On the Steady State Activity Levels in a Reactor-Regenerator System

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A method is proposed for computing the steady state activity levels at various points within a reactor-regenerator system in which the residence time distribution functions in the reactor and regenerator, the permanent deactivation function, and the temporary deactivation and activation functions are arbitrarily specified. A particularly simple solution to these equations is obtained when the temporary activation and deactivation functions are of exponential form. The latter equations are used to calculate values of the mean activity in the reactor for the limiting cases of piston type of flow and complete mixing under a variety of conditions.

The activity of catalyst particles circulated in a system consisting of a fluidized reactor and a fluidized regenerator changes owing to carbon deposition on and removal from the active surface and to sintering or sealing off of active surface making parts of the catalyst surface unavailable to the reactant charge. The activity of a catalyst particle is a function of its initial properties, its history within each of the units, the extent of reaction taking place within it, the reaction temperatures, and the time of exposure to cracking conditions. After a period of residence within a reactor under cracking conditions the activity of a catalyst particle decays, and upon subsequent exposure to the environment of the regenerator the activity of the catalyst particle increases depending upon the residence time and conditions within the regenerator. However the original activity of the fresh catalyst cannot, presumably, be attained even if its residence time in the regenerator is infinite. It is therefore convenient to postulate two types of deactivation: a regenerable or temporary type which can be reactivated in a regenerator environment, and a nonregenerable or permanent type which cannot be reactivated in a regenerator environment.

The effect of each type of deactivation can be illustrated by the following description of an operating system. Consider a reactor-regenerator combination charged with fresh catalyst and operated without supplying make-up catalyst as shown in Figure 1*a*. When one assumes that only temporary deactivation occurs, the mean activity levels within the reactor and regenerator will decrease and approach some finite steady state value as the time of operation increases. The steady state value will be a function of the operation conditions and the residence-time distribution within the reactor and regenerator and the nominal residence time within each unit. The greater the catalyst recirculation rate the higher the mean activity within each unit.

Consider the operation of the reactor and regenerator again as before, except that now both temporary and permanent deactivation can occur. As operation time increases, the mean activity levels within the reactor and regenerator will not approach a steady state value but will continue to decrease and approach either a value of zero activity or some very small activity level probably independent of the mean residence time and residence-time distribution within each of the units. However if fresh catalyst is continuously introduced in the reactor, as shown in Figure 1*b*, and an equal quantity continuously withdrawn from the catalyst stream going to the regenerator, the inventory in the units remains constant and the activity levels within the reactor and regenerator again approach finite steady state values. The magnitudes of the steady state values depend on the fresh catalyst feed rate in addition to the variables mentioned for the case of temporary deactivation only.

The purpose of this paper is to predict the steady state mean level of activity in the reactor and regenerator where the residence-time distribution, the permanent deactivation functions, and the temporary deactivation and activation functions are arbitrary functions of residence time. This problem is a generalization of some work by Pigford (*7*) who solved for time-dependent activity within a completely mixed reactor resulting from permanent deactivation and hence did not consider the reactor and regenerator separately. Pigford assumed that the fresh catalyst feed rate was a known but arbitrarily specified function of time.

RESIDENCE TIME DISTRIBUTION FUNCTION

Assume that the reactor shown in Figure 2 contains a large number of catalyst particles and has equal catalyst feed and removal rates to maintain constant inventory within the unit. If Q tagged catalyst particles are injected into the feed stream at time $t = 0$, and the number of tagged particles $q(t)$ having left the reactor at time t is counted, a plot of the form shown in Figure 2 can be obtained. On the assumption that this function is continuous, the number of tagged particles leaving in the interval from t to $t + dt$ is represented by the time derivative of the curve in Figure 2. The residence time distribution function $T'(t)$ is defined as

$$T'(t) \equiv \frac{1}{Q}\frac{dq(t)}{dt} \tag{1}$$

and has the property that

$$\int_0^\infty T'(t)\,dt = 1 \tag{2}$$

Also let

$$T(t) \equiv \int_0^t T'(\gamma)\,d\gamma \tag{3}$$

All catalyst particles entering at the same time have the same *a priori* probability of leaving the bed. The function $T'(t)$ however defines the relative probabilities of particles leaving having entered at different times.

The distribution function $T'(t)$ depends upon the type of mixing which occurs in the system. Distribution functions of engineering interest generally lie between the limits of no mixing, which corresponds to piston flow, and complete mixing; these limiting forms are shown in Figure 3. The reader is referred to the works of Danckwerts et al. (*4, 5*) and Singer et al. (*8*) for a detailed discussion of the residence time distribution function. The number of particles N remaining in the bed after an infinite time is

$$N = n\int_0^\infty [1 - \int_0^t T'(\gamma)\,d\gamma]dt \tag{4}$$

Therefore

$$\frac{n}{N}\int_0^\infty [1 - T(t)]dt = 1 \tag{5}$$

A particular set of residence time distribution functions of engineering interest is that obtained from m stages of equal volume in series. Complete mixing is assumed in each stage. The residence time distribution function for particles leaving the last stage in terms of the time they entered the first stage is

$$T'(\tau) = \frac{\tau^{m-1}}{(m-1)!} e^{-\tau} \quad (6)$$

where $T'(\tau)$ is the derivative with respect to τ:

$$\tau = \frac{mnt}{N} \quad (7)$$

When $m = 1$, the distribution function corresponds to a single completely mixed stage, and as $m \rightarrow \infty$, it approaches piston flow. The curves for several intermediate values of m are included on Figure 3.

