$$D_{A_o} = Z\,T^{3/2} \qquad (17)$$

Applying Equations (16) and (17) to (14) and (15), we get

$$M = \frac{1-\alpha_o}{\alpha_o}\;\frac{b\,h^+}{C_{B_o}L_o^2}\left[\frac{2\,A'\,Z}{a_{i_o}(\gamma+1)}\right]^{0.5} C_{A_s}{}^{0.617}\,T^{3/4}\,e^{-E/2RT}$$

$$P = \frac{h^+}{L_o}\left[\frac{(\gamma+1)\;Z}{2\,a_{i_o}\,A'}\right]^{0.5} C_{A_s}{}^{0.394}\,T^{3/4}\,e^{E/2RT}$$

The values of $\ln(M/C_{A_s}{}^{0.617}\,T^{3/4})$ vs. $1/T$ are plotted in Figure 2. These values can be fitted by a straight line with a correlation factor of 0.982. From the fit we get

$$M = 0.25\,C_{A_s}{}^{0.617}\,T^{3/4}\,e^{-9\,590/RT}$$

$$P = 0.26 \times 10^{-6}\,C_{A_s}{}^{0.394}\,T^{3/4}\,e^{9\,590/RT}$$

In order to obtain values for A' and Z, it would be necessary to assign values to h^+ and b. Values for h^+ were computed using Equation (13) and were found to be near unity. It is rather difficult to assign a value to b, although it is known that $1 < b < 2$.

CONCLUSIONS

The kinetics of the reaction between tungsten trioxide and carbon tetrachloride has been interpreted by a diffuse interface model, from which an order of reaction of 0.234 and an activation energy of 19 180 cal/g-mole have been determined.

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NOTATION

A' = constant in Equation (16)
a, a^* = total surface area per unit volume, cm^{-1}, dimensionless value = a/a_o
b = stoichiometric coefficient
C, C^* = molar concentration, g-mole/cm^3, dimensionless value = C/C_o
D, D^* = effective diffusivity, cm^2/s, dimensionless value = D/D_o
E = activation energy, cal/g-mole
h^+ = correction factor, defined in Equation (13)
h_o = generalized Thiele modulus, Equation (12)
k = reaction rate constant per unit surface area
K = equilibrium constant
L = characteristic length, $L = R_p/3$
M = variable defined in Equation (10)
P = variable defined in Equation (11)
r = reaction rate, g-mole/cm^3 s
R_p, R^* = pellet radius, cm, dimensionless radius = R_p/R_o
R = gas constant, cal/g-mole °K
T = temperature, °K
X = conversion
Z = constant in Equation (17)
α = external surface area/total surface area
γ = apparent reaction order
ϵ = porosity
θ = time, s

Subscripts

o = initial value
i = inner value
s = external surface area
A = gaseous reactant
B = solid reactant

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Catalyst Effectiveness Factor and Contacting Efficiency in Trickle-Bed Reactors

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In order to interpret or predict trickle-bed performance, attempts have been made to account for liquid maldistribution, deviation from plug flow, and for incomplete wetting of catalyst particles (Ross, 1965; Cecil et al., 1968; Murphree, 1964; Henry and Gilbert, 1973; Mears, 1974). It has been shown that liquid phase deviation from plug flow does not have significant effects on conversion in commercial and pilot scale trickle-bed reactors (Schwartz and Roberts, 1973). Application of Mears' (1971) criterion confirms the insignificance of dispersion effects. Although, in principle, external gas-liquid and liquid-solid mass transfer may affect the rate in large trickle-bed reactors, it appears that hydrodesulfurizers mainly operate in regimes free of these external effects. Effectiveness factors from 0.5 to 0.85 have been reported (Le Nobel and Choufoer, 1959; Van Zoonen and Douwes, 1963; Van Deemter, 1964; Adlington and Thompson, 1964; Satterfield, 1975). Finally, incomplete catalyst wetting as affected by the hydrodynamic regime in the bed was singled out as the most important parameter which determines reactor performance (Ross, 1965; Mears, 1974; Satterfield, 1975).

