# Optimum Effectiveness Factors for Porous Catalysts

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**In the manufacture of catalyst pellets from particles of powder, for example alumina, one of the parameters is pellet density. The opposing effects of density on surface available for reaction and on pore diffusion result in a specific pellet density for maximum reaction rate per unit volume of reactor. The method for predicting the optimum density and rate is presented for a first-order reaction. The data required are pore volumes and pore-size distributions as a function of density, as well as kinetic measurements. Such data are available for the ortho-para hydrogen reaction using a nickel oxide-on-alumina catalyst. Using this system as an illustration, it can be seen that the optimum effectiveness factors are less than unity and range from about 0.68 for ⅛-in. diam. spherical catalyst pellets to 0.29 for 1-in. pellets. Corresponding optimum densities are from about 1.3 to 0.6 g./cc.**

**The results demonstrate the possibility of a tailor-made pelleted catalyst for optimum reaction rate.**

When catalyst pellets are prepared from particles of catalyst powder, one of the variables is pellet density. For example, particles of alumina are commonly used as a carrier for metal and oxide catalysts. When such particles are compressed to form a pellet of high density, the diffusion resistance is relatively high because the macropore (space between particles volume) and mean diameter are both relatively small. Contrariwise, the reaction resistance is comparatively low because the high density provides a large surface available for reaction. For low-density pellets the macropore volume and diameter are large so that the diffusion resistance is low. However, the reduced mass of the pellet corresponds to a low surface area, and, hence, a high reaction resistance. The direct proportionality of mass and surface area results because the external surface of the particles is negligible with respect to the surface of the micropores within the particles. This is illustrated by data (2) for alumina pellets which show that the surface area, per unit mass, is essentially constant over a wide density range.

Because of these opposing effects there should be, for some reaction-catalyst systems, an optimum pellet density; that is, a density for which the reaction rate per pellet, $r_p$, would be a maximum. When the bulk void fraction in the catalyst bed is known, this rate can be converted to the more important design criterion of a maximum rate per unit volume of reactor $r_v$. There exists also an optimum effectiveness factor ($E_a$), not necessarily unity, which corresponds to the optimum density.

## RATE PER UNIT VOLUME OF REACTOR, $r_v$

If $n$ is the number of catalyst pellets per unit volume

$$r_v = n\, r_p \tag{1}$$

For spherical pellets in a catalyst bed of void fraction $\epsilon_B$

$$n = \frac{(1 - \epsilon_B)}{4/3\, \pi\, R_p^3} \tag{2}$$

Hence

$$r_v = \frac{1 - \epsilon_B}{4/3\, \pi\, R_p^3}\, r_p \tag{3}$$

The rate per pellet can be expressed in terms of the specific reaction rate per unit surface and an effectiveness factor $E_a$ for the macropores. Thus

$$r_p = k_s\, S_g\, (\rho_p\, 4/3\, \pi\, R_p^3)\, E_a\, f(y) \tag{4}$$

where the concentration function $f(y)$ depends upon rate equation; that is, first order, or more complicated form. Including $E_a$ permits the function to be in terms of concentrations at the external surface of the pellet. Since the rate expression used in Equation (4) is based upon a concentration measured as mole fraction, $y$, the specific reaction rate $k_s$ is a function of pressure as well as temperature. In general the value of $k_s$ would be a function of diffusion in the micropores within the catalyst particles (powder particles) and the specific rate constant on the surface of the micropores. However, the particles are generally small enough to make the micropore diffusion resistance negligible (3).

For isothermal and isobaric conditions, $k_s S_g$ is constant for variations in pellet density or radius $R$. The product is the specific reaction rate per unit mass of catalyst, $k_w$. Hence from Equations (3) and (4)

$$\frac{r_v}{(1 - \epsilon_B)\, f(y)} = k_w\, \rho_p\, E_a \tag{5}$$

The left side of Equation (5) is a measure of the rate per unit volume of reactor. When it is applied to pellets of the same size, the effect of density is manifested through its effect on $\rho_p$ itself, and on $E_a$. The effect of pellet size is determined solely through its effect on the macroeffectiveness factor, since $\epsilon_B$ is essentially independent of pellet size.

