where

$$\sigma = \alpha_o \sqrt{\frac{k}{\varphi}}\,|\nabla p|$$

may be useful for calculating the flow of a non-Newtonian fluid through porous media. Here, the dimensionless viscosity ratio $F(\sigma)$ is determined from capillary measurements and the constant α_o from a few measurements on linear cores for each rock type. (In principle, a single measurement is sufficient.)

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Ideas similar to those presented here but not available at the time have been given by T. J. Sadowski (*3*) and Stanley Middleman (*4*) where specific rheological models are assumed for the non-Newtonian fluid.

NOTATION

k = permeability, millidarcies
k_o = superposition permeability, millidarcies
p = pressure, atm.
r = radius, cm.
v = velocity, cm./sec.
A = area, sq. cm.
F = dimensionless viscosity ratio
L = length, cm.
Q = volumetric flow rate, cc./sec.
R = capillary radius, cm.
V = average pore velocity, cm./sec.
V_o = fluid superficial velocity, cm./sec.
α_o = superposition constant, cm./millidarcies$^{1/2}$
φ = porosity
σ = shear stress, g./sq. cm., lb./sq. in.
μ = viscosity, cp.
$\mu(\sigma_R)$ = apparent or tube average viscosity, cp.
μ_o = apparent viscosity (cp.) at a given reference value of shear stress

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The Influence of Surface Coverage on Catalytic Effectiveness and Selectivity. The Isothermal and Nonisothermal Cases

JOHN HUTCHINGS and JAMES J. CARBERRY

University of Notre Dame, Notre Dame, Indiana

Both nonisothermal and isothermal catalytic effectiveness factors are computed for kinetic rate laws of the Langmuir-Hinshelwood, Hougen-Watson type, involving surface coverage by reactant and products. Selectivity taxation is also treated and the significant influence of interphase heat and mass gradients surrounding the catalyst is displayed. The complexities of these real kinetic systems suggest caution in the use of prior generalizations based upon simpler rate laws.

Many analytical and numerical solutions have been set forth to assess quantitatively the influence of intraparticle heat and mass diffusion upon catalytic activity (*1*, *3*, *5* to *18*) and selectivity (*1*, *3*, *4*, *11*, *16*, *18*). While isothermal effectiveness and selectivity alteration are readily determined for linear kinetics by analytical means, nonlinear kinetic schemes and nonisothermality within the catalyst have required approximate solution or digital/analog simulation. It appears, however, that the most typical form of the catalytic rate law, that of Langmuir-Hinshelwood as elaborated, extended, and refined by Hougen and Watson, has not received attention commensurate with its prominence.

Implicit in the Langmuir-Hinshelwood, Hougen-Watson (L-H, H-W) model* is the notion of surface coverage by reactants and/or products, which coverage is essential to reaction. Clearly, simple first-order kinetics prevail for the reaction $C \rightarrow P$ when surface coverage by reactant and product is small, that is

$$\theta = \frac{K_1C}{[1 + K_1C + K_pP]} \rightarrow K_1C \text{ for } 1 >> K_1C + K_pP$$

then rate $= k\theta = kK_1C$.

Under these circumstances the isothermal effectiveness as well as the nonisothermal event is predictable in the light of prior work. However, while K_p may be large, yet

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* We are not defending the intrinsic reality of L-H, H-W implications, but merely recognizing its qualitative merit in the sense that Boudart has suggested.

James J. Carberry is at the University of Cambridge, Cambridge, England (1965-66).

K_pP negligible for low product concentration throughout a porous catalyst, it is clear that in the diffusion limited case a gradient in C is accompanied by a gradient in P such that P increases with depth of penetration. Thus the rate may be first order at the pore mouth yet within the pellet follow the nonlinear law.

$$\text{rate} = \frac{kK_1C}{1 + K_pP} \tag{1}$$

It would seem, then, that catalytic effectiveness treatments which ignore the real world of surface occupancy may be of limited utility to those engaged in the analysis and design of catalytic systems governed by kinetics more complex than can be expressed by first- or second-order laws.

