

NOTES

Low-Pressure Operation of the Union Carbide Gradientless Reactor

A gradientless reactor, developed at Union Carbide Corporation by J. M. Berty and co-workers (1,2), has been described for use in studying the catalytic kinetics of high pressure, moderate temperature, vapor phase reactions. A modified reactor that has been used successfully at higher temperatures (to 1100°F) has also been reported (3). By rapid internal recycling of the vapor phase the reactor is capable of performing at near-commercial conditions (temperature, pressure, mass velocity, etc.) or at nearly gradientless conditions, i.e., no external pellet heat or mass transfer limitations.

Berty (1) has recommended that a lower pressure limit of 45 psig be used "because at lower pressure and corresponding low gas densities it is difficult to maintain good mass velocities." High mass velocities are required to minimize the thickness of the stagnant boundary layer between the external catalyst surface and the bulk gas phase. However, for laboratory reactors, higher pressures are frequently neither desired nor convenient.

Experience with the modified gradientless reactor at Purdue (4) has shown that it can also be used at low pressure, i.e., 1 atm, provided certain conditions are met. It is the purpose of this note to point out some of the characteristics of this reactor under low-pressure operation where truly gradientless conditions may be difficult to achieve.

The reactor approximates a perfectly mixed vessel at atmospheric pressure and

over a wide range of temperatures, inlet flow rates, and impeller speeds. The flow profile, checked by a method similar to that described by Smith (5) and Berty (1) was found to be uniform across the bed as long as the recycle ratio was greater than about 20.

The only reliable method for determining whether bulk-to-surface heat or mass transfer limitations are significantly influencing the measured kinetics is by experimentation. This was tested by the CO oxidation by O₂ over chromia-silica catalyst granules 4 mm in diameter. Various temperatures and chromia loadings were used. Variation in the impeller speed from 750 to 1500 rpm produced a negligible change in the outlet CO₂ concentration provided that the reaction rate remained below about 3.3 (10⁻⁷) kg mol CO₂/s kg catalyst. At higher reaction rates the exit CO₂ concentration varied significantly with the linear velocity (mass flux) indicating heat and/or mass transfer limitations.

Since these experiments can be rather time consuming it would be preferable if there were a method whereby these heat and mass transfer gradients could be estimated a priori from pertinent catalyst and reaction parameters. Such a method will now be described.

The recycle mass flow rate can be estimated from a thermodynamic calculation (1,3). Assuming an adiabatic catalyst bed, the heat generated during a steady-state reaction is equal to the heat removed by the

recycle flow.

$$\Delta \dot{n} \Delta H = \dot{m} C_p \Delta T. \quad (1)$$

By measuring the change in moles of reactant and the temperature difference across the bed during reaction, the mass flow rate can be determined from Eq. (1).

Heat and mass transfer coefficients can now be calculated using the Colburn j_H and j_D correlations described by Bird *et al.* (6). These factors are then substituted into the following heat and mass balance equations over the catalyst pellet.

$$Q = r \rho_B \Delta H = h a \Delta T, \quad (2)$$

$$N_i = r \rho_B \nu_i = k_i a \Delta X_i. \quad (3)$$

The ΔT and ΔX_i can now be calculated directly. The mass flow rate has been previously estimated by Eq. (1) to be about 10^{-3} kg/s at 1500 rpm (2000 rpm is maximum impeller speed) and a vapor density of 0.84 kg/m³ (4). Assuming perfect gas behavior, this value will vary directly with either vapor density or impeller speed (750–2000 rpm) provided that large frictional resistances are not present (1). All of the previous calculations can now be combined to yield the following overall equations to estimate the temperature and concentration differences.

The constants in these equations are only valid for the original and modified-high-temperature reactor designs (1,2,3). On a more recent design both the size of the catalyst basket and the shape of the impeller were altered. Therefore, although the functionalities of the following equations remain the same, the constants must be reevaluated. The catalyst bed cross-sectional area of 1.79 (10^{-3}) m² was used to obtain the correlation for the mass velocity, G . The L/D_p factors should be included only when L/D_p exceeds 4; other-

wise the factors should be replaced by unity.

$$\text{Re} = \frac{G}{a \psi \mu} = \left[\frac{79.9 (10^{-6}) \frac{MP}{T} \left(\frac{\text{rpm}}{1500} \right) \left(\frac{4}{L/D_p} \right)^{\frac{1}{2}}}{a \psi \mu} \right] < 50, \quad (4)$$

$$\Delta T = 112 \frac{r \rho_B \Delta H \text{Pr}^{\frac{1}{3}}}{C_p (a \psi)^{1.51} (\mu)^{0.51}}$$

$$\times \left(\frac{T}{MP} \right)^{0.49} \left(\frac{\text{rpm}}{1500} \right)^{-0.49} \left(\frac{4}{L/D_p} \right)^{-0.25}$$

$$\Delta X_i = 47 (10^3) \frac{r \rho_B \nu_i}{(a \psi)^{1.51} (\text{Dim})^{0.67} \left(\frac{\mu}{M} \right)^{0.16}} \times \left(\frac{T}{P} \right)^{1.16} \left(\frac{\text{rpm}}{1500} \right)^{-0.49} \left(\frac{4}{L/D_p} \right)^{-0.25}, \quad (5)$$