The purpose of this paper is to summarize the previously reported expressions for interpretation of the effect of incomplete catalyst wetting on trickle-bed performance and demonstrate the link between catalyst effectiveness, as affected by internal diffusional limitations, and incomplete wetting.

REVIEW OF PREVIOUS MODELS

Most of the previously used expressions to account for incomplete catalyst wetting in trickle beds are summarized in Table 1. All of these with the exception of the last one, are based on the assumptions of plug flow of liquid, no external mass transfer limitations, isothermal conditions, first-order irreversible reaction with respect to the liquid reactant, nonvolatile liquid reactant, and no noncatalytic homogeneous liquid phase reaction.

Table 1. Suggested Performance Equations for Trickle-Bed Reactors

$$\ln\frac{1}{1-x} \propto \frac{k_{tc}H_{TL}}{\text{LHSV}} \tag{T1}$$

$$\tau_{1/2} = \tau_{1/2}{}^{c} + \frac{A'}{U_L{}^{b}} \tag{T2a}$$

$$\frac{1}{k_v} = \frac{1}{k_{tc}} + \frac{A}{U_L{}^{b}}; \quad 0.5 < b < 0.7 \tag{T2b}$$

$$\ln\frac{1}{1-x} \propto \frac{k_{tc}L_m{}^{1/3}}{(\text{LHSV})2/3} \tag{T3}$$

$$\ln\frac{1}{1-x} \propto L_m{}^{0.32}\,(\text{LHSV})^{-0.68}\,d_p{}^{0.18}\,\nu^{-0.15}\,(\sigma_c/\sigma)^{0.21}\,\eta_T \tag{T4}$$

$$\ln\frac{1}{1-x} = \Lambda_3\omega \tag{T5}$$

where

$$\Lambda_3 = \frac{N_{B_o}}{2}\,[1 + 4\Lambda_2/N_{B_o} - 1] \tag{T5a}$$

$$\Lambda_2 = \frac{1}{1/\Lambda_1 + 1/N_{st}} \tag{T5b}$$

$$\Lambda_1 = \frac{1}{f}\,[\phi_T \coth \phi_T - 1] \tag{T5c}$$

Ross (1965), in treating the data from commercial and pilot plant hydrodesulfurization reactors, assumed that k_v is proportional to $k_{tc}\,H_{TL}$which results in expression (T1). This is equivalent to asserting that liquid space time is the basic parameter in reactor performance. Bondi (1971) developed an empirical expression (T2*a*)in interpreting data for the hydrodesulfurization of heavy gas oil. This expression relates the space time required to achieve 50% conversion, $\tau_{1/2}$, to the analogous space time at complete wetting, $\tau^{c}{}_{1/2}$, and to liquid superficial velocity, U_L. This can also be written as Equation (T2*b*) in terms of previously defined constants. Henry and Gilbert (1973) extended Ross' (1965) formula by incorporating into it an available correlation for liquid holdup which resulted in expression (T3). Finally, Mears (1974) hypothesized that the apparent rate constant k_v is proportional to the true rate constant on completely wetted catalyst k_{tc} to the catalyst effectiveness factor η_T and to the contacting efficiency η_{CE}, that is, to the fraction of the external catalyst area wetted by liquid. By incorporating the correlation of Puranik and Vogelpohl (1974), which was developed for incomplete contacting in absorbers packed with different packing size and shape, Mears (1974) arrived to expression (T4). Sylvester and Pitayagulsarn (1974) reproduced the model of Suzuki and Smith (1970) for gas solid catalytic reactions and applied it without modification to three-phase systems in trickle beds. Incomplete wetting was accounted for by assuming only a portion of the reactor, that is, an effectively smaller volume, to be contributing to reactant conversion. This is, again, equivalent to assuming that a primary parameter is liquid space time. When for these trickle beds unimportant external mass transfer limitations and axial dispersion effects are neglected, the model expressed by Equations (T5) is reduced to Ross' (1965) expression with catalyst effectiveness factor added to it. It is important to note that the usual expressions for catalyst effectiveness factor in two-phase (gas-solid or liquid-solid) systems were used by Mears (1974) and Sylvester and Pitayagulsarn (1974).

