ν = kinematic viscosity, $(\text{length})^2/\text{time}$
ξ = scaled tangential distance, Equation (6)
ρ = density, $\text{mass}/(\text{length})^3$
σ = $\gamma\Delta\omega/\beta\Delta\theta$
τ = shear stress at surface, $\text{force}/(\text{length})^2$
ϕ_1, ϕ_2 = variables defined by Equations (4) and (5)
ω, ω_S, ω_∞ = mass fraction of component undergoing transfer, mass fraction at surface, mass fraction far from surface

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Combined Reactors: Formulation of Criteria and Operation of a Mixed Tubular Semifluidized Reactor

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Combined reactors in which the mixed reactor is followed by a tubular reactor can be optimal for a large number of simple adiabatic exothermal reactions. In the present paper, optimality criteria defined earlier for simple reactions involving a single reactant species have been extended to reactions involving two reactant species and for a system of consecutive reactions.

The oxidation of benzene has been studied in an adiabatic semifluidized mixed tubular (MT) reactor. A definite improvement is possible when the oxidation is carried out in this reactor, as observed by a comparison of the experimental results obtained in tubular, mixed, and MT reactors under adiabatic conditions.

The methods of optimizing the performance of a chemical reactor by introducing a temperature sequence in the case of stirred tank reactors and imposing an external temperature gradient in the case of tubular reactors have been described by Denbigh (*7*) who has also summarized (*8*) other important contributions in this area. In addition, the behavior of mixed and tubular reactors can also form a valuable basis for optimizing reactor performance.

In an elaborate analysis of mixing, Cholette, Blanchet, and Cloutier (*5, 6*) considered the case of a reactor which is partially mixed. The system was analyzed in terms of fully mixed and plug flow zones, and short circuiting was omitted from the analysis. The performance of a partially mixed reactor would then be determined by the location of the fully mixed zone in the reactor. Two cases were considered: the fully mixed zone is present in the first part of the reactor and the second part is in tubular flow, and the first part of the reactor is in tubular flow while the second part is fully mixed. These two combinations were called, respectively, MT and TM combinations. Equations were then proposed for simple chemical reactions of different kinetics to predict the performance of MT and TM combinations under isothermal conditions.

These investigators also considered adiabatic systems (again for simple reactions) and formulated equations for the optimum combination of the mixed and tubular portions of a combined reactor. The studies were then extended by Aris (*1*) and by Douglas (*9*) who presented the criteria for optimal combination for reactions in which a single reactant species is involved. Trambouze and Piret (*15*) have discussed the use of combined reactors for a system of three competing parallel reactions.

King (*13*) considered the MT combination and proposed equations for calculating the optimum combination under conditions where provision was made for cooling in the mixed zone and an intercooler between the two stages.

No experimental studies have so far been reported on combined reactors, but Babu Rao, Mukherjee, and Doraiswamy (*2*) have proposed a reactor for carrying out a chemical reaction under conditions of the MT combination. This reactor is based on the principle of semifluidization proposed by Fan and co-workers (*11*, *12*) and consists of a fluidizing portion at the bottom (which may be considered to approach fully mixed conditions) and a tubular portion at the top formed by introducing a tubular bundle at an appropriate position in the fluidizing column. The advantages and characteristic features of this reactor system have been discussed by Doraiswamy et al. (*2*, *3*).

The object of the present study is to develop generalized criteria for the optimality of adiabatic reactors of the combined type for simple and complex reactions and to experimentally examine these criteria for benzene oxidation by using the semifluidized MT reactor proposed earlier.

FORMULATION OF CRITERIA

The four significant factors affecting the rate of a reaction are temperature, concentration, residence time, and mixing. In the case of catalytic reactions, the time factor W/F can be used in place of residence time. Before the performance of a combined reactor is analyzed, it is first necessary to formulate an expression for the effect of variations in temperature and concentration on the behavior of tubular and stirred tank (mixed) reactors. This becomes easy in the case of adiabatic reactors, since the effect of temperature can be expressed in terms of variations in conversion. The two variables entering into a rate equation (temperature and concentration) can thus be reduced to a single variable, conversion. In the present analysis, two cases are considered: simple reactions (involving one or two reactant species) and complex reactions.

Simple Reactions

Consider the reaction

$$A \rightarrow \text{Products} \qquad (i)$$

If this reaction is carried out adiabatically, the heat effect can be related to the conversion by

$$T = T_0 + (\Delta T)\, x \qquad (1)$$

The usual Arrhenius equation

$$k = A_f \exp\left[-\frac{E}{RT}\right] \qquad (2)$$

can be modified to take into account the adiabatic temperature rise due to exothermicity by combining Equations (1) and (2), giving

$$k = k_0 \exp \alpha \left[\frac{Mx}{1+Mx}\right] \qquad (3)$$

where

$$\alpha = \frac{E}{RT_0} \text{ and}$$

$$M = \frac{\Delta T}{T_0}$$

Equation (3) expresses the rate constant at any temperature in terms of the rate constant at the inlet temperature (k_0) and two dimensionless terms, E/RT_0 and $\Delta T/T_0$.

