these calculations are given in Table 3. Values of physicochemical properties used, as measured or estimated in various ways (Ring, 1988), are given in Table 4.

Table 2. Summary of Trickle-Bed Performance Experiments

$T/°C$	$L_m/kg \cdot m^{-2} \cdot s^{-1}$	α_A	$\eta_o(PF)$	$\eta_o(DPF)$*	Pe**	η_{o+}
330	0.092	0.909	0.341	0.363	54.6	0.695
	0.139	0.813	0.365	0.380	58.4	
	0.186	0.740	0.393	0.405	61.2	
	0.278	0.644	0.447	0.458	65.2	
	0.371	0.518	0.424	0.432	68.3	
	0.557	0.444	0.522	0.529	73.1	
350	0.092	0.975	0.293	0.329	56.1	0.594
	0.139	0.939	0.351	0.376	60.1	
	0.186	0.894	0.377	0.398	63.0	
	0.278	0.775	0.382	0.395	67.3	
	0.371	0.672	0.380	0.390	70.4	
	0.557	0.596	0.451	0.459	74.8	
370	0.278	0.866	0.306	0.319	70.6	0.499
	0.371	0.785	0.308	0.319	73.8	
	0.557	0.705	0.369	0.379	78.8	

*Calculated using value of Pe in Col. 6.

**Calculated using correlation of Furzer and Michell (1970).

The general trends shown by η_o (decrease with increasing T, and increase with increasing L_m) are as expected.

Table 2 also gives the three values of η_o for totally wetted catalyst at the three T's, as obtained from k_a/k from the kinetics experiments in the autoclave. For the system used here, these are equal to the values of η_{o+}, as indicated in the table and as discussed above. The values of η_o obtained in the trickle-bed reactor are correspondingly lower than the values of η_{o+}, indicating that total wetting ($f = 1$) did not occur in the reactor even at the highest value of L_m ($0.557\ kg \cdot m^{-2} \cdot s^{-1}$). This is consistent with, e.g., the work of Koros (1976), who concluded that total wetting was achieved at $L_m = 4\ kg \cdot m^{-2} \cdot s^{-1}$.

Values of η_o were also calculated using the correlation of Hochman and Effron (1969) for Pe, which yields lower values than that of Furzer and Michell. However, these values of η_o were essentially independent of L_m at each temperature, contrary to the expected increase with increasing L_m (so as to approach the value for completely-wetted catalyst at high values of L_m). These values of η_o were not used further.

Other factors which might have effects for η_o turned out to be unimportant as estimated or observed: liquid-solid mass transfer resistance (by comparing the mass fluxes to and from the external catalyst surface, using a mass transfer coefficient calculated from the correlation of Tan and Smith, 1982), and change in catalytic activity (no significant deactivation for the 500-h period of operation).

Table 3. Trickle-bed Reactor: Catalyst and Bed Characteristics

Characteristics	Value
Bed	
Bed Depth (L)	0.51 m
Bed Diameter (d_B)	0.0254 m
Mass of Catalyst (m_c)	0.120 kg
Bed Voidage (ϵ_B)	0.412
Catalyst Bulk Density (ρ_B)	$495\ kg \cdot m^{-3}$
Catalyst	
Particle Diameter (d_p)	2.17×10^{-3} m
Particle Density (ρ_p)	$843\ kg \cdot m^{-3}$
Fresh Catalyst	
Pore Volume (PV_F)	$0.810\ cm^3 \cdot g^{-1}$
Surface Area (SA_F)	$141.2\ m^2 \cdot g^{-1}$
Particle Porosity (ϵ_P)	0.682

Table 4. Physicochemical Properties for the System

$T/°C$	$\rho_L/kg \cdot m^{-3}$	$10^4\,\mu_L/kg \cdot m^{-1} \cdot s^{-1}$	$10^9\,D_A/m^2 \cdot s^{-1}$
330	708	4.00	3.05
350	675	3.65	
370	651	3.23	

The main objective of this paper, comparison of the experimental values of η_o with the predictions of the MZEW model (Ring and Missen, 1986), is illustrated in Figures 1 to 3 for the three temperatures, with η_o plotted against f, the wetting efficiency. In each figure, the full lines represent the solution of the model for the upper limit, η_{o+}, and the lower limit, η_{o-}, and for two values of N: $N = 8$ (eight-zone model) and $N = 2$ (two-zone model), at the value of ϕ in each case (2.81 at 330°C, 3.69 at 350°C, and 4.75 at 370°C). The full lines were obtained using a program devised by Ring (1984). The comparison is complicated by uncertainty in the method to be used for estimating f from effective diffusivities: D_{ETa}/D_{ET} (Colombo et al., 1976) or $(D_{ETa}/D_{ET})^{1/2}$ (Sicardi, et al., 1980). Although Ramachandran et al. (1986) seem to indicate that the former corresponds closer to the external wetting, we have shown comparisons for both, with estimated error bars indicated for the former.