The relationship between $\rho_p$ and $E_a$ depends upon the macropore volume and pore size. This is a specific relationship since it is a function of the kind of carrier and amount and type of catalyst. However, the problem can be presented in a general form if the variables are taken as the diffusivity $D$ and density of the pellet. For example, for a first-order reaction the relationship between $E_a$ and $R_p$, $\rho_p$, and $D$ is given by the equations

$$E_a = 3\, \frac{h \coth h - 1}{h^2} \tag{6}$$

$$h = R_p \sqrt{\frac{k_w\, \rho_p\, RT}{DP}} \tag{7}$$

These equations are adaptations of the work of Thiele and Wheeler with $D$ related to the macropore volume and mean pore radius (3). Equations (5) to (7) can be conveniently represented graphically by plotting $r_v/f(y)$ as a function of $h$ and the dimensional group $Y = \rho_p\, k_w$. Such a plot is shown in Figure 1 for a limited range of values for the two parameters. Since the void fraction of fixed-bed reactors is

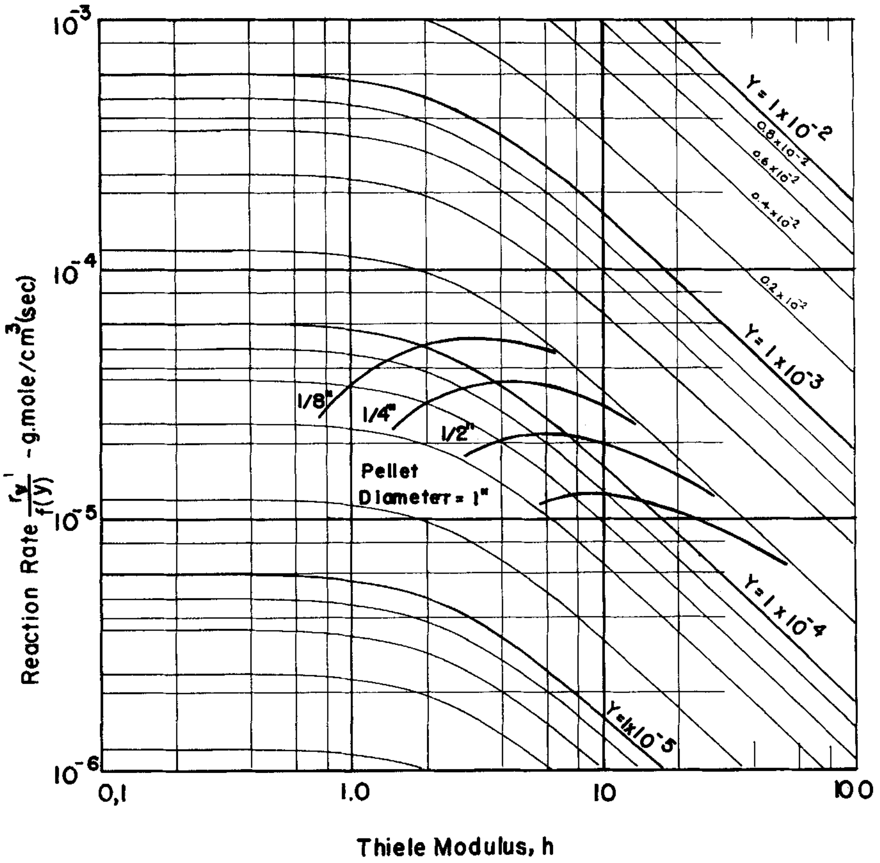

Fig. 1. Reaction rate as a function of parameters *y* and *h*.

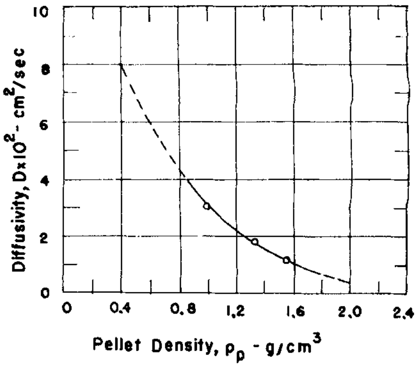

Fig. 2. Diffusivity-density relationship for nickel oxide and aluminum oxide catalyst.

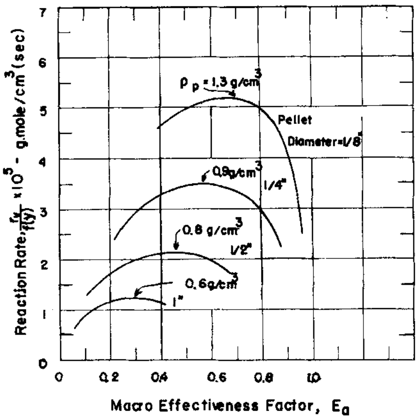

Fig. 3. Optimum reaction rate and effectiveness factor for hydrogen conversion (nickel oxide on aluminum oxide catalyst).

close to 0.4, the plot is based upon this value for $\epsilon_B$. The choice of a value for $\epsilon_B$ could be avoided by plotting the entire left side of Equation (5) as the ordinate in Figure 1.