The rate of reaction (i) is given by

$$r = \frac{dx}{d\theta} = k\,(1-x)^p\, C_{A0}{}^{p-1} \qquad (4)$$

By eliminating k from Equation (4), the adiabatic reaction rate for a tubular reactor can be expressed as

$$r = k_0\, C_{A0}{}^{p-1}\,(1-x)^p \exp\left[\alpha\frac{Mx}{1+Mx}\right] \qquad (5)$$

The residence time can then be computed from the equation

$$\theta_t = \int_0^x \frac{1}{r}\,dx = \frac{1}{k_0\, C_{A0}{}^{p-1}} \int_0^x \frac{dx}{\left(\exp \alpha \dfrac{Mx}{1+Mx}\right)(1-x)^p} \qquad (6)$$

On the other hand, for a mixed reactor, the holding time ($\theta_m{}'$) is given by

$$\theta_m{}' = \left(\frac{1}{r}\right) x \qquad (7)$$

It can be deduced, from simple reasoning that, under adiabatic conditions, the first part of an exothermal reaction can be advantageously carried out in a mixed reactor, the reaction being then completed in a tubular reactor. With this hypothesis, the combination will be optimal if ($\theta_m{}' + \theta_t$) is minimum. Thus the conversion to be achieved in the mixed reactor (x_m) will have the optimum value X_m if

$$\frac{d\theta_m{}'}{dx_m} + \frac{d\theta_t}{dx_m} = 0 \qquad (8)$$

X_m evidently is dependent on the values of the parameters α and M. By incorporating the equations for θ_t and θ_m [Equations (6) and (7)] in Equation (8), and representing the final conversion achieved by x_f, we obtain

$$\frac{d\left[\dfrac{x_m}{k_0\left(\exp \alpha \dfrac{Mx}{1+Mx_m{}'}\right)(1-x_m)^p}\right]}{dx_m} + \frac{\displaystyle\int_{x_m}^{x_f}\left[\dfrac{dx}{k_0\left(\exp \alpha \dfrac{Mx}{1+Mx}\right)(1-x)^p}\right]dx}{dx_m} = 0 \qquad (9)$$

Solving this equation and replacing x_m by the optimum value X_m, we get

$$\frac{1}{k_0\left(\exp \alpha \dfrac{MX_m}{1+MX_m}\right)} \left[\frac{pX_m}{1-X_m} - \frac{\alpha\, MX_m}{(MX_m+1)^2}\right] = 0 \qquad (10)$$

on (10) on simplification leads directly to

$$\frac{\alpha M}{(1 + MX_m)^2} = \frac{p}{(1 - X_m)} \qquad (11)$$

It may be noted that the criterion represented by Equation (11) is exactly identical with that derived by Aris (*1*) and by Douglas (*9*).

The treatment presented above can be extended to a reaction in which two reactant species are involved:

$$A + bB \rightarrow \text{Products} \qquad (ii)$$

If β is the ratio of the initial concentrations of B and A ($\beta = C_{B0}/C_{A0}$), and if b is the stoichiometric coefficient of the reactant B, the following criterion results:

$$\frac{p}{1 - X_m} + \frac{bq}{\beta - bX_m} = \frac{\alpha M}{(1 + MX_m)^2} \qquad (12)$$

x has now been replaced by the optimum value X_m, and p and q are the reaction orders with respect to A and B, respectively.

The optimality criterion for a reaction involving a single reactant species, represented by Equation (11), can be regarded as a special case of Equation (12), since, in the absence of the second component B, the two equations become identical.

Complex Reactions

Let us now consider the consecutive reaction

$$A \rightarrow R \rightarrow S \qquad (iii)$$

If both the steps of this reaction are exothermal, it is obvious that the amount of A converted and the amount of S formed will follow the same general pattern as for a simple reaction involving the conversion of a single reactant to products. However, the adiabatic temperature rise will now be caused by the heats of reaction of both the steps. For the intermediate product (R), it is also possible to define a criterion for the optimum combination of mixed and tubular reactors.

Let us assume that, at any instant, x moles of A are converted per mole fed and that y moles of S are formed. If the inlet temperature is T_0, by a treatment analogous to that for single reactions, it is possible to develop the following relationships for the rate constants of the two steps:

$$k_1 = k_{10} \exp \alpha_1 Z \qquad (13a)$$

and

$$k_2 = k_{20} \exp \alpha_2 Z \qquad (13b)$$

where

$$Z = \frac{M_1 x + M_2 y}{1 + M_1 x + M_2 y} \qquad (14)$$

$$M_1 = \frac{\Delta T_1}{T_0}; \quad M_2 = \frac{\Delta T_2}{T_0}$$

$$\alpha_1 = \frac{E_1}{RT_0}; \quad \alpha_2 = \frac{E_2}{RT_0}$$

On the assumption that each of the steps of reaction (*iii*) is first order, the following rate equation can be written for the formation of R in a tubular reactor:

$$\frac{dC_R}{d\theta} = k_1 C_A - K_2 C_R \qquad (15)$$

Since

$$C_A = C_{A0} (1 - x)$$

and

$$C_R = C_{A0} (x - y)$$

Equation (15) for the tubular reactor can be written as

$$\left[\frac{d(x - y)}{d\theta}\right]_t = \frac{dx}{d\theta} - \frac{dy}{d\theta} = k_1 (1 - x) - k_2 (x - y) \qquad (16)$$

Expressing k_1 and k_2 by Equations (13*a*) and (13*b*), respectively, we obtain

$$\left[\frac{d(x - y)}{d\theta}\right]_t = k_{10} (\exp \alpha_1 Z) (1 - x) - k_{20} (\exp \alpha_2 Z) (x - y) \qquad (17)$$