REACTOR DEACTIVATION AND REGENERATOR ACTIVATION FUNCTIONS

The discussion is first directed to the case in which only temporary deactivation is considered and no fresh catalyst is charged (Figure 1a). The activity of a catalyst particle leaving the reactor depends upon its activity when entering and its residence time therein. The functions $R(\theta_1)$ and $G(\alpha)$ relate the activity of a catalyst particle and its residence time in the reactor and regenerator, respectively. These functions are characteristic of the particular operating conditions within the units, and their qualitative forms are shown in Figure 4. Consider the history of a single particle entering the reactor with an activity $R(\theta)$. After residing a time t_{r_1} in the reactor the particle leaves with an activity $R(\theta_1 + t_{r_1})$ and enters the regenerator with an activity $G(\alpha_1) = R(\theta_1 + t_{r_1})$, and after residing for a time t_{g_1} it leaves the regenerator with an activity $G(\alpha_1 + t_{g_1})$. The particle then re-enters the reactor with an activity $R(\theta_1') = G(\alpha_1 + t_{g_1})$ where in the general case $R(\theta_1) \neq R(\theta_1')$.

This is undoubtedly a simplified picture of the real behavior of catalyst particles within the system because implicit in this description are the assumptions that all particles residing a definite time in the reactor or regenerator are exposed to identical environmental conditions and that the activity is a unique function of the carbon deposition. On a statistical basis the former assumption would appear to be reasonable, whereas the latter assumption may be untrue owing to heat treating of the deposit after many cycles. However the apparent temperatures are too low for appreciable graphization to occur.

STEADY STATE ACTIVITY LEVELS WITH TEMPORARY DEACTIVATION

$F(\theta)$ and $H(\alpha)$ have properties such that

$$\int_0^\infty F(\theta)\, d\theta = 1 \quad (8)$$

$$\int_0^\infty H(\alpha)\, d\alpha = 1 \quad (9)$$

The mean activity of a stream of catalyst particles having an age distribution given by $F(\theta)$ is therefore

$$\overline{A_i} = \int_0^\infty F(\theta)\, R(\theta)\, d\theta \quad (10)$$

If the age distribution of the feed does not change with time, the mean activity of the catalyst particles entering and leaving the reactor is given by Equations (10) and (11), respectively:

$$\overline{A_o} = \int_0^\infty \int_0^\infty F(\theta) R(\theta + t_r) T_R'(t_r)\, dt_r\, d\theta \quad (11)$$

Equation (11) can be stated in words as follows. All particles entering the reactor of age θ will leave the reactor with a distribution of ages according to the distribution $T_R'\ (t_r)$, and a particle of age θ residing for a time t_r in the reactor will leave with an activity $R(\theta + t_r)$.

The particles leaving the reactor enter the regenreator (Figure 1a); therefore the average activity of the stream entering the regenerator is $\overline{A_o}$, which is also represented by

$$\overline{A_o} = \int_0^\infty H(\alpha)\, G(\alpha)\, d\alpha \quad (12)$$

and the stream leaving the regenerator has a mean activity $\overline{A_i}$ given by

$$\overline{A_i} = \int_0^\infty \int_0^\infty H(\alpha) G(\alpha + t_g) T_G'(t_g)\, dt_g\, d\alpha \quad (13)$$

The mean activity within the reactor and regenerator can be represented in terms of the above functions:

$$\overline{A_R} = \frac{n}{N_R} \int_0^\infty \int_0^\infty F(\theta)\, R(\theta + t_r) [1 - T_R(t_r)]\, dt_r\, d\theta \quad (14)$$

$$\overline{A_G} = \frac{n}{N_G} \int_0^\infty \int_0^\infty H(\alpha) G(\alpha + t_g) [1 - T_G(t_g)]\, dt_g\, d\alpha \quad (15)$$

In the general case the solution to Equations (14) and (15) can be obtained after Equations (10) through (13) have been solved simultaneously to determine the functions $F(\theta)$ and $H(\alpha)$.

