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Oxidation of Naphthalene in Packed-Bed Reactor with Catalyst Activity Profile: A Design Scheme for Improved Reactor Stability and Higher Product Yield

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Vapor phase catalytic oxidation of naphthalene to phthalic anhydride using air is usually carried out in packed-bed tubular reactor at 350° to 400°C. Under the same conditions, phthalic anhydride also undergoes oxidation, giving undesirable products. Both the reactions are extremely exothermic.

The heat of reactions is removed by using molten salt as a coolant. However, owing to high exothermicity of the reactions, the temperature rises sharply in the catalyst bed to a maximum (hot spot temperature) and subsequently decreases. To prevent rapid catalyst deterioration, the hot spot temperature must be kept within bounds while a generally high temperature is maintained throughout the remainder of the reactor to give high conversion. In practice this means the reactor must be operated near the unstable region. This causes critical problems because the hot spot is very sensitive to the inlet temperature and inlet naphthalene concentration. Small increases in the latter variables can cause a normally stable reactor to become unstable, leading to runaway and explosion.

Calderbank et al. (1969) and Caldwell and Calderbank (1969) suggested the use of a mechanical mixture of inert and active catalyst pellets to reduce the activity in the front part of the bed in order to control the temperature and thereby increase the stability of the reactor. Apparently, this technique with graded beds of increasing catalytic activity has been used for many years industrially, but little has been written about it.

An alternate approach is to dilute a catalyst with inerts prior to pelleting in order to produce a series of catalysts with similar catalytic characteristics but of reduced activity. Koros and Nowak (1967) have suggested this means of varying the activity of a catalyst. This latter approach, with a diluted catalyst used, has several advantages over the mechanical mixture of inert and active pellets referred to herein as the diluted bed.

The practical problem of nonuniform distribution of catalyst and inert pellets is possible with diluted beds. A distribution having too many active pellets in close proximity in the hot spot region could lead to reactor instability, particularly when a small ratio (8 to 10) of reactor to particle diameter is used as in the case of

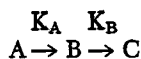
naphthalene oxidation. This problem will be entirely avoided if diluted catalysts are used. Also, the use of diluted catalysts will make the temperature between the catalyst and the bulk gas lower than the corresponding difference in a diluted bed of catalyst, because the external heat transfer area is increased for the diluted catalyst proportional to the dilution ratio. This is particularly important in the vicinity of the hot spot and leads to a more stable reactor. A comparison of two catalyst beds of the same activity per unit volume of reactor will show that the bed composed of diluted catalyst will have the smaller Thiele parameter than one formed by diluting the bed with inerts; consequently, the selectivity for the reaction system with the intermediate as the desired product will be higher for the diluted catalyst (Wheeler, 1951), particularly in the region of the hot spot. Indeed, Watanabe et al. (1968) oxidized o-xylene to phthalic anhydride for a prolonged period using a reactor with four different activities, product selectivity being about 20% higher than for the reactor with uniform but relatively high activity. The higher selectivity is partly due to the use of catalyst with lower activity and partly due to reduced hot spot temperature. As far as handling the pellets, loading the reactor, and regeneration of catalyst bed are concerned, it seems that there is no advantage of one approach over the other.

It appears, therefore, that reactors with pellets of diluted catalyst offer greater opportunities for increased stability and selectivity than mechanical mixtures of active and inert pellets, and as a consequence attention will be given to how the diluted catalyst activity should be distributed in the bed. It appears that superior performance is associated with catalyst bed having four different activities, a short section of high activity to start the reaction, a longer section of substantially reduced activity in the vicinity of the hot spot zone to induce stability, followed by sections of increasing activity to give high conversion. This will be compared to beds of uniform activity.

KINETICS AND REACTOR MODEL

The reactions involved during naphthalene oxidation can be represented as

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where A is naphthalene, B is phthalic anhydride, and C is the oxidation products of B. Also, based on experimental observations by different workers, the rates for both the steps have been taken to be first order in the corresponding species and zero order in oxygen concentration, since oxygen is in large excess (more than an order of magnitude).

In case of naphthalene oxidation, radial temperature differences of 20° to 45°C have been reported. The temperature differences of such magnitude necessitate the consideration of the radial variation of temperature in the modeling of the reactor, particularly when the stability of the reactor is being considered (Carberry and White, 1969).