If we accept the conclusion of Ramachandran et al. (1986), and the validity of the previous comparison (Ring and Missen, 1986) with the data of Herskowitz (1978), the MZEW model with a value of $N = 8$, say, represents the experimental values of η_o better than the simpler two-zone model. This avoids the need for introducing enhancement factors for the mass transfer coefficients involved, as proposed by Turek and Lange (1981), El-Hisnawi et al. (1982), and Mills and Duduković (1983, 1984). We do not attach particular significance to the value of N being 8, but rather to N being >2. Furthermore, N should be viewed as an effective parameter describing a simplistic approximation to a complex wetting pattern that includes regions of external catalyst particle surface both nonwetted and wetted by flowing and stagnant liquid. The experimental data of Paraskos et al. (1975)

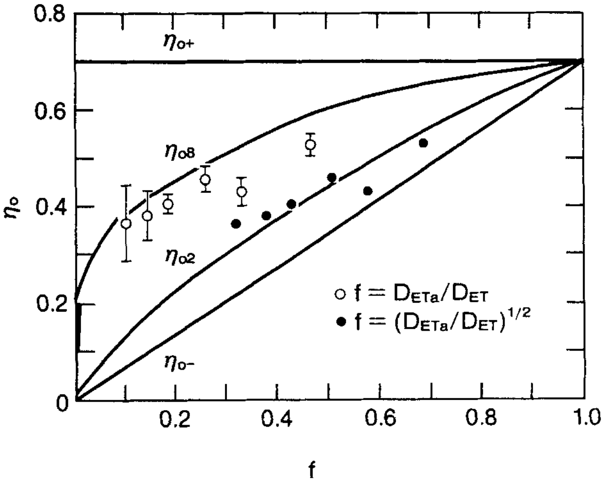

Figure 1. Experimental (points) vs. predicted (full curves) η_o's at 330°C.

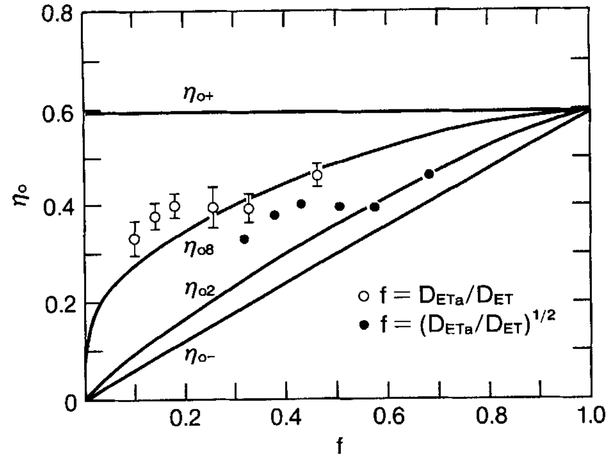

Figure 2. Experimental (points) vs. predicted (full curves) η_o's at 350°C.

can also be interpreted qualitatively using the concept of a number of zones greater than 2 (Ring, 1988).

Because of the uncertainty associated with f, this is not complete proof that the MZEW model is better. A more complete proof would require that experimental work be carried out at values of ϕ much greater than 3.5. Under such conditions, wetting efficiency is important but wetting geometry is not (Ring and Missen, 1986, Figure 6). Such a situation would allow determination as to which definition of f is applicable. Similar experimental work with another model system displaying $\phi \gg 3.5$ would be required.

Figures 1 to 3 show that the difference between the MZEW model (with $N = 8$) and the two-zone model for $f < 0.5$ can be as much as 200%, somewhat greater than the value of 40% pointed out previously but based on $f \geq 0.5$.