As noted by Satterfield and Sherwood (*10*), the effects of intraparticle diffusion upon complex kinetic schemes such as the Hougen-Watson type have not been studied in a general way. Chu and Hougen (*5*) considered the isothermal case describing the surface catalyzed oxidation of nitric oxide which involved adsorption of reactant nitric oxide as intermediate, as well as product nitrogen dioxide. Charts are presented displaying isothermal effectiveness factors for this and comparable systems.

Petersen (*9*) established a criterion for diffusion influence applicable to isothermal reaction involving inhibition by product. Roberts and Satterfield (*12*) have presented a comparatively general treatment of isothermal effectiveness for Hougen-Watson kinetics. However, in view of the number of parameters (rate constants, diffusivities, adsorption coefficients) which characterize typical surface rate laws, no hope exists of generalizing concisely nonisothermal effectiveness for such systems, no less selectivity. General trends can be detected, however, for both isothermal and nonisothermal circumstances in terms of surface coverage by reactant and/or product.

DETAILS

Consider the system $C \rightarrow P$ governed by the rate expression

$$\text{rate} = \frac{kK_1C}{1 + K_1C + K_pP} \tag{2}$$

Rephrased in dimensionless form where $f = C/C_o$, the diffusion-reaction relation is

$$C_o D \nabla^2 f = \frac{k K_1 C_o f}{[1 + (K_1C_o - K_pC_o)f + K_pC_o(p + 1)]} \tag{3}$$

By assuming a flat plate geometry and specifying its half thickness in terms of a sphere $L = R/3$, Equation (3) then becomes

$$\frac{d^2f}{dz^2} = \left(\frac{R^2 k_o}{9 D C_o}\right) \frac{K_1C_o f \cdot \exp\left[-\frac{E}{RT_o}\left(\frac{T_o}{T} - 1\right)\right]}{[1 + K_1C_o - K_pC_o)f + K_pC_o\,(p + 1)]} \tag{4}$$

where $p = P_o/C_o$ and $z = X/L$. The modified Thiele modulus is, then

$$\psi = \frac{R}{3}\sqrt{\frac{k_o}{D C_o}} \tag{5}$$

while the effectiveness factor η is

$$\eta = \frac{\left(\frac{df}{dz}\right)_{z=1}}{\psi^2} \frac{[1 + (K_1C_o - K_pC_o) + K_pC_o\,(p + 1)]}{K_1C_o} \tag{6}$$

The thermal energy equation is ($y = T/T_o$)

$$\frac{d^2y}{dz^2} = \frac{L^2(-\Delta H)}{\lambda\, T_o}\,(\text{rate}) \tag{7}$$

which when combined with (4) defines

$$\beta = \frac{C_o}{T_o}\frac{(-\Delta H)D}{\lambda} \tag{8}$$

while $k = k_o \exp\left[\frac{-E}{RT_o}\left(\frac{1}{y} - 1\right)\right]$

The absorption coefficients are considered to be relatively temperature independent. Thus the absorption coefficients and the parameters ψ, β, and E/RT_o govern the nonisothermal effectiveness. Equations (4) and (7) were solved with a UNIVAC 1107, employing the implicit technique of Thomas which permits stable solution with a flux boundary condition (2). In this case (3)

$$z = 1 \begin{cases} f = 1 + \dfrac{1}{(N_{Nu})_m}\left(\dfrac{df}{dz}\right)_{z=1} \\ y = 1 + \dfrac{1}{(N_{Nu})_h}\left(\dfrac{df}{dz}\right)_{z=1} \end{cases} \tag{9}$$

$$z = 0 \quad df/dz = dy/dz = 0$$

where

$$(N_{Nu})_m = \frac{k_gL}{D} \text{ and } (N_{Nu})_h = \frac{hL}{\lambda} \tag{10}$$

Sample results are presented in Figures 1 and 2 for $(N_{Nu})_m = (N_{Nu})_h = \infty$. In each figure both the exothermal and isothermal effectiveness factors are displayed for cases illustrating the influence of increasing product adsorption under conditions of modest coverage by reactant (Figure 1, $K_1C_o = 1$), and in Figure 2, an instance in which strong adsorption of reactant exists ($K_1C_o = 10$).