In the model, a steady state plug flow reactor having cylindrical symmetry and pseudo homogeneous rate expression (Petersen, 1965) is used. The axial conduction of heat and the axial eddy dispersion of heat and mass are taken to be negligible compared to the convective transport. Also, the inlet temperature for the reactants is taken to be the same as the coolant temperature, which is constant. Based on calculations, the effectiveness factor for the catalyst pellet is assumed constant but not unity.

The conservation equations describing the reactor with the above assumptions can be written as

$$-\frac{\partial Y_A}{\partial \eta} + \left(\frac{d_p}{R_o}\right) \left(\frac{L}{R_o}\right) \frac{1}{Pe_{MR}} \left[\frac{\partial^2 Y_A}{\partial \xi^2} + \frac{1}{\xi} \frac{\partial Y_A}{\partial \xi} \right] - \frac{\overline{ML}}{\rho_o U_o} R_A \epsilon_A = 0 \quad (1)$$

$$-\frac{\partial Y_B}{\partial \eta} + \left(\frac{d_p}{R_o}\right) \left(\frac{L}{R_o}\right) \frac{1}{Pe_{MR}} \left[\frac{\partial^2 Y_B}{\partial \xi^2} + \frac{1}{\xi} \frac{\partial Y_B}{\partial \xi} \right] + \frac{\overline{ML}}{\rho_o U_o} [R_A \epsilon_A - R_B \epsilon_B] = 0 \quad (2)$$

$$-\frac{\partial \tau}{\partial \eta} + \left(\frac{d_p}{R_o}\right) \left(\frac{L}{R_o}\right) \frac{1}{Pe_{HR}} \left[\frac{\partial^2 \tau}{\partial \xi^2} + \frac{1}{\xi} \frac{\partial \tau}{\partial \xi} \right] + \frac{L}{\rho_o U_o C_p T_o} [(-\Delta H_A) R_A \epsilon_A + (-\Delta H_B) R_B \epsilon_B] = 0 \quad (3)$$

The boundary and initial conditions are

$$\begin{aligned} \frac{\partial Y_A}{\partial \xi} = \frac{\partial Y_B}{\partial \xi} = 0, \quad \frac{\partial \tau}{\partial \xi} = 0 \quad \text{at} \quad \xi = 0 \\ \frac{\partial Y_A}{\partial \xi} = \frac{\partial Y_B}{\partial \xi} = 0, \quad -k_e \frac{\partial \tau}{\partial \xi} = R_o h_w (\tau - \tau_c) \quad \text{at} \quad \xi = 1 \\ Y_A = Y_{Ao}, \quad Y_B = 0, \quad \tau = 1 \quad \text{at} \quad \eta = 0 \end{aligned}$$

In the above equations

$$\begin{aligned} R_A &= K_A C_A = K_A (\rho_M Y_A) \\ &= (1 - \epsilon) \rho_s S_p K_A' \exp\left(-\frac{E_A}{R_g T}\right) (\rho_M Y_A) \quad (4) \end{aligned}$$

$$\begin{aligned} R_B &= K_B C_B = K_B (\rho_M Y_B) \\ &= (1 - \epsilon) \rho_s S_p K_B' \exp\left(-\frac{E_B}{R_g T}\right) (\rho_M Y_B) \quad (5) \end{aligned}$$

In the present work, the term activity means the product of all the terms before the exponential in Equations

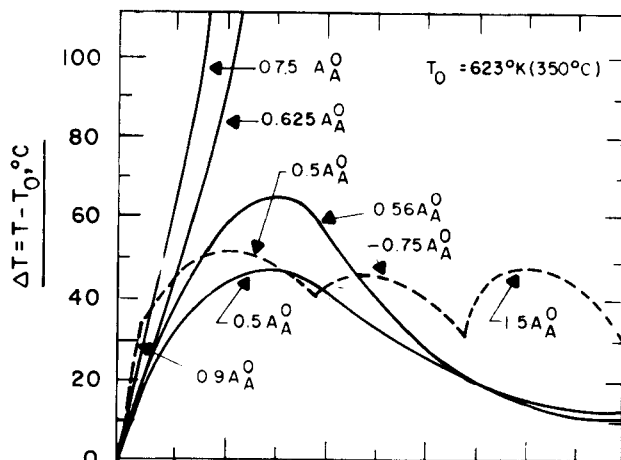


Fig. 1. Comparison of axial temperature profiles.