Define two functions $P(\epsilon)$ and $Q(\eta)$ in such a way that $P(\epsilon)\, d\epsilon$ and $Q(\eta)\, d\eta$ are the fractions of particles leaving the reactor and regenerator respectively having ages between ϵ and $\epsilon + d\epsilon$ and $\eta + d\eta$. It follows therefore that

$$P(\epsilon) = \int_0^\epsilon F(\theta) T_R'\ (\epsilon - \theta)\, d\theta \quad (16)$$

and

$$Q(\eta) = \int_0^\eta H(\alpha) T_G'(\eta - \alpha)\, d\alpha \quad (17)$$

Furthermore

$$F(\theta) d\theta = - Q(\eta) d\eta \quad (18)$$

$$P(\epsilon) d\epsilon = - H(\alpha) d\alpha \quad (19)$$

Since the activity $R(\epsilon)$ of a particular group of particles leaving the reactor is equal to $G(\alpha)$, α can be functionally related to ϵ by the use of the original activity curves shown in Figure 4. Let these functions be $\alpha(\epsilon)$ and $\epsilon(\alpha)$ which are, respectively, the values of age α necessary to give the same catalyst activity as particles having an age ϵ and vice versa. Clearly θ and η are related by the functions $\eta(\theta)$ and $\theta(\eta)$ and are, respectively, identical to $\alpha(\epsilon)$ and $\epsilon(\alpha)$. From Equations (17), (18), and (19) one obtains

$$F(\theta) = \eta'(\theta) \int_\infty^\theta P(\epsilon) T_G'[\eta(\theta) - \alpha(\epsilon)] d\epsilon \quad (20)$$

where $\eta'(\theta)$ is the derivative of $\eta(\theta)$ with respect to θ, and the limits have been changed to correspond to the new variable ϵ. Substituting for $P(\epsilon)$ from Equation (16) one gets

$$F(\theta) = \eta'(\theta) \int_\infty^\theta T_G'[\eta(\theta) - \alpha(\epsilon)] \int_0^\epsilon F(\phi) T_R'(\epsilon - \phi) d\phi\, d\epsilon \quad (21)$$

Reversing the order of integration by standard procedures one obtains directly

$$F(\theta) = \eta'(\theta) \int_0^\infty F(\phi) \int_\infty^\phi T_G'[\eta(\theta) - \eta(\epsilon)] T_R'(\epsilon - \phi) d\epsilon\, d\phi - \eta'(\theta) \int_0^\theta F(\phi) \int_\theta^\phi T_G'[\eta(\theta) - \alpha(\epsilon)] T_R'(\epsilon - \phi) d\epsilon\, d\phi \quad (22)$$

In more standard form Equation (22) becomes

$$F(\theta) = \eta'(\theta) \int_0^\infty K_1(\theta, \phi) F(\phi) d\phi - \eta'(\theta) \int_0^\theta K_2(\theta, \phi) F(\phi) d\phi \quad (22a)$$

where

$$K_1(\theta, \phi) = \int_\infty^\phi T_G'[\eta(\theta) - \alpha(\epsilon)] T_R'(\epsilon - \phi) d\epsilon$$

$$K_2(\theta, \phi) = \int_\theta^\phi T_G'[\eta(\theta) - \alpha(\epsilon)] T_R'(\epsilon - \phi) d\epsilon$$

These Kernel functions can be evaluated provided the residence time distribution functions and the activation and deactivation functions are known.

Equation (22a) is a linear, homogeneous, integral equation and can be solved in general by numerical procedures. The reader is referred to the iterative method as a means of obtaining a solution.*

* See for example page 468 of reference 6.

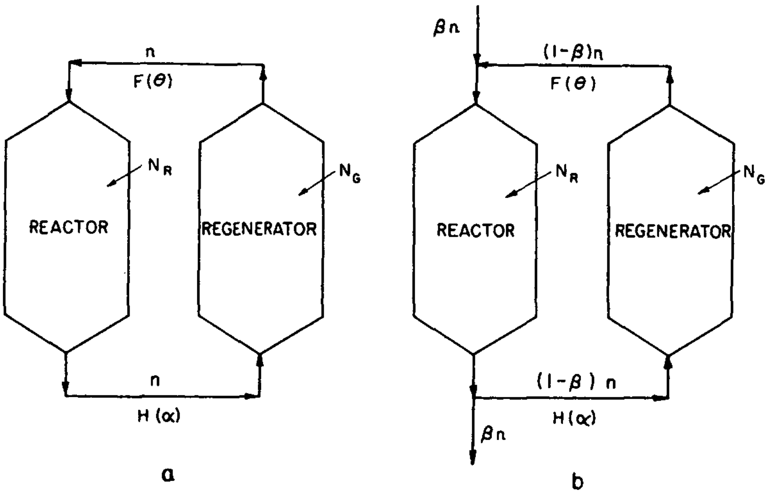

Fig. 1. Reactor-regenerator flow systems: *a*, case of temporary activation; *b*, case of temporary and permanent deactivation.

PERMANENT DEACTIVATION

When catalytic particles exhibit the property of permanent deactivation as a function of the residence time within the reactor-regenerator unit, a steady state activity level is maintained only when fresh catalyst is fed to the units. The level of activity of course depends upon the rate at which fresh catalyst is introduced. The flow diagram of the units is shown in Figure 1*b*. The recirculation is $(1-\beta)n$ particles per unit time, and the number of particles entering and leaving the reactor is n. The rate of addition of fresh catalyst particles to the system is βn. An equal number of particles is withdrawn from the stream leaving the reactor in order to keep the inventory constant.