For the fully mixed reactor, the corresponding equation is

$$\frac{x_m - y_m}{\theta} = k_{10} (\exp \alpha_1 Z) (1 - x_m) - k_{20} (\exp \alpha_2 Z) (x_m - y_m) \qquad (18)$$

It has been shown by Douglas (*9*) that the criterion for the optimality of the MT combination is the equality of the slopes of the mixed and tubular conversion curves shown in Figure 1. This criterion is equivalent to that formulated by Aris and mathematically represented by

$$\frac{dr}{dx} = 0 \qquad (19)$$

If the right-hand side of Equation (18) is represented by ϕ, we have by differentiation

$$\left[\frac{d(x - y)}{d\theta}\right]_m = \left(\frac{\delta\phi}{dx_m'}\right)_y \left(\frac{dx_m}{d\theta}\right) + \left(\frac{\delta\phi}{dy_m}\right)_x \left(\frac{dy_m}{d\theta}\right) \qquad (20)$$

According to the criterion demanding the equality of the slopes, we have

$$\left[\frac{d(x - y)}{d\theta}\right]_t = \frac{d(x_m - y_m)}{d\theta} \qquad (21)$$

A comparison of Equations (16) and (20) shows that if Equation (21) holds

$$\left(\frac{\delta\phi}{\delta x_m'}\right)_y = -\left(\frac{\delta\phi}{\delta y_m'}\right)_x \qquad (22)$$

Substituting for ϕ, differentiating, and replacing x_m and y_m by their optimum values X_m and Y_m, we obtain

$$\frac{k_{10} \exp \alpha_1 Z_m}{k_{20} \exp \alpha_2 Z_m} = \frac{\alpha_2 [x_m - y_m]}{\alpha_1 [1 - x_m] - \dfrac{H^2}{M_1 + M_2}} \qquad (23)$$

where Z_m is the value of Z at $x = X_m$, and $y = Y_m$ and is given by

$$Z_m = \frac{M_1 X_m + M_2 Y_m}{1 + M_1 X_m + M_2 Y_m} \qquad (24)$$

and

$$H = (1 + M_1 X_m + M_2 Y_m)$$

Equation (23) can be expressed in a slightly different form to give the final criterion

$$S_i \exp \alpha' Z_m = Sa = \frac{\alpha_2 (X_m - Y_m)}{\alpha_1 (1 - X_m) - \dfrac{H_2}{M_1 + M_2}} \qquad (25)$$

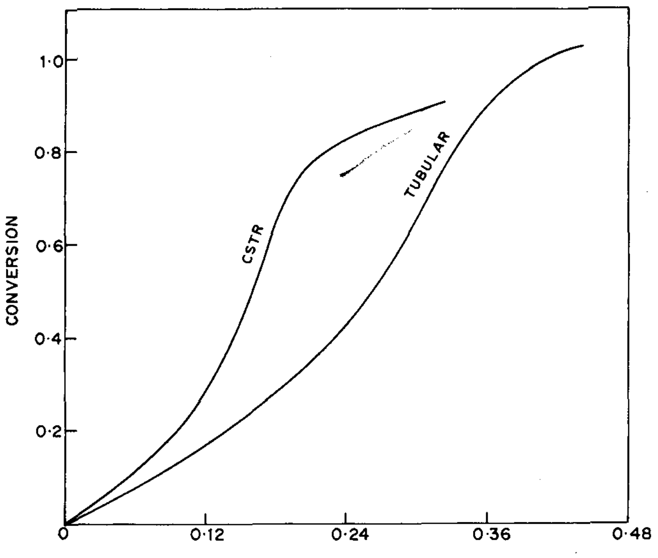


Fig. 1. Plot of conversion vs. residence time for adiabatic mixed and tubular reactors.

where

$$\alpha' = \frac{E_1 - E_2}{RT_0}$$

$$S_i = \frac{k_{10}}{k_{20}}$$

S_i represents the isothermal selectivity of the reaction at the inlet temperature, and the product $S_i \exp \alpha' Z_m$, denoted by S_a, may be regarded as an adiabatic selectivity which is obviously a function of temperature (and the kinetic parameter $E_1 - E_2$) and varies from point to point in the reactor.

A similar analysis can be applied to a more complicated case in which the order of the first and second steps of the reaction are p and q, respectively, resulting in

$$S_a = \frac{1}{C_{A0}{}^{p-q}} \frac{\alpha_2 (X_m - Y_m)^q}{(1 - X_m)^{p-1} \alpha_1 (1 - X_m) - \dfrac{pH^2}{M_1 + M_2}} \quad (26)$$

When both the steps are first order, Equation (26) reduces to Equation (25).

If the conditions are so chosen that the second step of the consecutive reaction does not take place, then M_2, E_2, and y are all zero, and Equation (26) reduces to Equation (11) which defines the criterion for a simple reaction of q^{th} order. This may be regarded as constituting proof of the correctness of Equation (26).