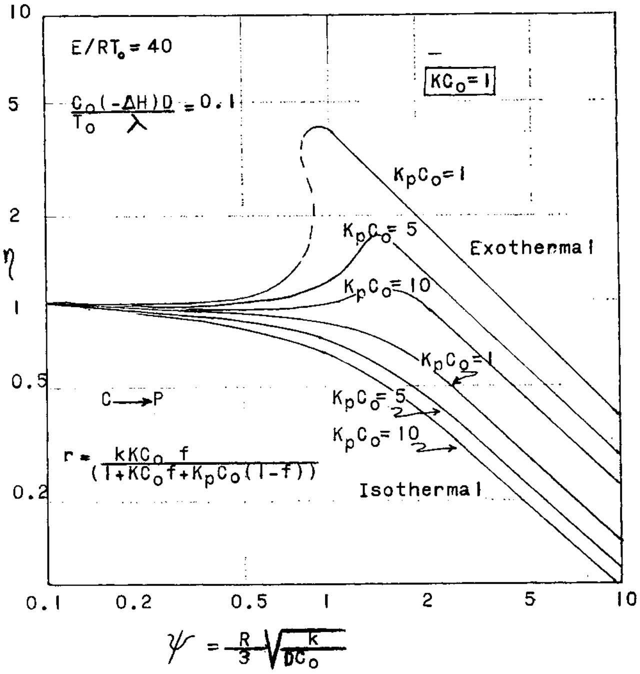

Fig. 1. Influence of product adsorption upon nonisothermal and isothermal intraparticle effectiveness for L-H,H-W rate model involving modest coverage by reactant.

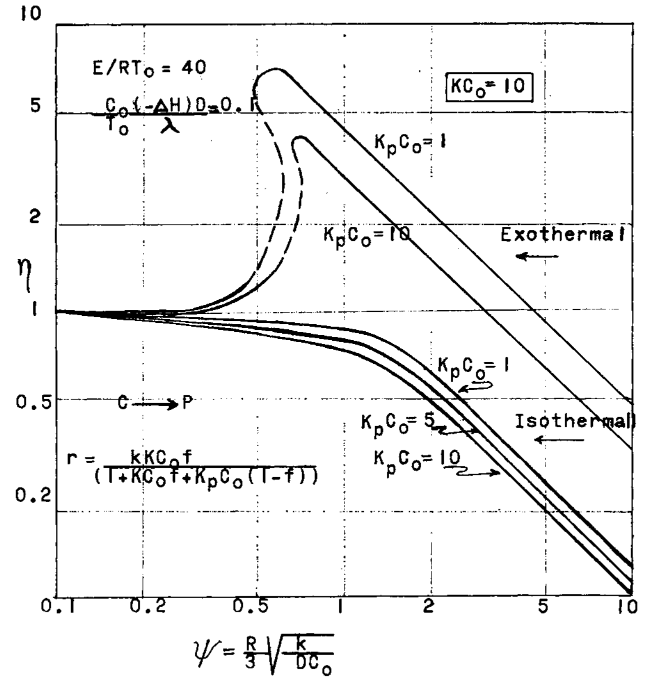

Fig. 2. Influence of product adsorption upon nonisothermal and isothermal intraparticle effectiveness for L-H,H-W rate model involving high coverage by reactant.

In Figure 3 the influence of interphase transport of heat and mass upon intraparticle effectivenes is displayed for a specific case involving a bulk phase mass transfer limitation $[(N_{Nu})_m = 1]$ in the absence of an interphase heat transfer limitation $[(N_{Nu})_h = \infty]$, and a fluid phase heat transfer limitation $[(N_{Nu})_h = 1]$. In all figures the dashed regions correspond to the instability regimes discussed by Weisz and Hicks (*17*).

DISCUSSION

The interphase gradient effects are marked, particularly that due to the fluid phase heat transfer limitation $[(N_{Nu})_h = 1]$. Effectiveness is enhanced some thirtyfold, while an interphase mass transport limitation reduces the nonisothermal effectiveness by about a factor of 5. The reference case is, of course, effectiveness in the absence of both mass and temperature gradients in the fluid film bathing the catalyst. In any system the mass transfer Nusselt number is related to its heat transfer analog by

$$(N_{Nu})_h = (N_{Nu})_m \frac{\rho C_p D}{\lambda}$$

which for reasonable values of $\rho C_p D/\lambda$ for gases and catalysts commonly encountered, suggests that $(N_{Nu})_m \cong 10^3 (N_{Nu})_h$. Consequently, a system found to be free of interphase mass gradients may well be characterized by a small and influential value of the heat transfer Nusselt number.