Two main points emerge from the previous studies. First, incomplete wetting was always accounted for in a global way by assuming that a fraction of a reactor is not wetted, that is, reactor scale incomplete contacting was considered. Second, the expression for the effectiveness factor for a single pellet was always based on existing formulas for single fluid phase systems, that is, for completely internally and externally wetted pellets. However, for reactors that operate in the regime free of external transport effects, as is here the case, it is the particle scale phenomena, that is, particle scale incomplete contacting and effectiveness of partially wetted pellets that affect reactor performance profoundly, especially if reactor scale incomplete contacting is eliminated by proper design. It is, therefore, of interest to show that catalyst effectiveness factor and incomplete wetting are strongly coupled phenomena which cannot necessarily be expressed in the regime of interest by a single product of catalyst effectiveness for a completely wetted pellet and fraction of external area wetted as suggested by Mears (1974).

PROPOSED APPROXIMATE MODEL

Based on the assumptions cited in the previous section, the basic differential mass balance for the trickle-bed reactor is

$$F_o dx = r_{RV} dV = r_{cvi}\,\eta_{TB}\,(1-\epsilon) \tag{1}$$

Owing to the fact that most of the liquid reactants are practically nonvolatile at the operating conditions used, and that often one deals with dilute reactants, for example, in desulfurizations, it can be assumed that the reaction is liquid reactant limited and proceeds only on the catalyst surface effectively wetted by liquid. If one assumes a uniform pore size distribution, then the fraction of internal

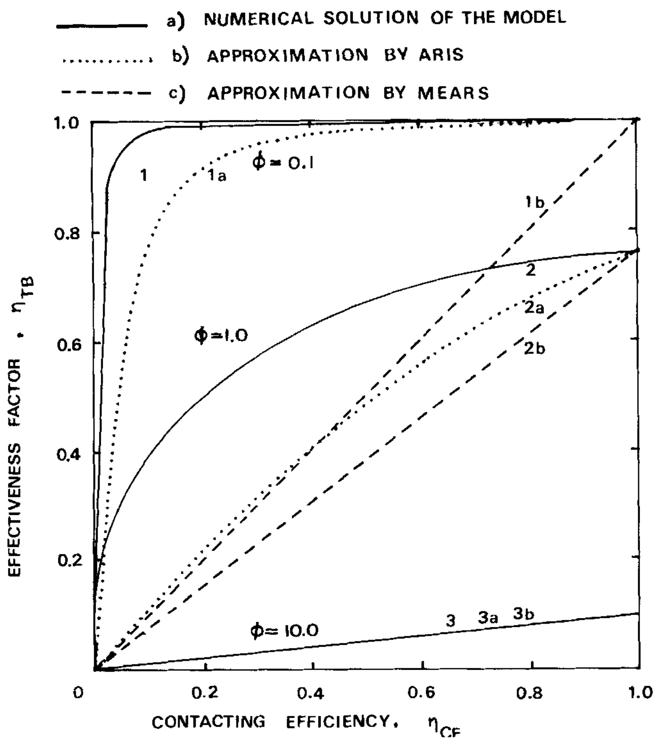

Fig. 1. Effectiveness factor in partly externally wetted catalyst pellets.

catalyst area wetted is equal to the fractional pore fill-up. Under these conditions, the effectiveness factor for a partially wetted catalyst pellet in a trickle-bed reactor for a reaction occurring only in the liquid filled pore region of the pellet can be defined by

$$\eta_{TB} = \frac{\text{(actual rate on a partially wetted pellet)}}{\left(\begin{array}{l}\text{ideal maximum rate at bulk conditions}\\ \text{on a completely wetted pellet}\end{array}\right)}$$

$$= \frac{\text{(actual rate per unit volume of partially wetted pellet)}}{\left(\begin{array}{l}\text{ideal maximum rate per unit volume of completely}\\ \text{wetted pellet}\end{array}\right)} \times \left[\begin{array}{l}\text{fraction of}\\ \text{pellet actually}\\ \text{internally}\\ \text{wetted}\end{array}\right] \tag{2}$$