TABLE 1. PARAMETERS USED IN THE MODEL

d_p	$= 2.54 \times 10^{-3} \text{ m}$	E_A	$= 83.7 \times 10^3 \text{ J/g mole}$
D_t	$= 2.54 \times 10^{-2} \text{ m}$	E_B	$= 180.0 \times 10^3 \text{ J/g mole}$
L	$= 3.05 \text{ m}$	ϵ	$= 0.4$
Pe_{MR}	$= 10$	A_A^o	$= 4.97 \times 10^6 \text{ 1/s}$
Pe_{HR}	$= 10.74$	A_B^o	$= 1.20 \times 10^{13} \text{ 1/s}$
G	$= 1.35 \text{ kg/m}^2 \cdot \text{s}$	P_o	$= 2.03 \times 10^5 \text{ N/m}^2$
h_w	$= 127.8 \text{ J/s/m}^2 \cdot \text{K}$	Y_{Ao}	$= 0.75\%$
k_e	$= 0.61 \text{ J/s} \cdot \text{m} \cdot \text{K}$	T_o	$= 623^\circ \text{K or } 628^\circ \text{K}$
ΔH_A	$= -1886 \times 10^3 \text{ J/g mole}$	T_c	$= 623^\circ \text{K or } 628^\circ \text{K}$
ΔH_B	$= -3268 \times 10^3 \text{ J/g mole}$	ϵ_A	$= 0.96$

(4) and (5). Furthermore, since K_A/K_B is quite large and ϵ_A is close to unity, ϵ_B has been assumed to be unity.

To take into account the change in concentration of A and B due to pressure drop during flow through packed bed, the Ergun equation (Bird et al., 1960) was solved simultaneously with the above equations. The differential equations were solved numerically by using the Crank-Nicholson six-point technique (Lapidus, 1962). The activity profile used in the present work was chosen by a trial-and-error approach. The parameters used in the representative computations presented here are listed in Table 1.

RESULTS AND DISCUSSION

The axial temperature profiles for uniform and non-uniform activities are shown in Figure 1. The temperature profile for the relatively low uniform activity exhibits the typical maximum or hot spot temperature. The extreme sensitivity of the temperature maximum leading to instability or runaway due to small increases in activity is also exhibited. Lower uniform activities correspond to increased stability but, of course, at the expense of conversion for the same reactor length.

For the reactor with four different layers of catalyst activity the temperature profile is more uniform (Figure 1). The first short length of high activity gets the reaction started, and a second larger length is of reduced activity to maintain stability while successive layers of increased activity permit increased conversion. It is also of interest that the lower activity in Section II stabilizes the reactor, even though Section I contains a very active catalyst. Watanabe et al. (1968) in their experimental work used four catalysts having relative activities of 0.45, 0.68, 0.85, and 1.0 contained in 8, 17, 33, and 42% of the reactors respectively, the activities increasing monotonically from the reactor entrance.

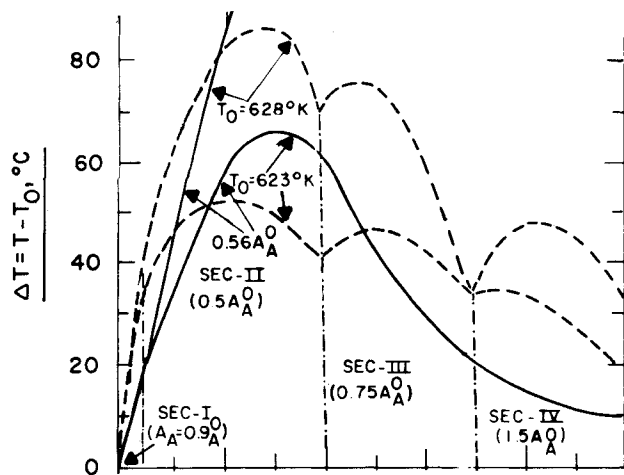


Fig. 2. Effect of inlet temperature perturbation on the axial temperature profile.

Figure 1 further shows that the hot spot zone contains three times less activity relative to the highest activity per unit volume. If a reactor with mixture of catalyst and inert pellets is used, one out of every three pellets would be active in this zone. By comparing this distribution with that in a reactor having variable activity catalyst, it appears, as mentioned in the introduction, that the latter approach would enhance selectivity and stability.