X_m and Y_m of Equation (26) represent the optimum conversion to be achieved in the mixed reactor. In order to solve for X_m and Y_m, it is obviously necessary to formulate a second equation in these variables. This can be easily done by deriving an expression similar to Equation (11) for the total conversion of A. In this case, however, the adiabatic temperature rise will be caused by both the reactions in the consecutive scheme. Thus, Equation (5) (which has been derived for a simple reaction) will now take the form

$$r = k_0 \, C_{A0}{}^{p-1} \left[\exp \alpha \frac{M_1 x + M_2 y}{1 + M_1 x + M_2 y} \right] (1 - x)^p \quad (27)$$

While for the simple reaction (*i*) the optimality criterion according to Aris was defined by Equation (19), in this particular case this criterion would have to be modified, since two variables are involved (x and y). It can be intuitively seen that at the optimum

$$\left(\frac{\delta r}{\delta x}\right)_y = \left(\frac{\delta r}{\delta y}\right)_x = 0 \quad (28)$$

Applying this condition to Equation (27) and rearranging, we get the following criterion for the overall disappearance of A (with x and y replaced by X_m and Y_m):

$$\frac{\alpha\,(M_1 - M_2)}{(1 + M_1 X_m + M_2 Y_m)^2} = \frac{p}{1 - X_m} \quad (29)$$

When the second reaction in the consecutive scheme is absent, M_2 and Y_m become zero, and Equation (29) reduces to Equation (11) for a simple reaction.

For a consecutive reaction of known kinetics, Equations (26) and (29) can be simultaneously solved to provide the optimum conversions X_m and Y_m. Thus, the following hypothetical problem will be solved for illustration.

Let

$$k_{10}/k_{20} = 2$$
$$\alpha_1 = \alpha_2 = 20$$
$$M_1 = 2; M_2 = 1$$
$$p = q = 1$$

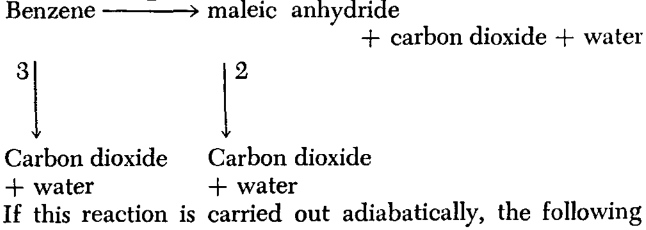
Incorporating these values into Equations (26) and (29) and solving them simultaneously, we obtain

$$X_m = 0.670$$
$$Y_m = 0.237$$

APPLICATION OF THE OPTIMALITY CRITERION TO BENZENE OXIDATION IN AN MT REACTOR

In order to experimentally examine the possibility of using the MT semifluidized bed reactor proposed earlier (2) for an exothermic reaction, it would evidently be desirable to choose a simple reaction of precisely known kinetics. On the other hand, it is also necessary to choose a reaction in which large throughputs are essential, so that the semifluidized condition is easily obtained. For this reason, the oxidation of benzene was chosen as a suitable reaction in spite of its complex nature. Since, as shown later, the oxidation of benzene can, for all practical purposes, be regarded as a single step reaction (with empirical kinetics), the choice of this reaction is justifiable.

Vaidyanathan and Doraiswamy (*16*) have made a complete kinetic analysis of this reaction in terms of the scheme represented below (using a vanadium-molybdenum catalyst):



If this reaction is carried out adiabatically, the following relationship will hold good:

$$T = T_0 + (\Delta T_1) x_1 + (\Delta T_2) x_2 + (\Delta T_3) x_3 \quad (30)$$

where x_1, x_2, and x_3 represent, respectively, the moles benzene converted to maleic anhydride through step (1), moles maleic anhydride reacting according to step (2), and moles benzene directly combusted according to step (3). ΔT_1, ΔT_2, and ΔT_3 represent the adiabatic temperature rises at total conversion for the three respective steps.

Emmett (*10*) and Marek and Hahn (*14*) have shown that the heat of reaction for the overall reaction can be taken as the average of the heat of reaction for total combustion and that for maleic anhydride formation, that is, steps (1) and (3) of the scheme represented above. With this assumption, Equation (30) can be simplified to Equation (1), where x represents the mole fraction of benzene disappearing and ΔT the total adiabatic temperature rise for the overall conversion of benzene corresponding to Emmett's single average value of ΔH (14,265 B.t.u./lb.mole).

If the oxidation of benzene can be represented in terms of a single heat of reaction, reaction (*iii*) can be expressed (for the present purpose) in a simplified form as

$$\text{Benzene} \rightarrow \text{Products} \qquad (iv)$$

The analysis employed for simple reactions can now be used, provided the activation energies of the three steps are of the same order of magnitude. Vaidyanathan and Doraiswamy (*16*) have shown that the activation energies of all three steps are of the order of 1.5×10^4 B.t.u./lb.mole in the lower temperature range, 310° to 350°C. (a fact which has also been observed by other investigators) or about 2.0×10^4 B.t.u./lb.mole in the high temperature range, 350° to 400°C., thus making it possible to apply the criterion represented by Equation (11) for the oxidation of benzene. It must be remembered that what is involved here is the overall disappearance of benzene, irrespective of the selectivity of the reaction for maleic anhydride.

Experimental

An experimental program was organized to investigate the oxidation of benzene to verify the optimality criterion for simple reactions. For this purpose the semifluidized MT reactor proposed by Doraiswamy and collaborators (*2*) was used, together with the tubular and mixed reactors operated independently.

The experimental set-up consisted of a prereaction section, reactors, and product treatment apparatus. A schematic diagram of the assembly, which was similar to that used by Vaidyanathan and Doraiswamy (*16*), is shown in Figure 2.