It has been established earlier (Aris, 1957) that in two-phase systems the effectiveness factor for particles of irregular shape can be represented by

$$\eta_T = \frac{\tanh \phi_T}{\phi_T} \tag{3}$$

where the Thiele modulus ϕ_T for first-order reaction is

$$\phi_T = \frac{V_P}{S_{\text{ext}}} \sqrt{\frac{k_{tc}}{D_{\text{eff}}}} \tag{4}$$

The above expression leads at steady state conditions to acceptable results with errors not exceeding 20% (Aris, 1975).

This approach can now be extended to the incompletely wetted catalyst particle in trickle beds by viewing such a particle as being of irregular shape, where the volume contributing to reaction is V_{eff} and the effective external area over which the reactant is supplied is S_{eff}. If η_{CE} and η_i represent the fraction of external area wetted and the fraction of internal volume wetted, respectively, then the modified modulus becomes

$$\phi_{TB} = \frac{\eta_i}{\eta_{CE}} \phi_T \tag{5}$$

The effectiveness factor in trickle-bed reactors is now obtained by substituting Equation (5) into Equation (3) and by using the latter one in Equation (2):

$$\eta_{TB} = \eta_i \frac{\tanh\left(\dfrac{\eta_i}{\eta_{CE}} \phi_T\right)}{\dfrac{\eta_i}{\eta_{CE}} \phi_T} = \eta_{CE} \frac{\tanh\left(\dfrac{\eta_i}{\eta_{CE}} \phi_T\right)}{\phi_T} \tag{6}$$

The integrated form of Equation (1) should be thus modified to read

$$\ln\left(\frac{1}{1-x}\right) = \frac{V(1-\epsilon)}{Q_L} k_{tc}\, \eta_{TB} \tag{7}$$

and should replace the expressions of Table 1.

This demonstrates that the catalyst effectiveness factor for liquid first-order reaction is a function of the ratio of the characteristic internal diffusion and reaction time ϕ_T, external contacting efficiency η_{CE}, and internal pore fill-up η_i. Expression (6) reduces to the product of $\eta_{CE}\eta_T$, as used by Mears (1974) only if $\phi_T >> 1$ or $\eta_i/\eta_{CE} \approx 1$.

$$\phi_T >> 1; \quad \eta_{TB} \sim \frac{\eta_{CE}}{\phi_T} = \eta_{CE}\, \eta_T \tag{6a}$$

In the first case, the internal pore diffusional limitations are severe, and the effectiveness factor is very low; thus reaction occurs only in a narrow zone (shell) close to the exterior surface.

$$\eta_i/\eta_{CE} = 1; \quad \eta_{TB} = \eta_{CE}\, \eta_T \tag{6b}$$

The second case implies that the pores in the catalyst pellet are not interconnected and that the fraction of internal wetting corresponds to external wetting. This in general is not the case when dealing with real catalysts and hydrocarbon feeds.

For small modulii, that is, very slow reactions, expression (6) reduces to

$$\eta_{TB} \approx \eta_i \left[1 - \frac{1}{3}\left(\frac{\eta_i}{\eta_{CE}} \phi_T\right)^2\right] \tag{6c}$$

The ratio of the maximum reaction rate and the maximum rate of internal diffusional transport, that is, the Thiele modulus ϕ_T, determines whether the catalyst effectiveness factor will be primarily affected by external or internal incomplete wetting. For large modulii, η_{CE} is the dominant variable, for small modulii, η_i becomes the important parameter. This conclusion is in agreement with common sense judgment. At large internal diffusional resistance ($\phi_T >> 1$), reaction occurs in a narrow zone close to the external surface, and the utilization of the catalyst is proportional to the fraction of external area wetted (η_{CE}) over which the reactant is supplied to the reaction zone. In completely kinetically controlled regime ($\phi_T << 1$), catalyst utilization is proportional to the internal volume wetted (η_i) since even a diminished wetted external area does not reduce the transport of reactants sufficiently to affect the rate.