Scale-up and approximate models for η_o

The implications of the results of this work for scale-up and/or design of trickle-bed reactors are as follows. For a short bed and an isothermal, single-reaction system, the liquid-space-velocity-based procedure should use the axial dispersion model for the bed-scale and the MZEW model for the particle-scale description of the (pilot-plant) process. For commercial units with relatively deep beds, in which the superficial liquid velocities are 20 to 40 times greater, the plug-flow model and η_o for totally wetted catalyst should be used. The latter and k can both be obtained from batch reactor experiments. In addition, reliable correlations are required for Pe and f. For partially-wetted catalyst, η_o should be calculated rigorously with the program devised by Ring (1984), or, failing that, η_o should be obtained from an approximate model as described below.

One of the objectives of this work is the development of an approximate model for η_o for the (isothermal) case of a nonvolatile limiting reactant (as here), as an alternative to the detailed numerical solution by computer of the continuity equation. One form proposed previously (Ring and Missen, 1986) involves weighting the two limiting solutions, η_{o+} and η_{o-}, with an arbitrary weighting function $g(\phi, L_m)$. For spherical particles, this becomes

$$\frac{1}{\eta_o} = (1 - g)\frac{1}{\eta_{o+}} + g\frac{1}{\eta_{o-}}$$

$$= \frac{\phi^2}{3fBi_L} + [1 - g(\phi, L_m)(1 - f^{-1})]\frac{1}{\eta}. \quad (10)$$

Another approximate model can be developed based on the approximation of the two-zone model proposed by Duduković (1977). The latter can be written for a spherical particle as

$$\eta_o = 3(f/\phi)^2[(\phi/f)\coth(\phi/f) - 1]. \quad (11)$$

If we decrease the dependence of η_o on f by replacing f by $f^{p(\phi, L_m)}$, where $p(\phi, L_m) < 1$, Eq. 11 becomes

$$\eta_o = 3(f^p/\phi)^2[(\phi/f^p)\coth(\phi/f^p) - 1]. \quad (12)$$

Figure 4 compares the experimental values of η_o obtained at 330°C with the approximate models in Eqs. 11 and 12, the latter with p arbitrarily chosen to be constant at 0.5. In both cases, f was calculated as D_{ETa}/D_{ET}. With this method of calculating f and the value of p chosen, there is good agreement with the experimental data. For the use of Eq. 10, the information gener-

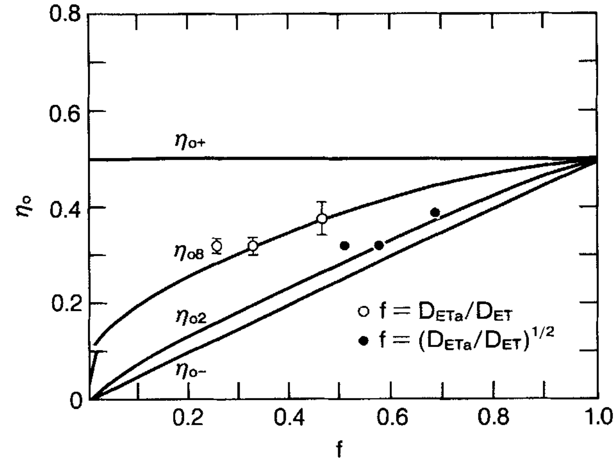

Figure 3. Experimental (points) vs. predicted (full curves) η_o's at 370°C.

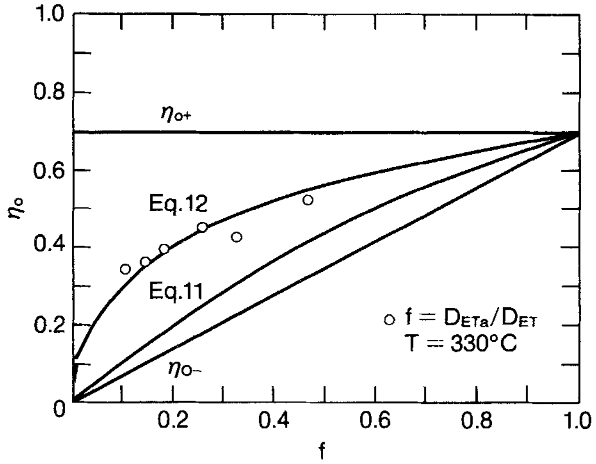

Figure 4. Experimental η_o's (points) vs. approximate models (full curves).

ated in this work is insufficient to establish $g(\phi, L_m)$, but it appears to be more dependent on L_m than is $p(\phi, L_m)$, and ranges from 0.3 to 0.5. Because of this, Eq. 12 appears to be more useful as an approximate model.