The permanent deactivation function is given by $K(t)$ ranging in magnitude between 1 and 0 as t varies between 0 and ∞ and where t is the total residence time of catalyst particles within the reactor and regenerator units. The function $K(t)$ is assumed to be independent of the temporary deactivation functions, and $1-K(t)$ represents a loss in activity which cannot be regenerated by exposure to the regenerator environment. The form of this function has been studied by Small et al. (9), although it is not clear at what temperature experiments should be made in order to correspond to the reacting system.

It is necessary therefore to solve for the residence-time distribution of particles in the system in terms of arbitrarily specified residence time distribution functions $T_R'(t_r)$ and $T_G'(t_g)$, and the parameters β, n, N_R, and N_G.

A schematic diagram of the system is shown on Figure 5, wherein βn untagged particles are fed and removed continuously and $(1-\beta)n$ particles are recirculated. If at time $t \geqq 0$ βn tagged particles are continuously fed to the system at point A, the fraction of the tagged particles in various parts of the system will depend upon t. Let the fractions of tagged particles at points C and D be given by the functions $F(t)$ and $H(t)$, respectively. These two functions can be inter-related by the equations below in terms of the residence-time distributions in the reactor and the regenerator.

$$\beta n \int_0^t T_R'(\gamma)\, d\gamma + (1-\beta)n \int_0^t F(t-\gamma)T_R'(\gamma)d\gamma = n\,H(t) \tag{23}$$

$$(1-\beta)n \int_0^t H(t-\gamma)T_G'(\gamma)d\gamma = (1-\beta)n\,F(t) \tag{24}$$

The formal solution to this set of equations can be obtained in terms of the Laplace transforms (2) of the functions which are represented by small script letters:

$$\mathcal{L}\{H(t)\} = h(s)$$
$$\mathcal{L}\{F(t)\} = f(s) \tag{25}$$

From Equations (3), (23), (24), and (25)

$$h(s) = \beta t_R(s) + (1-\beta)\, f(s) t_R'(s) \tag{26}$$

$$f(s) = h(s) t_G'(s) \tag{27}$$

Therefore:

$$h(s) = \frac{\beta t_R(s)}{1-(1-\beta)t_G'(s)t_R'(s)} \tag{28}$$

$$f(s) = \frac{\beta t_G'(s) t_R(s)}{1-(1-\beta)t_G'(s)t_R'(s)} \tag{29}$$

The evaluation of the functions $h(t)$ and $F(t)$ has been reduced to the problem of finding the inverses of their Laplace transforms in Equations (28) and (29) for arbitrary forms of the residence time distribution functions and the fraction of the recirculation stream.

The function $F(t)$ is the fraction of tagged particles in stream C at the time t units after the introduction of tagged particles. Since no tagged particles entered the system prior to zero time, all tagged particles have resided in the system a time equal to or less than t.

Let

$$\frac{dF(t)}{dt} \equiv F'(t) \tag{30}$$

and

$$\frac{dH(t)}{dt} \equiv H'(t) \tag{31}$$

Consider now a reactor-regenerator system in which fresh catalyst is fed and used catalyst removed at a rate βn for a very long period of time as shown in Figure 1*b*. The residence-time distribution of the particles in streams C and D approach those given by $F'(t)$ and $h'(t)$, respectively, and the mean permanent deactivations of the streams are, respectively

$$\overline{K_C} = \int_0^\infty K(t)\,F'(t)\,dt \tag{32}$$

and

$$\overline{K_D} = \int_0^\infty K(t)\,h'(t)\,dt \tag{33}$$

Moreover the permanent deactivations of the catalyst leaving the reactor and regenerator which entered from streams C and D, respectively, are

$$\overline{K}_r = \int_0^\infty F'(t) \int_0^\infty K(t+t_r)\, T_R'(t_r)\, dt_r\, dt \tag{34}$$

$$\overline{K_g} = \int_0^\infty H'(t) \int_0^\infty K(t+t_g)\, T_G'(t_g)\, dt_g\, dt \tag{35}$$

The mean permanent deactivation of the stream leaving the reactor which entered as fresh feed is

$$\overline{K_{rf}} = \int_0^\infty K(t_r)T_R'(t_r)\,dt_r \tag{36}$$

Finally the mean permanent deactivations of the particles in the reactor originating from fresh feed without recirculation and from stream C are, respectively

$$\overline{K_{Rf}} = \frac{n}{N_R}\int_0^\infty K(t_r)[1-T_R(t_r)]dt_r \tag{37}$$

$$\overline{K}_R = \frac{n}{N_R} \int_0^\infty F'(t) \int_0^\infty K(t + t_r) [1 - T_R(t_r)]\, dt_r\, dt \qquad (38)$$

and the mean permanent deactivation in the regenerator is

$$\overline{K}_G = \frac{n}{N_G} \int_0^\infty H'(t) \int_0^\infty K(t + t_g) [1 - T_G(t_g)]\, dt_g\, dt \qquad (39)$$

STEADY STATE ACTIVITY LEVELS WITH TEMPORARY AND PERMANENT DEACTIVATION

Throughout this treatment permanent and temporary deactivation phenomena have been assumed to be independent. Permanent deactivation depends only upon residence time within the reactor-regenerator set, whereas temporary deactivation depends upon a detailed history of the residence of catalyst pellets in the reactor and regenerator. It is possible therefore to combine the treatments from the previous sections to predict the activity levels in various parts of the units for the case where fresh catalyst is fed to the units and used catalyst is removed at a rate to maintain constant catalyst inventory. The activity of catalyst for carrying out chemical reaction is given by the product of the two activities.