The exact mathematical analysis of the effectiveness factor in partially wetted catalyst pellets is beyond the scope of this paper and will be presented elsewhere. However, as an illustration, the numerical solution for the effectiveness factor of an exact model for a completely internally and partly externally wetted catalyst of slab geometry is compared to the approximate formula based on the work of Aris (1957) and suggested in this paper and to the expression of Mears (1974). The comparison is presented in Figure 1. Aris' (1957) formula can be used as a lower bound except at very low modulii and extremely low external wetting. Mears' (1974) expression is valid only for high modulii ($\phi_T \geqq 10$).

CONCLUSIONS

Catalyst effectiveness factor in trickle-bed reactors is a function of the Thiele modulus ϕ_T, incomplete external wetting η_{CE}, and fractional pore fill-up η_i. An approximate formula derived in this paper accounts for all three variables. This indicates that the evaluation of contacting efficiencies by applying reactor performance equations to reaction studies is prone to numerous errors. In order to predict catalyst effectiveness factors, some independent means of evaluating η_{CE} and η_i (Schwartz et al., 1976) have to be used. In general, existing correlations for η_{CE} are unsatisfactory (Schwartz et al., 1976), and correlations for η_i are nonexistent. Fractional pore fill-up will depend on catalyst pore structure and physical properties (particularly surface tensions) of the gas-liquid-solid system involved. Failure to recognize that either η_{CE} or η_i, depending on the range of ϕ_T, are the primary variables affecting catalyst effectiveness in trickle-bed reactors may explain the difficulties previously encountered in interpreting trickle-bed data based on expressions in Table 1.

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NOTATION

A = constant in Equation (T2*b*)
A' = constant in Equation (T2*a*)
b = constant in Equations (T2)
D_{eff} = effective diffusivity of the liquid reactant in catalyst particle, cm^2 s^{-1}
d_p = diameter of catalyst pellet, cm
E_z = axial dispersion coefficient, cm^2 s^{-1}
F_o = inlet molar feed rate of the liquid reactant, moles^{-1}
$f = \dfrac{U_L d_p}{2D_{\mathrm{eff}}(1-\epsilon)}$ = parameter in Equation (T5*c*), dimensionless
H_{TL} = total liquid holdup, cm^3 liquid/cm^3 reactor, dimensionless
k_f = external mass transfer coefficient, cm s^{-1}
k_v = reaction rate constant, cm^3 liquid/cm^3 catalyst and second, s^{-1}
k_{tc} = true reaction rate constant, s^{-1}
L_m = liquid superficial mass velocity, g cm^{-2}s^{-1}
LHSV = liquid hourly space velocity, hr^{-1}
$N_{Bo} = \dfrac{U_L\, d_p}{2E_z}$ = Bodenstein number for axial dispersion in question (T5*a*), dimensionless
$N_{St} = \dfrac{3(1-\epsilon)k_f}{U_L}$ = Stanton number in Equation (T5*b*), dimensionless
Q_L = liquid flow rate, cm^3 s^{-1}
r_{RV} = reaction rate per unit reactor volume, mole cm^{-3} s^{-1}
r_{cvi} = maximum reaction rate at bulk conditions per unit volume of completely wetted catalyst pellet, mole cm^{-3} s^{-1}
S_{eff} = effectively wetted external area of catalyst pellets, cm^2
S_{ext} = total geometric external area of catalyst pellets, cm^2
U_L = liquid superficial velocity, cm s^{-1}
V = reactor volume, cm^3
V_{eff} = effectively wetted volume of catalyst pellets, cm^3
V_p = total geometric volume of catalyst pellets, cm^3
x = fractional conversion of the liquid reactant, dimensionless
z = axial distance in the reactor, cm