The effects of perturbation of the inlet temperature on the axial temperature profile for the uniform and nonuniform activity are shown in Figure 2, the uniform activity of $0.56 A_A^0$ being chosen for comparison. Although the reactor with uniform activity is stable at an inlet temperature of 623°K , it becomes unstable when the inlet temperature is increased to 628°K . However, under the same conditions the reactor with nonuniform activity profile is stable at both temperatures.

The product yield for the above two reactors has been compared in Figure 3. A meaningful basis for comparison is to consider product yield for reactors having the same amount of activity. Hence the comparison is at $\eta = 1$ and $\eta = 0.78^*$ for the uniform and nonuniform beds, respectively. Accordingly, the overall yield is 5% higher for the nonuniform reactor, although this reactor is 22% smaller than the uniform one. Although the overall selectivity for the reaction under consideration was about the same with both the reactors, experimental results of Watanabe et al. (1968) demonstrate that very pronounced increase of selectivity can be achieved by using reactors with variable activity bed for other industrially important reactions. Thus, the nonuniform reactor corresponds to much better stability, significantly smaller length, substantially increased yield, and in many cases higher overall selectivity. All these facts make the nonuniform reactor preferable to the uniform one.

NOTATION

A_A, A_A^0 = activity and reference activity for $A \rightarrow B$
 C_A, C_B = concentration of A, B
 C_p = heat capacity of reaction mixture
 d_p, D_t = diameter of catalyst pellet and reactor tube
 E_A, E_B = activation energy
 G = superficial mass velocity
 h_w = heat transfer coefficient at the reactor wall
 $\Delta H_A, \Delta H_B$ = heat of reaction
 K_A', K_B', K_A, K_B = intrinsic rate coefficient, global rate coefficient
 k_e = effective thermal conductivity of catalyst bed

* This comes from: $(0.05)(0.9) + (0.35)(0.50) + (0.30)(0.75) + (0.08)(1.5) = 0.56$ and $0.05 + 0.35 + 0.30 + 0.08 = 0.78$.

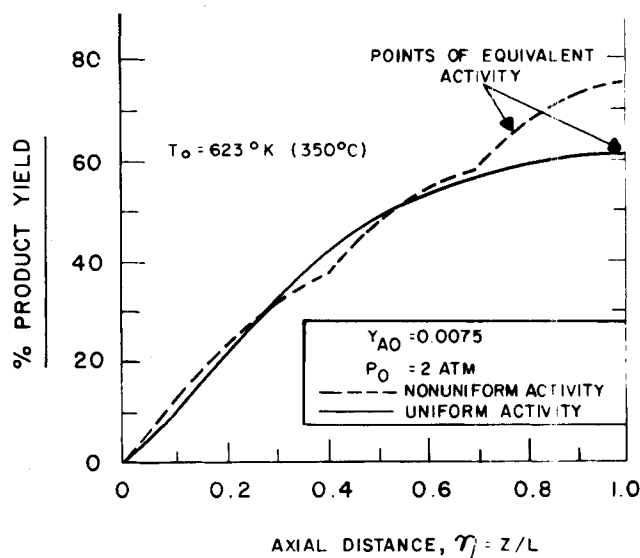


Fig. 3. Product yield of phthalic anhydride for the reactor with uniform and nonuniform catalyst activities.

L = length of the reactor tubes
 \bar{M} = average molecular weight of the feed mixture
 P_0 = inlet pressure
 Pe_{MR}, Pe_{HR} = Peclet number for mass, heat transfer in radial direction
 r = radial coordinate
 R_A, R_B = rate of reaction
 R_0 = radius of reactor tubes
 S_p = specific surface of catalyst pellet
 T_0, T_c = inlet temperature, coolant temperature
 U_0 = inlet superficial velocity
 Y_A, Y_B = dimensionless concentration, $C_A/\rho_M, C_B/\rho_M$
 z = axial coordinate

Greek Letters

ϵ_A, ϵ_B = catalyst effectiveness factor
 ϵ = porosity of catalyst bed
 ξ = dimensionless radial distance r/R_0
 η = dimensionless axial distance, z/L
 τ, τ_c = dimensionless temperature, $T/T_0, T_c/T_0$
 ρ_0 = density of feed mixture
 ρ_M = molar density of feed mixture
 ρ_s = density of catalyst particle

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