If the age-distribution functions of the catalyst are time independent in all parts of the unit, the equation for mean activities can be immediately written. With reference to Figure 1*b* the mean activity of catalyst entering the reactor $\overline{A}_i$ is

$$\overline{A}_i = \beta + (1 - \beta)\overline{K}_G \int_0^\infty F(\theta) R(\theta) d\theta \qquad (40)$$

Similarly the activity of catalyst leaving the reactor $\overline{A}_o$ is

$$\overline{A}_o = \beta \overline{K}_{rf} \int_0^\infty R(t_r) T'(t_r) dt_r + (1 - \beta) \overline{K}_r \int_0^\infty F(\theta) \int_0^\infty R(\theta + t_r) T'(t_r) dt_r\, d\theta \qquad (41)$$

In accordance with Figure 1*b* a fraction $(1 - \beta)$ of the particles leaving the reactor enter the regenerator; therefore the mean activity of the stream entering the regenerator is also $\overline{A}_o$, which can be represented also by

$$\overline{A}_o = \overline{K}_D \int_0^\infty H(\alpha) G(\alpha) d\alpha \qquad (42)$$

and the activity of the stream leaving the regenerator $\overline{A}_i - \beta$ is given by

$$\overline{A}_i - \beta = (1 - \beta) \overline{K}_G \int_0^\infty \int_0^\infty H(\alpha) G(\alpha + t_g) T_G'(t_g) dt_g\, d\alpha \qquad (43)$$

The mean activities of particles within the reactor and regenerator are $\overline{A}_R$ and $\overline{A}_G$, respectively, where

$$\overline{A}_R = \frac{n}{N_R} \beta \overline{K}_{Rf} \int_0^\infty R(t_r) [1 - T_R(t_r)] dt_r + \frac{n}{N_R} (1 - \beta) \overline{K}_R \int_0^\infty F(\theta) \int_0^\infty R(\theta + t_r) [1 - T(t_r)] dt_r\, d\theta \qquad (44)$$

and

$$\overline{A}_G = \frac{n}{N_G} \overline{K}_G \int_0^\infty H(\alpha) \int^\infty G(\alpha + t_g) [1 - T_G(t_g)] dt_g\, d\alpha \qquad (45)$$

If $K(t) = 1$ from $0 \leq t \leq \infty$ and β is allowed to go to zero, Equations (33) through (38) reduce to the temporary deactivation case described by Equations (10) through (15).

In the general case the mean activity in the reactor can be obtained by the use of Equations (22*a*) and (44). It is proposed however to approximate the $R(\theta)$ and $G(\alpha)$ by an exponential function in order to calculate mean activity levels under varying conditions.

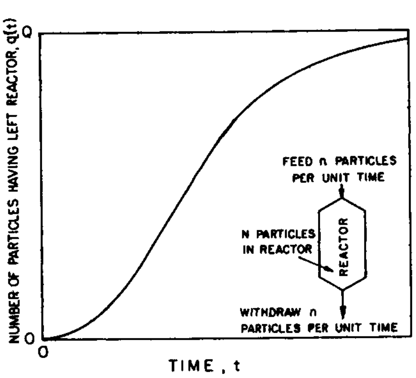

Fig. 2. Residence time distribution in reactor.

ACTIVATION AND DEACTIVATION CURVES OF EXPONENTIAL FORM

Let

$$R(\theta) = e^{-k_r \theta} \qquad (46)$$

and

$$G(\alpha) = 1 - e^{-k_g \alpha} \qquad (47)$$

Substituting Equation (46) into (40) and (41) one gets

$$\overline{A}_i = \beta + (1 - \beta) \overline{K}_G \int_0^\infty e^{-k_r \theta} F(\theta) d\theta \qquad (48)$$

and

$$\overline{A}_o = \beta \overline{K}_{rf} \int_0^\infty e^{-k_r t_r} T'(t_r) dt_r + (1 - \beta) \overline{K}_r \int_0^\infty e^{-k_r \theta} F(\theta) d\theta \int_0^\infty e^{-k_r t_r} T_R'(t_r) dt_r \qquad (49)$$