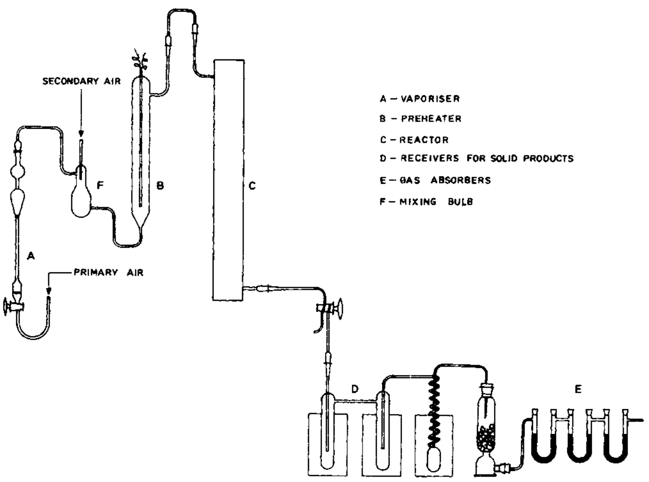


Fig. 2. Experimental setup.

Dry primary air was introduced through a benzene reservoir into the reactor. Secondary air was supplied directly from a compressor after it was mixed with the primary air as shown in the Figure 2. The amount of benzene consumed during the reaction was noted from the drop in level in the benzene reservoir.

Three reactors were used during this study: tubular, mixed, and semifluidized MT reactors. These are shown schematically in Figure 3. The same reactor could be used as tubular or mixed, the only difference being in its operation. In the case of the mixed reactor, the feed was introduced at the bottom so that the catalyst in the reactor was in a state of vigorous fluidization (thus ensuring reasonably good mixing). On the other hand, for the tubular reactor, the flow was downward in order to avoid fluidization. The reactor dimensions, which are given in the figure, were such as to ensure plug flow when the feed was passed from the top.

The MT reactor was similar in construction to that described earlier (*2*). A tubular bundle was placed at an appropriate position in the fluidizing column, and the bottom fluidizing portion corresponded to the mixed reactor. In this particular case, the column (beneath the restraining plate) could itself be regarded as a tubular reactor, since the diameter of the column was quite small (1 in.). However, in order to conform to the MT reactor proposed (*2*), a tubular bundle was inserted at the top, the bundle consisting of four tubes of 0.35 in. diameter each.

The mechanics of solids distribution in a semifluidized MT reactor has been studied by Babu Rao and Doraiswamy (*3*), and the following equation has been proposed:

$$\frac{G_s}{G_t} = k(Ar)^{-0.15}\,(Sf)^{-0.186} \qquad (31)$$

where

$$Ar \text{ (Archemedes number)} = \frac{Dp^3 g_c\, \rho_s(\rho_s - \rho_F)}{\mu^2}$$

$$Sf \text{ (semifluidization number)} = \frac{(W - W_p)}{(h - h_s)^3 \rho_s}$$

$$k = \frac{4.62^*}{(D)^{-0.372}} \quad (D \text{ is in feet})$$

From this equation, it is possible to determine the quantity of solids in the fluidized and tubular sections of the reactor assembly for a given set of operating conditions. In the reactor shown in Figure 2, provision was made for discharging the fluidizing solids during a run in order to enable experimental determination of the proportion of mixed portion in the combined reactor. During a run the discharge valve was opened momentarily and the solids in the fluidizing portion emptied. This was weighed and the fraction of the mixed portion in the reactor assembly determined. This procedure was repeated for several initial experiments in order to verify Equation (31), and it was found that the results could be reproduced to within 5 to 10%. In all the subsequent runs, the fluidizing portion was not weighed separately, and the proportion of solids in the mixed and tubular portions was calculated from Equation (31).

All the reactors were heated by electrical resistance wire through appropriate autotransformers. The reactors were

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[*] The value of 17.3 given in reference *3* is wrongly printed, and a suitable erratum will appear soon.

heavily lagged to give surface temperatures not exceeding 40° to 50°C., thus ensuring near adiabatic conditions. Provision was made for measuring the temperature at the inlet to the reactor and at various points in the fluidized and tubular reactors by a sliding thermocouple. In the case of the MT reactor, while an arrangement was provided for measuring the temperature in the fluidizing portion, no attempt was made to measure the temperature in the tubular section.

The products of reaction consisted of unreacted benzene, maleic anhydride, water, and carbon dioxide. These were estimated by standard procedures. Only those runs in which the material balance could be established to within 3% were accepted for reactor analysis.

The catalyst used was the same as that employed by Vaidyanathan and Doraiswamy *(16)*, consisting of vanadium and molybdenum oxides on silica gel. The method of preparation of the catalyst and its principal properties have been described by them.

Experiments were carried out at an inlet temperature of 380°C. and at benzene-air ratios of 1 : 170, 1 : 200, and 1 : 250. The time factor was defined as the ratio W/F. The time factor was varied by changing the feed rate and the catalyst quantity, and the range covered was 50 to 350. Since Vaidyanathan and Doraiswamy *(16)* found that there is a shift in the activation energy at a temperature of about 350°C., inlet temperature less than 350°C. would lead to a situation where both the activation energy regimes might become operative. An inlet temperature of 380°C. was therefore used in all the runs (for convenience in computation). As shown later, this is a justifiable procedure.

The Optimality Criterion

This part of the work is concerned with the estimation of X_m by the following methods.