Not all values of *h* and *Y* in Figure 1 are permissible. This is because the density of the pellet affects the diffusivity. The specific relationship is determined by the reaction-catalyst system. A quantitative treatment has been developed and tested for alumina pellets (*3*). For a first-order reaction, with equal-molal counter diffusion of reactant and product and no micropore diffusion resistance, the result is

$$D = \frac{\epsilon_a^2}{\frac{1}{D_b} + \frac{1}{\overline{D}_{ka}}} + \frac{\epsilon_i^2(1 + 3\epsilon_a)}{1 - \epsilon_a} \; \frac{1}{\frac{1}{D_b} + \frac{1}{\overline{D}_{ki}}} \qquad (8)$$

When the density of the pellet changes, $\epsilon_a$, $\epsilon_i$, and $\overline{D}_{ka}$ vary; the latter quantity changes because the mean macropore radius changes. On the other hand, the micropores are not affected* so that $\overline{D}_{ki}$ is constant. Hence for the case in mind, Equation (8) determines the permissible value of *D*, and therefore *h*, for a given density. To determine *h* and $\rho_p k_w$ for a series of densities requires pore volume and pore-size distribution data for the pellets over the density range. The result is a curve superimposed on Figure 1 showing the allowable values of *h, Y, and* $r_v/f(y)$. The effect of size of pellet would be indicated as a separate curve for each pellet diameter.

## ILLUSTRATION FOR ORTHO-PARA HYDROGEN CONVERSION

The use of Figure 1 to evaluate the optimum pellet density requires $k_w$, as well as the macropore volumes and sizes. Sufficient information of this kind was recently obtained (*1*) for the ortho-para hydrogen reaction to illustrate the method. Pellets of three different densities of nickel oxide on aluminum oxide were studied at −196°C. and 1 atm. pressure. The reaction-rate measurements, to obtain $k_w$, and pellet geometry data were first employed to determine the diffusivity-density curve shown in Figure 2. Then permissible values of *h* were obtained for each $\rho_p$ using Equation (7). Calculations were carried out for pellet diameters of 1/8 in., 1/4 in., 1/2 in., and 1 in., and the results are shown by the heavy lines in Figure 1. Each curve represents the effect of pellet density and shows an optimum rate per unit volume of reactor. As expected, the optimum rate increases as the pellet diameter decreases.

While not indicated on Figure 2 there is a specific density and effectiveness factor for each pellet size. These values are given in Figure 3 which shows $r_v/f(y)$ vs. $E_a$. The optimum effectiveness factors vary from about 0.68 for the 1/8 in. diam. pellet down to 0.29 for the 1 in. size. For this system of relatively fast reaction rate, high $k_w$, and small macropores, the optimum effectiveness factors are significantly less than unity. Optimum densities for each pellet size are shown on the curves.

## CONCLUSIONS

It has been shown than an optimum density may exist for catalysts prepared by pelleting microporous particles. This presents the possibility of tailor-making catalyst pellets to give a maximum reaction rate per unit volume of reactor and, hence, an optimum reactor design. The data needed to determine the optimum density are pore volumes and pore-size distributions. Routine and rapid methods are readily available for making such measurements. Therefore, whenever diffusion resistances are significant it would be rewarding to accompany rate studies with these physical measurements.

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* If the pelleting pressure is high enough, the microporous particles presumably can be crushed. Data for alumina (*2*) indicate that this does not occur except at an extremely high pressure.

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## NOTATION

$D$ = effective diffusivity in catalyst pellet, sq.cm./sec.
$\overline{D}_{ka}$ = mean Knudsen diffusivity in the macropores, sq.cm./sec.
$\overline{D}_{ki}$ = mean Knudsen diffusivity in the micropores, sq.cm./sec.
$D_b$ = bulk diffusivity, sq.cm/sec
$E_a$ = effectiveness factor (macropores) for catalyst pellet
$f(y)$ = concentration function representing order of reaction
$k_w$ = specific reaction rate, g. mole/(sec.) (g. of catalyst) for first-order reaction, based upon concentration measured as mole fraction
$k_s$ = specific reaction rate, g. mole/(sq.cm. of catalyst surface) (sec.) for first-order reaction
$h$ = Thiele parameter for catalyst pellet
$n$ = number of pellets per unit volume of reactor
$P$ = total pressure, atm.
$r_p$ = rate of reaction per pellet, g. moles/sec.
$r_v$ = rate of reaction per unit volume of reactor, g. moles/(sec.) (cc.)
$R$ = gas constant, (cc.) (atm.)/(g. mole) (°K.)
$R_p$ = radius of spherical catalyst pellet, cm.
$S_g$ = surface area of catalyst per unit mass, sq.cm./(g. of catalyst)
$T$ = temperature, °K.
$y$ = mole fraction
$Y$ = $k_w \rho_p$, g. mole (sec.) (cc. of pellet)
$\epsilon_B$ = void fraction in bed of catalyst pellets
$\epsilon_a$ = macropore void fraction within catalyst pellet
$\epsilon_i$ = micropore void fraction within catalyst pellet
$\rho_p$ = density of catalyst pellet

## LITERATURE CITED

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3. Wakao, Noriaki, and J. M. Smith, "Diffusion and Reaction in Porous Catalysts," submitted to *Ind. and Eng. Chem., Fund. Quarterly.*

# INFORMATION RETRIEVAL*

**Estimation of enthalpies: multicomponent hydrocarbon mixtures at their saturated vapor and liquid states,** Stevens, W. F., and George Thodos, **A.I.Ch.E. Journal, 9,** No. 3, p. 293 (May, 1963).