Given the rather dramatic influence of $(N_{Nu})_h$ upon effectiveness, one might expect that variations in ψ caused by particle size variation, for example, will generate reaction rate particle size data exhibiting a sudden rate increase at a critical particle size. Such a phenomenon has been observed by Fulton and Crosser (*6*).

In the case where $(N_{Nu})_m = (N_{Nu})_h = \infty$, Figures 1 and 2 reveal that increasing product adsorption reduces effectiveness in general, and specifically, the system characterized by modest surface coverage by reactant is inhibited more severely by product than one characterized by strong adsorption of reactant.

As surface reaction rate is proportional to surface coverage by reactant it is instructive to consider θ values as a function of f for the range of adsorption coefficients under consideration.

K_IC_o	K_pC_o	θ_o vs. f $f =$ 1	0.5	0.1
1	1	0.5	0.25	0.05
1	10	0.5	0.077	0.009
10	1	0.91	0.77	0.34
10	10	0.91	0.45	0.09

Viewed in the light of reactant surface coverage and its alteration due to product adsorption, the trends manifested in Figure 1 and 2 are not unexpected.

Further, for given values of β, E/RT, ψ, and modest product adsorption, the nonisothermal effectiveness is greater for the Hougen-Watson kinetic form than is found in the simple first-order system treated by Carberry (*3*), Metzner (*14*), and Weisz and Hicks (*17*). As the Hougen-Watson form can often be approximated by a power law rate formulation

$$\frac{kc}{1 + KC} \cong k'C^n \qquad (11)$$

where $n < 1$, than the fact that higher η values are found simply reflects the fact that the apparent kinetics approach zero order with increasing reactant adsorption. For zero order kinetics display the highest effectiveness, while higher and negative orders (strong product adsorption) reveal lower effectiveness factors for given values of the diffusion reaction moduli.

These conclusions may be further supported by considering another surface process, for example, olefin hydrogenation. Such an example also permits an assessment of reactant species diffusivity differences. Consider the rate law

$$\text{rate} = \frac{k(A)(B)}{(1 + K_BB)} \qquad (12)$$

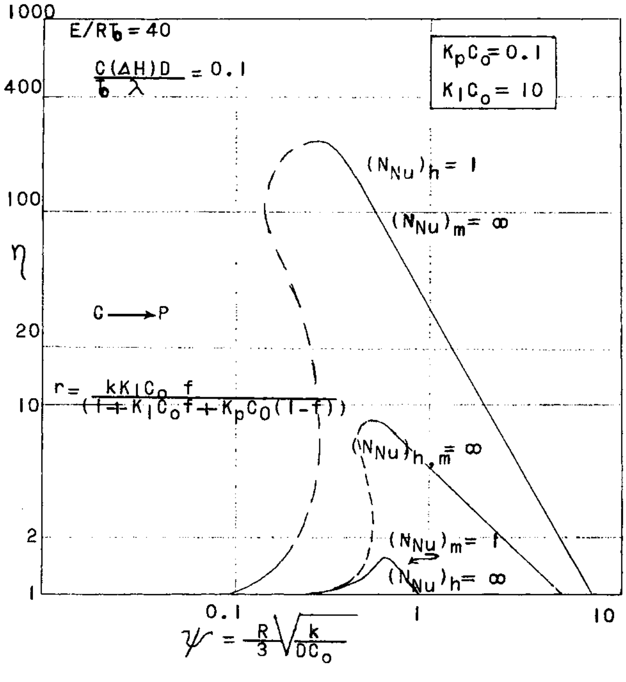

Fig. 3. Influence of interphase heat $(N_{Nu})_h$ and mass $(N_{Nu})_m$ transport upon nonisothermal intraparticle effectiveness.

for $\psi_a = 1$ and $\psi_B = 1.93$ ($D_B/D_A = \gamma = 3.74$) the following results are obtained under isothermal conditions.