Substituting Equation (48) into (49) one obtains

$$\overline{A}_o = \left\{ \beta \overline{K}_{rf} + (\overline{A}_i - \beta) \left(\frac{\overline{K}_r}{\overline{K}_G} \right) \right\} t_R'(k_r) \qquad (50)$$

where

$$t_R'(k_r) = \int_0^\infty e^{-k_r t_r} T_R'(t_r)\, dt_r \qquad (51)$$

Substituting Equation (40) into (35) and (36) one gets

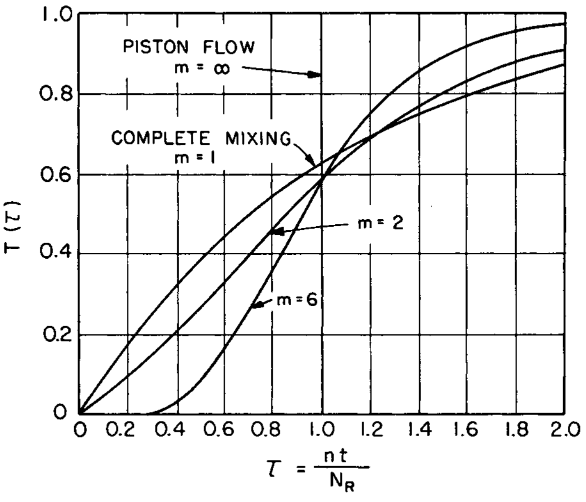

Fig. 3. Residence time distribution in reactor for piston flow, complete mixing, and intermediate cases.

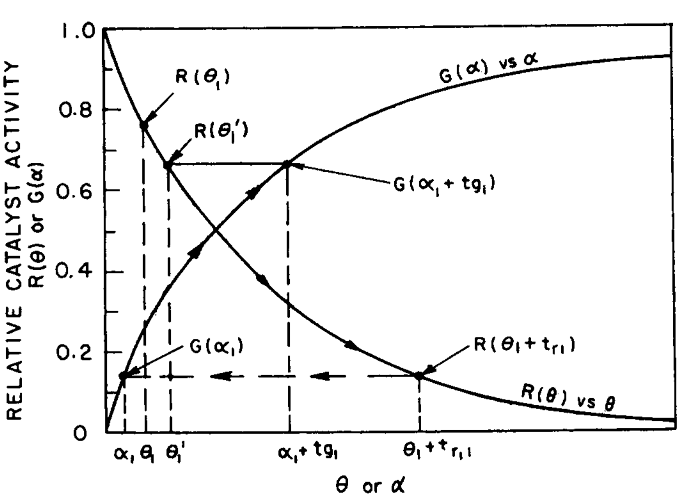

Fig. 4. Temporary reactor deactivation and regenerator activation curves.

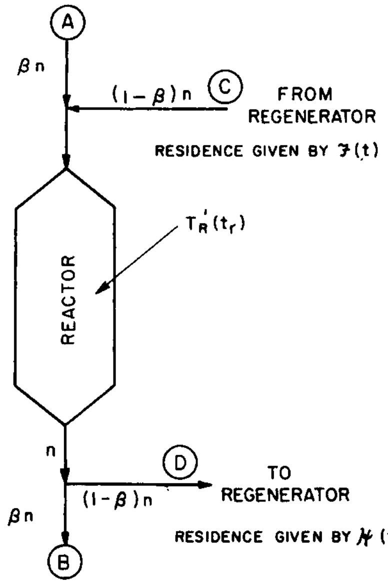

Fig. 5. Reactor regenerator flow system for case of temporary and permanent deactivation.

$$\overline{A}_o = \overline{K}_D[1 - \int_0^\infty e^{-k_g\alpha} H(\alpha)\, d\alpha] \quad (52)$$

$$\overline{A}_i - \beta = (1-\beta)\overline{K}_C \int_0^\infty \int_0^\infty [1 - e^{-k_g(\alpha+t_g)}] H(\alpha)\, T_G'(t_g)\, dt_g\, d\alpha \quad (53)$$

When one performs the integration of Equation (53) and substitutes Equation (52)

$$\overline{A}_i - \beta = (1-\beta)\left(\frac{\overline{K}_C}{\overline{K}_D}\right)[\overline{K}_D + (\overline{A}_o - \overline{K}_D)\mathfrak{t}_G'(k_g)] \quad (54)$$

where

$$\mathfrak{t}_G'(k_g) = \int_0^\infty e^{-k_g t_g}\, T_G'(t_g)\, dt_g$$

Substituting Equation (50) into (54) and solving for $\overline{A}_i$ one obtains

$$\overline{A}_i = \beta + \frac{(1-\beta)[\overline{K}_C\overline{K}_D + \overline{K}_C(\beta\overline{K}_{r_f}\mathfrak{t}_R'(k_r) - \overline{K}_D)\mathfrak{t}_G'(k_g)]}{\overline{K}_D - (1-\beta)\,\overline{K}_r\mathfrak{t}_R'(k_r)\,\mathfrak{t}_G'(k_g)} \quad (55)$$

Finally from Equation (44) the mean activity in the reactor is computed:

$$\overline{A}_R = \frac{n}{N_R}\{\beta\overline{K}_{R_f}\int_0^\infty e^{-k_r t_r}[1-T_r(t_r)]dt_r + (1-\beta)\overline{K}_R\int_0^\infty e^{-k_r\theta} F(\theta)\, d\theta \int_0^\infty e^{-k_r t_r}[1-T_R(t_r)]dt_r\} \quad (56)$$

When one substitutes for $(\overline{A}_i-\beta)/(\overline{K}_C)$ from Equation (48) into (56)

$$\overline{A}_R = \frac{n}{N_R}\left[\beta\overline{K}_{R_f} + \frac{\overline{K}_R}{\overline{K}_C}(A_i - \beta)\right]\int_0^\infty e^{-k_r t_r}[1 - T_R(t_r)]dt_r \quad (57)$$

Expressions for $\overline{A}_o$ and $\overline{A}_G$ can be developed similarly.