1. In accordance with the method proposed by Aris *(1)*, a curve of $1/r$ vs. x was drawn by using the rate equation proposed by Vaidyanathan and Doraiswamy *(16)*, which can be expressed in the form

$$r = (k_1 + k_3)p_B \qquad (32)$$

The curve shown in Figure 4 exhibits a minimum as expected (at the point M). It may be noted that although more than one minimum (or maximum) is possible for a solid catalyzed heterogeneous reaction (1), in this particular case a single minimum is observed within the operating range. The value of x corresponding to M gives the optimum conversion X_m that should be achieved in the mixed portion of the combined reactor. At $T_o = 380$°C. and benzene-air ratio = 1 : 170, as shown in the figure, $X_m = 0.15$. As is to be expected, practically the same value (0.152) is obtained from Equation (11) by using the parametric values reported by Vaidyanathan and Doraiswamy *(16)*.

2. The optimality criterion is also given by the equality of the slopes of the conversion vs. time curves for the mixed and tubular reactors. Representative plots of x vs. W/F for the mixed and tubular reactors at an inlet temperature of 380°C. and benzene-air ratio of 1 : 170 are shown in Figure 5. Each of these curves can be represented by a polynomial. Thus

$$x_t = a_1\left(\frac{W}{F}\right) + b_1\left(\frac{W}{F}\right)^2 + c_1\left(\frac{W}{F}\right)^3 \qquad (33)$$

and

$$x_m = a_2\left(\frac{W}{F}\right) + b_2\left(\frac{W}{F}\right)^2 + c_2\left(\frac{W}{F}\right)^3 \qquad (34)$$

where

$$a_1 = 1.7773 \times 10^{-3}$$
$$b_1 = -3.8038 \times 10^{-6}$$
$$c_1 = 4.6765 \times 10^{-9}$$
$$a_2 = 2.0555 \times 10^{-3}$$
$$b_2 = -5.3440 \times 10^{-6}$$
$$c_2 = 6.0974 \times 10^{-9}$$

Differentiation of these equations leads to

$$\frac{dx_t}{d(W/F)} = a_1 + 2b_1\left(\frac{W}{F}\right) + 3c_1\left(\frac{W}{F}\right)^2 \qquad (35)$$

$$\frac{dx_m}{d(W/F)} = a_2 + 2b_2\left(\frac{W}{F}\right) + 3c_2\left(\frac{W}{F}\right)^2 \qquad (36)$$

By simultaneous solution of these equations, it is possible to determine the value of x at which

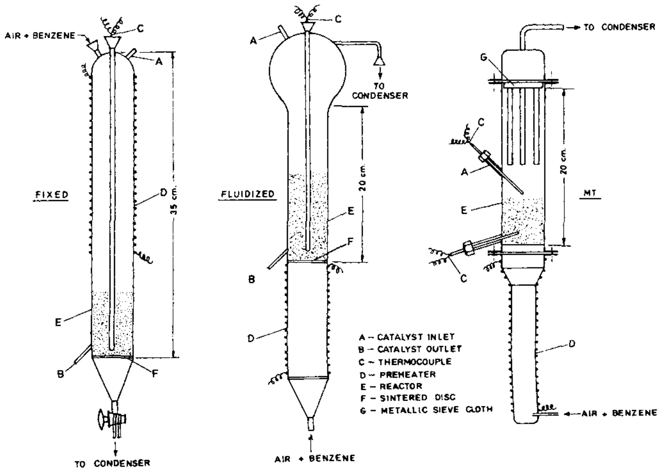

Fig. 3. Reactor details.

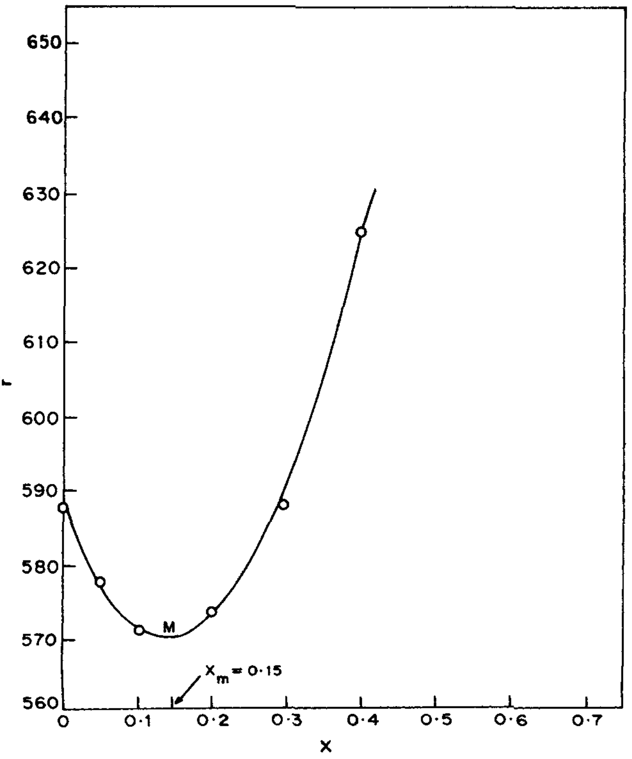

Fig. 4. Experimental graph of $1/r$ vs. x.