Re > 50,

$$\Delta T = 428 \frac{r \rho_B \Delta H \text{Pr}^{\frac{1}{3}}}{C_p (a \psi)^{1.41} (\mu)^{0.41}} \times \left(\frac{T}{MP} \right)^{0.59} \left(\frac{\text{rpm}}{1500} \right)^{-0.59} \left(\frac{4}{L/D_p} \right)^{-0.30}, \quad (6)$$

$$\Delta X_i = 181 (10^3) \frac{r \rho_B \nu_i}{(a \psi)^{1.41} (\text{Dim})^{0.67} \left(\frac{\mu}{M} \right)^{0.26}} \times \left(\frac{T}{P} \right)^{1.26} \left(\frac{\text{rpm}}{1500} \right)^{-0.59} \left(\frac{4}{L/D_p} \right)^{-0.30}. \quad (7)$$

Equations (4) and (5) or (6) and (7) can now be used to calculate reasonable approximations to the temperature and concentration differences between the catalyst surface and vapor phase. All parameters in equations (4)–(7) are easily obtainable except for the reaction rate, which must be estimated beforehand. A sample calculation

utilizing the previous reaction data,

$$\begin{aligned}
 T &= 515^\circ\text{K}, \\
 P &= 10^5 \text{ N/m}^2 (\approx 1 \text{ atm}), \\
 r_{\text{PB}} &= 2.2 (10^{-4}) \text{ kg mol/s m}^3 \text{ cat}, \\
 a\psi &= 945 \text{ m}^{-1}, \\
 \mu &= 31 (10^{-6}) \text{ kg/m s}, \\
 M &= 36.1, \\
 \Delta H &= -286 (10^6) \text{ J/kg mol}, \\
 C_p &= 710 \text{ J/kg }^\circ\text{K}, \\
 \text{Pr} &= 0.68, \\
 X_{\text{CO}_2} &= 0.036, \\
 D_{\text{CO}_2\text{-Ar}} &= 4.1 (10^{-5}) \text{ m}^2/\text{s}, \\
 &60\% \text{ Ar diluent,} \\
 &1500 \text{ rpm,}
 \end{aligned}$$

yields $\Delta T = 0.6^\circ\text{K}$ and $\Delta X_{\text{CO}_2} = 6.9 (10^{-5})$. Clearly, this is near the limit of gradientless operation, which is consistent with the experimental results mentioned earlier.

Equations (4) and (5) or (6) and (7) show the effects of changing catalyst and reaction parameters, and they yield the limit of reaction conditions available for gradientless operation of the Union Carbide Reactor.

List of Symbols

a	Interfacial area per unit volume of bed, m^{-1}
C_p	Bulk gas heat capacity, $\text{J/kg }^\circ\text{K}$
Dim	Effective gas-phase binary diffusivity of i , m^2/s
L	Catalyst bed depth, m
G	Mass flux, $\text{kg/m}^2 \text{ s}$
h	Heat transfer coefficient, $\text{W/m}^2 \text{ }^\circ\text{K}$
k	Mass transfer coefficient, $\text{kg mol/m}^2 \text{ s}$
D_p	Catalyst particle diameter, m
\dot{m}	Mass flow rate, kg/s
M	Average molecular weight of vapor
N_i	Molar flux of species i , $\text{kg mol/m}^2 \text{ s}$
P	Pressure, N/m^2
Pr	Prandtl number
Q	Rate of heat production, $\text{J/m}^3 \text{ s}$
r	Reaction rate, $\text{kg mol CO}_2/\text{s kg catalyst}$
Re	Modified Reynolds number, $G/a\psi\mu$

rpm	Impeller revolutions per minute
T	Temperature, $^\circ\text{K}$
ΔH	Heat of reaction, J/kg mol
$\Delta \dot{n}$	Absolute reaction rate, kg mol/s
ΔT	Temperature difference between external catalyst surface and vapor phase, $^\circ\text{K}$
ΔX_i	Composition difference between external catalyst surface and vapor phase, species i
μ	Viscosity, kg/m s
ν_i	Stoichiometric coefficient
ρ_B	Catalyst bed density, kg/m^3
ψ	Empirical coefficient depending on particle shape (γ): spheres, 1.00; cylinders, 0.91

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