The solution to the case of temporary deactivation alone can be obtained from Equations (55) and (57) if one lets $K(t) = 1$ and β go to zero. The resulting equations are

$$\overline{A}_i = \frac{1 - \mathfrak{t}_G'(k_g)}{1 - \mathfrak{t}_R'(t_r)\,\mathfrak{t}_G'(k_g)} \quad (58)$$

$$\overline{A}_R = \frac{n}{N_R}\overline{A}_i \int_0^\infty e^{-k_r t_r}[1 - T_R(t_r)]dt_r \quad (59)$$

Activation and deactivation functions for a particular set of operating conditions are difficult to measure accurately. Blanding (*1*) has measured activity vs. time curves and found that the activity is roughly proportional to the 0.5 power of time. Values of the mean reactor activity may be approximated by fitting an exponential function to the important range of time. However, if warranted, a solution to this problem can be obtained numerically by solving Equation (22). It should be mentioned that the problem can also be solved by a Monte-Carlo method (see reference *1*) in which the residence time that a particle spends in each unit as it cycles is determined by dice weighted according to the residence-time distributions therein.

In the following section the equations previously developed will be applied to more specific cases to illustrate their use.

ILLUSTRATIVE CALCULATIONS

When one considers only temporary deactivation, the steady state activity level within the reactor can be computed from Equations (58) and (59). These equations are easily solved for the limiting cases of complete mixing and piston flow in both the reactor and regenerator. For the first case let $N_R = N_G$ and $k_r = k_g$.

The residence time distribution function for complete mixing is

$$T_{RM}'(t_r) = \frac{n}{N_R} e^{-\frac{n}{N_R}t_r} \quad (60)$$

From Equation (58)

$$\overline{A}_{iM} = \frac{1+\epsilon}{2+\epsilon} \quad (61)$$

where

$$\epsilon = \frac{k}{\lambda};\ k = k_r = k_g;\ \text{and}\ \lambda = \frac{n}{N_R} = \frac{n}{N_G}$$

$$\overline{A}_{RM} = \frac{1}{\epsilon + 2} \quad (62)$$

For the case of piston flow through the reactor and regenerator all particles spend the same time, N/n, in each unit.

$$\overline{A}_{iP} = \frac{1 - e^{-\epsilon}}{1 - e^{-2\epsilon}} \quad (63)$$

$$\overline{A}_{RP} = \frac{(1 - e^{-\epsilon})^2}{(1 - e^{-2\epsilon})} \quad (64)$$

Figure 6 shows the activity in the reactor as a function of ϵ. Note that the highest activity of 0.50 is a result of letting $k_r = k_g$.

For the case of $k_g = 5k_r$ and $N_R = N_G$, the corresponding expressions for the activity in the reactor for complete mixing and piston flow are, respectively:

$$\overline{A}_{RM} = \frac{5}{(5\epsilon + 6)} \quad (65)$$

and

$$\overline{A}_{RP} = \frac{(1 - e^{-\epsilon})(1 - e^{-5\epsilon})}{\epsilon(1 - e^{-6\epsilon})} \quad (66)$$

where now $\epsilon = (k_r)/(\lambda)$.
The highest activity is now 5/6 which results from making $k_g = 5k_r$. Note that the highest activity levels approached in Figures 6 and 7 are discontinuous at zero; obviously when k_r is equal to zero, the activity must be 1.0. Values of the mean activity in the reactor are plotted in Figure 7 as a function of ϵ. Figures 6 and 7 show the advantages of piston flow over complete mixing.

If both permanent and temporary deactivation are considered, then $\mathcal{F}'(t)$ and $\mathcal{H}'(t)$ must be calculated in order to evaluate the mean activities $\overline{K}$'s in Equations (55) and (57). For the case of complete mixing for equal size reactor and regenerator

$$\left.\begin{aligned} T_R'(t) &= T_G'(t) = \lambda e^{-\lambda t} \\ \text{and} \quad & \\ T_R(t) &= 1 - e^{-\lambda t} \end{aligned}\right\} \quad (67)$$

Therefore from Equations (28) and (29) the Laplace transformations of the functions $'(t)$ and $'(t)$ are

$$\left.\begin{aligned} h'(s) &= \frac{\beta\lambda(s+\lambda)}{(s+\lambda)^2 - \lambda^2(1-\beta)} \\ f'(s) &= \frac{\beta\lambda^2}{(s+\lambda)^2 - \lambda^2(1-\beta)} \end{aligned}\right\} \quad (68)$$

Inverting the transformations by the method of partial fractions one gets

$$\mathcal{H}'(t) = \beta\lambda e^{-\lambda t}\cosh\lambda(\sqrt{1-\beta})t \quad (69)$$

$$\mathcal{F}'(t) = \frac{\beta}{\sqrt{1-\beta}}\lambda e^{-\lambda t}\sinh \lambda(\sqrt{1-\beta})t \quad (70)$$