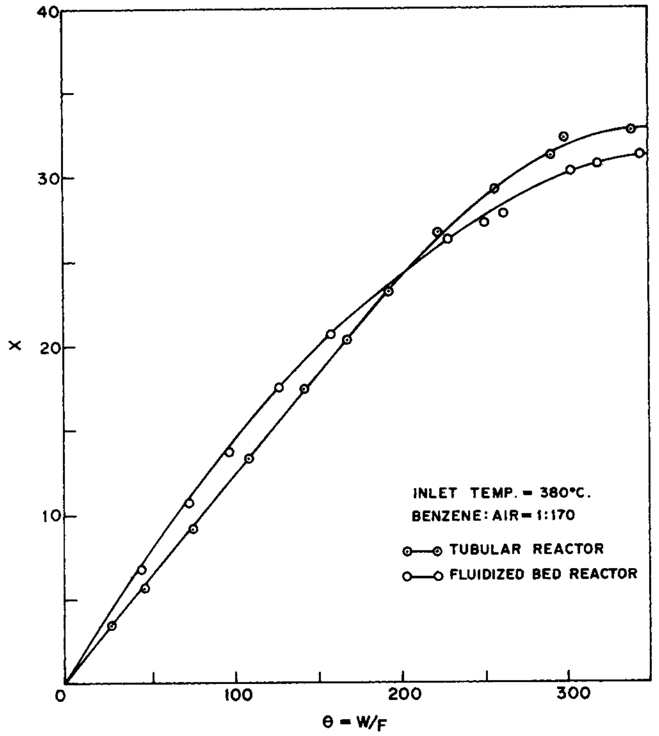

Fig. 5. Experimental conversion vs. residence time plots for tubular and mixed (fluidized) reactors.

$$\frac{dx_t}{d(W/F)} = \frac{dx_m}{d(W/F)}$$

Thus

$$X_m = 0.158$$

It may be pointed out that the second method involves actual experimental values from mixed and tubular reactors, while the first is based on kinetics alone. Since data on the use of these methods have not so far been reported, the agreement between the methods shown above is noteworthy and demonstrates the practical utility of the optimality criterion; this will be further elaborated in the following section.

Operation of the MT Semifluidized Reactor

A series of runs was carried out at $T_0 = 380°C.$ and at different values of W/F, and the experimental data obtained are recorded in reference 4. The amount of catalyst in the mixed (fluidized) portion is given by W_F; X_{MT} represents the total conversion obtained in the combined reactor, and x_t represents the conversion in a tubular reactor for the same value of W/F in the MT reactor and was obtained by preparing plots of the type shown in Figure 6 for different benzene-air ratios.

In Figure 6, x_{MT} is plotted as a function of m' defined by

$$\left(\frac{W_F}{F}\right) = m'\left(\frac{W}{F}\right)$$

or

$$m' = \frac{\theta_m}{\theta} \qquad (37)$$

for a benzene-air ratio of 1 : 170 and inlet temperature of 380°C. It is evident that there is a noticeable improvement in conversion as m' is increased, reaching a definite maximum and then gradually decreasing. The improvement obtained in the MT combination is clearly discernible, particularly at higher values of θ. Obviously no maximum is possible when $\theta \lesseqgtr \theta_m$.

The optimum value of m' for any W/F (or θ) can be obtained from Figure 6 by noting the maximum in the corresponding curve. Then from Equation (37) θ_m (corresponding to the mixed portion) can be obtained. θ_m calculated in this manner has a value of 108, which represents the average for the different values of θ included in Figure 6 for values of $\theta \gtrless \theta_m$.

It is also possible to calculate θ_m from Equations (6) and (32) by using the theoretical values of X_m listed in Table 1. The resulting θ_m values are also given in the same table, thus making it possible to compare the optimum residence time in the mixed portion obtained from the theoretical procedures with the experimental value. Comparisons have been made at three different ratios of benzene:air in Table 1 by using the experimental data reported by Babu Rao (*4*). The agreement between the theoretical value of θ_m and the experimental values obtained in the MT reactor should be regarded as satisfactory, considering the fact that the fluidized portion of the MT combination does not actually correspond to a fully mixed system (but only approaches it).

SUMMARY AND CONCLUSIONS

1. The optimality criterion for a simple reaction in which a single reactant goes to products has been developed by a method which minimizes the residence times in the mixed and tubular portions, and this criterion is shown to be identical with that derived by Aris (*1*) and by Douglas (*9*) by other methods. The optimality criterion for a reaction in which two reactant species are involved has also been presented.

2. A complex reaction system consisting of two consecutive steps has been considered, and criteria have been derived for the optimality of both the steps.

3. By using some simplifying assumptions, the oxidation of benzene has been studied in an MT semifluidized

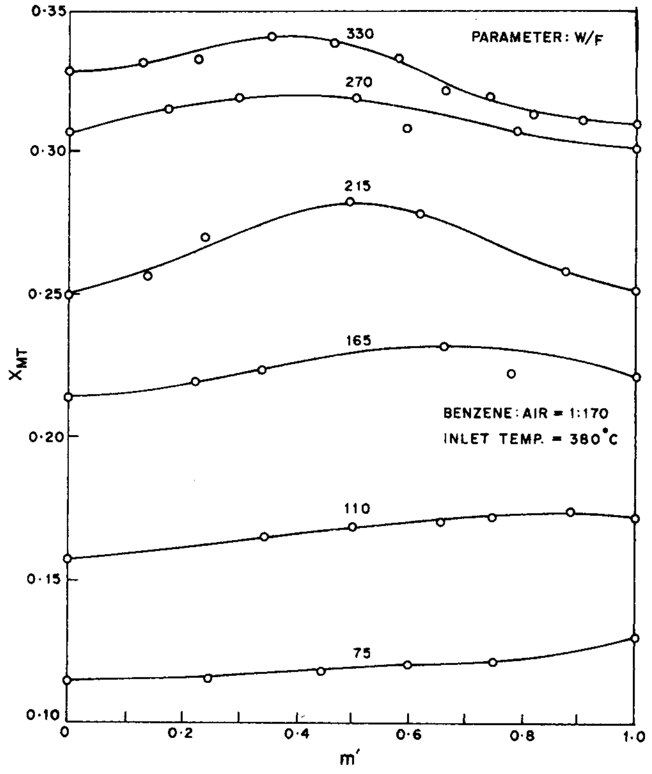

Fig. 6. Plot of x_{MT} vs. m' for semifluidized MT reactor at 380°C.