A_o/B_o	K_B	η
1	0	0.465
3	0	0.48
3	0.5	0.57
3	1	0.66
3	5	0.96

If equality of reactant diffusivities is assumed the computed effectiveness is 0.64 for $K_B = 0$. It is evident that in this bimolecular case, pseudo first-order kinetics are approached with increasing values of K_B.

SELECTIVITY IN COMPLEX H-W SYSTEMS

The influence of intraparticle diffusion under isothermal (*4, 9, 10, 16, 18*) and nonisothermal (*1, 3, 11*) conditions for yield sensitive reactions such as

$$A \rightarrow B \rightarrow C$$

is well known for cases involving simple kinetics, that is, first order. Consider the case

$$A + B \overset{k_1}{\rightarrow} C \overset{k_2}{\rightarrow} G$$

where a Rideal mechanism prevails, that is, gaseous A reacts with adsorbed B. Specifically, let

$$\text{rate} = -\frac{dA}{dt} = \frac{A \cdot B \cdot (4.68) \exp\left[-17.63\left(\frac{1}{y} - 1\right)\right]}{[1 + 10^{-2} B + 5 \times 10^{-3} C + 10^{-1} G]} \tag{13}$$

that is, G, the undesired by-product is more strongly absorbed than reactants or product C. The rate constant ratio $k_1C_o/k_2 = 4$, $E/RT_o = 17.63$ for each step,* and $\beta = 0.03$. With a diffusion limitation product C is prone to further undesired reaction, creating G which reduces surface coverage (inhibition), which in turn reduces the rate of formation of C. For this specific case, the nonisothermal point yield of product C, dC/dA, is tabulated below for particle radii of 1 and 2 mm.

Particle radius	Ψ_a	η_a	η_c	η_G	dC/dA	ΔT
1 mm.	1	0.7	0.62	2.9	0.89	5.5°C.
2 mm.	2	0.42	0.31	4.8	0.72	14°C.

These computed results dramatize the influence of both heat and mass transport as well as inhibition upon yield of a desired intermediate. While those factors contributing to yield loss are not isolated here, a comparison with the first-order consecutive system (*3*) for the same values of ψ_1, and ψ_2 indicates a 93% yield under isothermal-diffusion free conditions, and a 92% nonisothermal yield for values of β and E/RT identical to the L-H, H-W case for a 1 mm. particle radius. Evidently, complex kinetics involving inhibition by a product leads to further yield loss. Other more complex yield sensitive schemes presently are being assessed in our program.

CONCLUSIONS

Intraparticle heat and mass gradients affect Langmuir-Hinshelwood, Hougen-Watson rate formulations in a complex fashion. Some general trends can be qualitatively anticipated. However, the simple cases set forth and analyzed in this paper suggest caution in dealing with these reaction schemes. Reaction order can vary with position within a porous particle giving rise to activity and selectivity alterations not anticipated with precision in prior analyses which are limited to reactions involving low surface coverage.

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NOTATION

A, B, C, G, P = molecular species or concentration
C_o = bulk fluid phase reactant concentration
D = intraparticle diffusivity
E = activation energy
f = reduced concentration C/C_o
ΔH = reaction enthalpy change
k = rate constant
k_g = bulk mass transfer coefficient
K_1 = reactant adsorption coefficient
K_p = product adsorption coefficient
L = average single pore length = $R/3$
n = reaction order
$(N_{Nu})_m$ = mass transport Nusselt number, k_gL/D
$(N_{Nu})_h$ = heat transport Nusselt number, hL/λ
p = ratio of initial product to reactant P_o/C_o
R = radius of spherical catalyst or gas constant
T = absolute temperature
X = distance within pore
y = reduced temperature T/T_o
z = reduced pore depth X/L

Greek Letters

β = heat generation parameter, Equation (8)
γ = species diffusivity ratio
ψ = Thiele modulus, Equation (5)
η = catalytic effectiveness factor, Equation (6)
θ = surface coverage
λ = thermal conductivity of pellet

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* Clearly, if $E_1 > E_2$ an intraparticle $+\Delta T$ enhances yield of C, the intermediate.