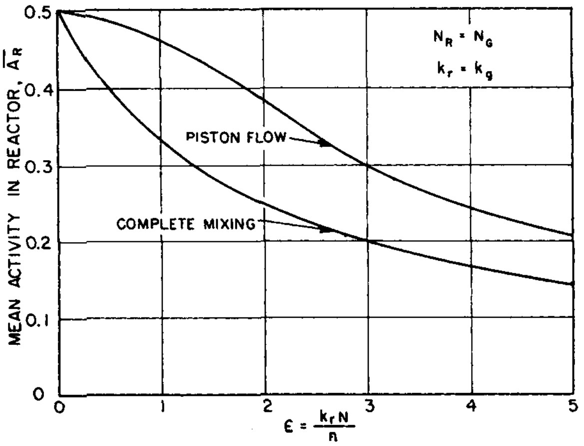

Fig. 6. Mean activity within reactor for the case of temporary deactivation.

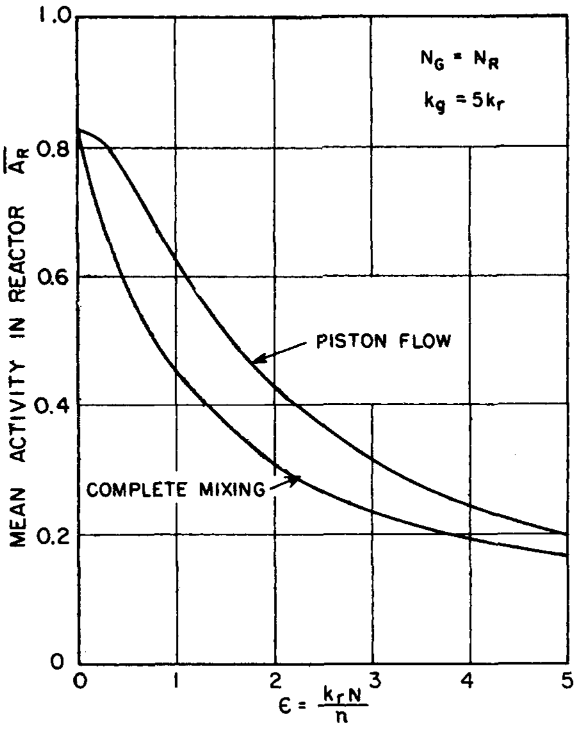

Fig. 7. Mean activity within reactor for the case of temporary deactivation.

Equations (69) and (70) may now be substituted into Equations (26) through (39) along with the appropriate function $K(t)$ to evaluate mean activities of various streams in the reactor-regenerator system.

CONCLUSIONS

This paper has dealt with a very complex subject, many details of which are not yet known. A method has been developed for calculating the mean activity levels of catalyst particles at various points within a reactor-regenerator system from arbitrarily assumed residence-time and deactivation and activation functions. The analysis developed in this paper is quite general, and although it is subject to certain idealizations regarding the temporary activation and deactivation functions, it should tentatively serve as a means of interpreting the values of mean activities and their variation with operating variables in terms of laboratory data on catalyst behavior and residence-time characteristics of reactors and regenerators.

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NOTATION

- $\overline{A}$ = mean activity
- $F(\theta)$ = age-distribution function in reactor feed
- $F(t)$ = fraction of particles leaving regenerator having entered the system at time t or less
- $F'(t)$ = time derivative of $F(t)$
- $G(\alpha)$ = temporary activation function
- $H(\alpha)$ = age-distribution function in regenerator feed
- $H(t)$ = fraction of particles leaving reactor having entered the system at time t or less
- $H'(t)$ = time derivative of $H'(t)$
- k = constant defined by Equations (46) and (47)
- $K(t)$ = permanent deactivation function
- $\overline{K}$ = mean permanent deactivation
- m = number of completely mixed stages in series
- n = feed rate to reactor
- $P(\xi)$ = age distribution in regenerator feed
- N = number of particles within reactor or regenerator
- q = number of tagged particles having left reactor
- $Q(\eta)$ = age distribution in reactor feed
- Q = number of tagged particles introduced into reactor
- $R(\theta)$ = temporary deactivation function
- t = time
- $T'(t)$ = residence-time distribution function
- $T(t)$ = defined by Equation (3)

Greek Letters

- α = catalyst age in regenerator
- β = fraction of reactor feed stream which is fresh catalyst
- ϵ = k/λ
- λ = n/N
- η = $\alpha + t_g$
- θ = catalyst age in reactor
- ξ = $\theta + t_r$
- τ = dimensionless time

Subscripts

- G and g = regenerator
- i = stream entering reactor
- o = stream leaving reactor
- M = complete mixing
- P = piston flow
- R and r = reactor

Other Notation

Small letters $f(s)$, $f'(s)$, $h(s)$, $h'(s)$, $t(s)$, and $t'(s)$ represent the Laplace transforms of the corresponding capitalized functions.

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