**Key Words:** Enthalpy-2, Mixtures-10, Hydrocarbons-10, Paraffins-10, Saturated Vapor-10, Saturated Liquid-10, Nonideal Behavior-10, Reduced Temperature-1, Critical Compressibility Factor-1, Enthalpy Corrections-10, Distillation Calculations-10, Digital Computers-10, Molecular Weight-6.

**Abstract:** Relationships between enthalpy and temperature at zero pressure have been developed for the normal paraffins through octane in their gaseous states. The enthalpies of mixtures of these substances can be established from the enthalpies and mole fractions of the individual components. A method is also presented for the calculation of the enthalpies of these mixtures in their saturated liquid and vapor states. Enthalpies calculated by the methods of this study were found to be in excellent agreement with experimental data.

**Continuous models for polymerization,** Zeman, Ronald, and Neal R. Amundson, **A.I.Ch.E. Journal, 9,** No. 3, p. 297 (May, 1963).

**Key Words:** Polymerization-8, Mechanism-8, Reactions-8, Reactors-8, Equations-8, Calculus-10, Numerical-10, Distribution-8, Design-10, Computers-10.

**Abstract:** In polymerization systems, conceptually, an infinite number of reactions take place. The mathematical description of such systems leads to infinite sets of rate equations. In this paper, a new technique for solving these equations is presented. The technique considers the degree of polymerization as a continuous variable, and reduces the infinite set of algebraic equations of a continuous stirred tank reactor to a single ordinary differential equation and the infinite set of ordinary differential equations of a batch reactor to a single partial differential equation. These differential equations are solved for a variety of polymerization mechanisms. Numerical examples are included.

**Effect of carbon monoxide in causing nonuniform gasification of graphite by carbon dioxide,** Austin, L. G., and P. L. Walker, Jr., **A.I.Ch.E. Journal, 9,** No. 3, p. 303 (May, 1963).

**Key Words:** Carbon-1, Carbon Dioxide-1, Carbon Monoxide-2, Kinetics-7, Mass Transfer-6, Gasification-8.

**Abstract:** The effect of internal mass transport on the reaction of porous carbons with carbon dioxide was considered employing a rate equation, rate $= k_1 p_{CO_2}/(1 + k_2 p_{CO} + k_3 p_{CO_2})$. The equation of combined mass transport and chemical effects was solved numerically, using rate constants from the literature. The results showed that nonuniformity of reaction can exist where the usual Thiele criteria for integer order reactions would predict uniform rate.

**The laminar-turbulent transition for fluids with a yield stress,** Hanks, Richard W., **A.I.Ch.E. Journal, 9,** No. 3, p. 306 (May, 1963).

**Key Words:** Critical Reynolds Number-2, Onset of Turbulence-7, 8, Laminar-Turbulent Transition-7, Annuli-8, Parallel Plates-8, Pipe Flow-8, Hedstrom Number-2, 6, Bingham Plastic Flow-6, Powell-Eyring Model-1, 6, Fluid Flow-6, Stability of Flow-7, Stability Parameter-2, 7, Bingham Plastic Model-1, 6, Yield Stress-6, Visco-Plastic Flow-6.

**Abstract:** Theoretical expressions are presented for the critical Reynolds number for flow of Bingham fluids in pipes and concentric annuli and between parallel plates. The calculations for pipe flow agree well with literature data for $N_{He} < 10^5$ where $N_{He} = \rho \tau_0 d^2/\eta^2$.

Discrepancies between the data and calculations for large Hedstrom numbers are explained as owing to the inadequacy of the Bingham model. Calculations performed using the more realistic Powell-Eyring model, for a set of data having $N_{He} > 10^6$, resulted in closer agreement between theory and experiment, confirming the plausibility of the failure of the Bingham model.

(*Continued on page 423*)

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* For details on the use of these key words and the A.I.Ch.E. Information Retrieval Program, see **Chem. Eng. Progr., 57,** No. 5, p. 55 (May, 1961), No. 6, p. 73 (June, 1961); **58,** No. 7, p. 9 (July, 1962).