Greek Letters

ϵ = bed porosity, cm^3 voidage/cm^3 reactor, dimensionless
η_{CE} = external contacting efficiency, fraction of external area wetted, dimensionless
η_i = fractional pore fill-up, dimensionless
η_T = catalyst effectiveness factor given by Equation (3), dimensionless
η_{TB} = catalyst effectiveness factor in trickle-bed reactors, dimensionless
Λ_1, Λ_2, Λ_3 = parameters defined in Equations (T5), dimensionless
ν = kinematic viscosity, cm^2 s^{-1}
σ = surface tension of liquid, dyne cm^{-1}
σ_c = critical surface tension of the solid defined as the liquid surface tension at which cosine of the contact angle equals one, dyne cm^{-1}
$\tau_{1/2}$ = actual space time required to reach 50% conversion, s
$\tau^c{}_{1/2}$ = space time at complete wetting required for 50% conversion, s
ϕ_T = Thiele modulus defined by Equation (4), dimensionless
ϕ_{TB} = modified modulus in trickle beds defined by Equation (5), dimensionless
$\omega = \dfrac{2z}{d_p}$ = axial coordinate, dimensionless

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An Improved Corresponding States Method For Liquid Heat Capacities

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In a recent paper (Tarakad and Danner, 1977) we have discussed the development of a new set of corresponding states parameters for nonpolar and polar fluids. These parameters were used to correlate both pure and cross second virial coefficients. In this paper we discuss the use of the new parameters in correlating configurational liquid heat capacities.

The fourth parameter Φ, developed in the previous paper, was defined in terms of the second virial coefficient. We, therefore, assume that this parameter accounts for the polar contribution to the interactions involving two molecules at a time. However, while Φ is based on two-body interactions, it is to be used primarily as an indicator of overall polar and association effects. The magnitude of these effects may be assumed to be proportional, whether we are concerned with two-, three-, or more body interactions. Thus, the two-body measure may well be expected to be able to correlate the overall effects of polarity.

DEVELOPMENT OF THE CORRELATION

Using a theoretical equation developed by Rowlinson (1959), Bondi (1966) obtained the following semitheoretical correlation for the configurational liquid heat capacity of normal fluids:

$$\frac{C_\sigma - C_p{}^o}{R} = 2.56 + \frac{0.436}{1 - T_r} + \delta\left[17.11 + \frac{25.2}{T_r}(1 - T_r)^{1/3} + \frac{17.42}{1 - T_r}\right] \quad (1)$$

where δ is related to the Pitzer acentric factor by $\delta = 0.40\omega$. This equation (usually referred to as the Rowlinson-Bondi equation) was developed using data on liquid argon. Though Equation (1) has not been widely used, it does offer an excellent starting point for developing a correlation for standard fluids. (See our previous paper for the definition of standard fluids.)

In the newly developed corresponding states formulation, the radius of gyration $\overline{R}$ is the size-shape parameter. A functional form identical to Equation (1) will not adequately fit standard fluid data when $\overline{R}$ is used in place of δ as the size-shape parameter. This is because of the nonlinear relationship between $\overline{R}$ and δ (or ω, the Pitzer acentric factor). Several modifications of Equation (1) were tried so as to best fit a selected set of experimental points for fifty-eight standard fluids in the temperature range $0.35 < T_r < 0.96$. The following equation was chosen:

$$\left[\frac{C_\sigma - C_p{}^o}{R}\right]_{\substack{\text{standard}\\ \text{fluid}}} = 1.136 + \frac{0.297}{1 - T_r} + \frac{0.718(1 - T_r)^{1/3}\overline{R}}{T_r} + \frac{0.012\,\overline{R}^2}{T_r} + 1.01\,T_r{}^3\overline{R} \quad (2)$$

All the data used were for the saturated liquid. Since this already fixes one degree of freedom, Equation (2) contains no terms in P_r.

When $\overline{R}$ is zero (that is, for simple, monoatomic fluids), Equation (2) does not correctly represent the data on liquid argon. By replacing the constant 1.136 by 2.85, however, C_σ for argon can be predicted with only 0.7% average deviation. Thus, for simple fluids, the recommended equation is

$$\left[\frac{C_\sigma - C_p{}^o}{R}\right]_{\substack{\text{simple}\\ \text{fluids}}} = 2.85 + \frac{0.297}{1 - T_r} \quad (3)$$

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