Conclusions

To consider the effects of wetting efficiency, f, and wetting geometry on η_o in a short trickle-bed reactor, we have made a comparison of experimentally determined values of η_o, at varying values of f, with models that take wetting geometry into account. These effects are both important. The effect of f can be seen directly in Figures 1 to 3, independent of any model used. The nature of the experimentation, however, is such that the effect of wetting geometry cannot be considered without reference to the framework of models used. These are considered in turn, followed by implications for scale-up.

With regard to f, η_o increases as f increases, as expected. However, even at the highest value of L_m used, corresponding to the highest value of f, η_o is less than its value for totally-wetted catalyst (which is equivalent to η_{o+} for the system used here).

With regard to wetting geometry, the conclusion that the MZEW model (e.g., with $N = 8$) represents the effect of this better than the two-zone model is based on the assumption that f can be estimated as D_{ETa}/D_{ET} (Colombo et al., 1976), rather than as $(D_{ETa}/D_{ET})^{1/2}$ (Sicardi et al., 1980). Apart from this, for the system investigated, the difference between the values of η_o calculated from the two models can be as much as 200%, with the MZEW value being higher.

Equation 12 appears to provide a useful approximate model for η_o as a substitute for the rigorous solution of the MZEW model, but further development of such a model requires more experimental data such as obtained here. Furthermore, for practical applications, Eqs. 6 and 7 for η_{o+} and η_{o-} may give useful bounds on η_o, even if they are not directly involved in an approximate solution, as in Eq. 10.

Before the MZEW model can be used for scale-up purposes with more confidence, the uncertainty arising from the method of determining f needs to be resolved. This could be attempted by experimental work similar to that described here but at relatively large values of ϕ (>50, say) to eliminate the effect of wetting geometry and focus on the effect of f itself. Any possible effect of molecular diffusivity of tracer on f should also be explored.

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Notation

A = preexponential factor in Arrhenius equation for k
Bi_g = Biot number for nonwetted region
Bi_L = Biot number for wetted region = $(d_p/2)\epsilon_p k_{Ls}/D_{EA}$
c = concentration of limiting reactant A in internal liquid holdup
c_s = sulfur concentration in liquid sample, ppm wt
C^0_{DMDS} = *initial concentration of dimethyldisulfide*, $cm^3 \cdot g^{-1}$
d_p = particle diameter, mm
D = molecular diffusivity, $m^2 \cdot s^{-1}$
D_{ax} = axial dispersion coefficient, $m^2 \cdot s^{-1}$
D_E = effective diffusivity, based on void cross section, $m^2 \cdot s^{-1}$
E_A = activation energy in Arrhenius equation for k
f = wetting efficiency, ratio of wetted area to total external area of particle
g = weighting parameter in Eq. 10
h_i = borders between zones, radians, $i = 0, 1, 2, \ldots, N$
k = (intrinsic) reaction rate constant, $kg_{oil} \cdot kg_{cat}^{-1} \cdot s^{-1}$
k_{Ls} = liquid-solid mass transfer coefficient, $m \cdot s^{-1}$
L = depth of bed, m
L_m = mass superficial liquid velocity, $kg \cdot m^{-2} \cdot s^{-1}$
N = number of zones
p = parameter in Eq. 12
P = pressure, MPa
Pe = Peclet number = $u_L L/D_{ax}$
r = radius of spherical particle
t = time
T = temperature, °C or K

Greek letters

α_A = fractional conversion of A(DBT)
ϵ_p = particle porosity
η = catalyst effectiveness factor for totally wetted particle
η_o = overall effectiveness factor
η_{o+} = upper limit for overall effectiveness factor; in this system, $\eta_{o+} \equiv \eta_o$ for totally-wetted catalyst
η_{o-} = lower limit for overall effectiveness factor
η_{o2} = overall effectiveness factor for two-zone wetting
η_{o8} = overall effectiveness factor for eight-zone wetting
θ = angular coordinate, radians
μ_L = viscosity of liquid, $kg \cdot m^{-1} \cdot s^{-1}$
ρ_L = density of liquid, $kg \cdot m^{-3}$
ρ_p = particle density, $kg \cdot m^{-3}$
ϕ = Thiele modulus = $(d_p/2)(k\rho_p/\rho_L D_{EA}\epsilon_p)^{1/2}$

Subscripts

a = apparent
A = dibenzothiophene (DBT)
NW = nonwetted
T = tracer
W = wetted

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