TABLE 1. COMPARISON OF OPTIMUM X_m AND θ_m VALUES

Benzene:air	From criterion Equation (11)*		Method of slopes		θ_m from Figure 6
	X_m	θ_m	X_m	θ_m	
1:170	0.152	88.0	0.158	90.2	108.0
1:200	0.158	89.4	0.164	92.3	104.0
1:250	0.165	90.5	0.160	92.5	109.0

* The graphical method of Aris will give the same value.

bed reactor as well as in tubular and fluidized bed reactors. It has been found that the optimality criterion developed for a reaction of this type is satisfactorily borne out by the experimental results.

NOTATION

A = reactant
A_f = frequency factor
Ar = Archimedes number, dimensionless
C_A = concentration of A, (lb.)/(cu.ft.)
C_{A0} = initial concentration of A, (lb.)/(cu.ft.)
C_R = concentration of R, (lb.)/(cu.ft.)
d = diameter of particle, ft.
D = diameter of reactor, ft.
E = energy of activation, B.t.u./(lb.mole)
F = feed rate of benzene, (lb.mole)/(hr.)
g_c = acceleration due to gravity, (ft.)/(hr.^{2})
G_s = semifluidization velocity, (lb.)/(hr.)(sq.ft.)
G_t = terminal velocity, (lb.)/(hr.)(sq.ft.)
h = overall height of the semifluidized reactor, ft.
h_s = height of the initial static bed, ft.
H = as defined in the Equation (24)
ΔH = heat of reaction, B.t.u./(lb.mole)
k = rate constant, (lb.mole)/(lb.cat.)(hr.)(atm.)
k_1 = rate constant for formation of maleic anhydride, (lb.mole)/(lb.cat)(hr.)(atm.)
k_{10} = rate constant at inlet temperature for formation of maleic anhydride, (lb.mole)/(lb.cat.)(hr.)(atm.)
k_3 = rate constant for combustion of benzene, (lb. mole)/(lb.cat.)(hr.)(atm.)
k_{30} = rate constant at inlet temperature for combustion of benzene, (lb.mole)/(lb.cat.)(hr.)(atm.)
m = mixed reactor
m' = fraction of catalyst in the mixed zone
M = dimensionless ratio $(\Delta T/T_0)$
M_1 = dimensionless ratio $(\Delta T_1/T_0)$
M_2 = dimensionless ratio $(\Delta T_2/T_0)$
p = order of reaction
P_B = partial pressure of benzene, atm.
q = order of reaction
r = rate of reaction, (lb.mole)/(hr.)(lb.cat.)
R = intermediate product
S = final product
S_a = adiabatic selectivity, defined by Equation (25)
S_f = semifluidization number, dimensionleess
S_i = isothermal selectivity, defined by Equation (25)
t = tubular reactor
T = temperature of an adiabatic reaction at any conversion, °K.
T_0 = initial temperature, °K.
ΔT = adiabatic temperature rise, °K.
ΔT_1 = adiabatic temperature rise, defined by Equations (16a) and (30), °K.
ΔT_2 = adiabatic temperature rise, defined by Equations (16b) and (30), °K.
ΔT_3 = adiabatic temperature rise, defined by Equation (30), °K.
W = weight of the catalyst at the static condition of the bed (same as initial weight of the catalyst or total weight in MT reactor), lb.
W_F = weight of the catalyst in the fluidized reactor or fluidized portion of MT reactor, lb.
W_p = weight of the catalyst in the tubular reactor, lb.
x = moles of A converted per mole fed
x_1 = conversion of benzene to maleic anhydride
x_2 = conversion of maleic anhydride to carbon dioxide
x_3 = conversion of benzene to carbon dioxide by combustion
x_f = final conversion in the tubular part of the MT reactor
X_m = optimum conversion in the mixed reactor
x_m = any conversion in the mixed reactor
x_{MT} = conversion in the MT reactor
x_t = conversion in the tubular reactor
y = conversion of $A \rightarrow S$
Y_m = optimum conversion $A \rightarrow S$ in the mixed reactor
y_m = conversion $A \rightarrow S$ in the mixed reactor
Z = constant defined by Equation (14)
Z_m = constant Z evaluated at optimum values of x_m and y_m and defined by Equation (24)

Greek Letters

α = defined by Equation (3)
α_1 = defined by Equation (13b)
α_2 = defined by Equation (13b)
α' = defined by Equation (25)
ρ = ratio of initial concentrations of B and A
θ = residence time
θ_m = optimum residence time in the mixed reactor
θ_m' = residence time in the mixed reactor
θ_t = residence time in the tubular reactor
ϕ = right-hand side of Equation (18)
ρ_F = density of the fluid, lb./(cu.ft.)
ρ_s = density of the solid, lb./(cu.ft.)
μ = viscosity of the fluid, lb./(hr.)(ft.)

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