On the Interdependence of Temporary and Permanent Deactivation in a Reactor-Regenerator System

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Under a given catalyst replacement policy for a reactor-regenerator system, the mean steady state activity in either vessel is a function of both permanent and temporary (regenerable) deactivation. In calculating the mean activity, catalyst particles that undergo an appreciable degree of permanent deactivation per cycle cannot be considered to have time independent temporary and permanent deactivation. This became apparent when the authors used Petersen's analytic solution [*AIChE J.*, **6**, 488 (1960)] to test a numerical technique applied to a more complex system.

Petersen assumed that permanent and temporary deactivation phenomena can be treated as being time independent. That is, the mean of actual activity can be taken as the product of mean permanent activity and the mean temporary activity. While this becomes nearly true after the first cycle, it is definitely not true for freshly added (makeup) catalyst.

Consider the first pass through the reactor of new catalyst added at the reactor inlet. As it leaves the reactor, the residence time distributions are identical for both temporary and permanent deactivation. That is, a particle of long residence in the first pass will be strongly deactivated in both permanent and temporary activity. For first-order deactivation (exponential decay) and continuous stirred tank reactor (CSTR), the mean activity after the first pass through the reactor is

$$\overline{A_0} = \int_0^\infty e^{-pt}\, e^{-k_r t}\, \lambda e^{-\lambda t}\, dt \qquad (1)$$

where p is the permanent deactivation rate constant, k_r is the temporary deactivation rate constant, and $1/\lambda$ is the mean residence time or,

$$\overline{A_0} = \frac{\lambda}{p + k_r + \lambda} \qquad (2)$$

But Petersen's approach gives

$$\overline{A_0} = \overline{K_{rf}} \cdot \frac{\lambda}{k_r + \lambda} \qquad (3)$$

or,

$$\overline{A_0} = \frac{\lambda}{p+\lambda} \cdot \frac{\lambda}{k_r + \lambda} \neq \frac{\lambda}{p + k_r + \lambda} \qquad (4)$$

where $\overline{K_{rf}}$ is the mean permanent deactivation in the first pass of fresh catalyst through the reactor. Thus, except for small values of p, Petersen's value of $\overline{A_0}$ is not correct.

The activity leaving the regenerator during the first cycle and activities of subsequent cycles may be calculated in a similar fashion; however, the algebraic manipulations soon become overwhelming. Therefore, the authors have modified Petersen's approach in his equations (40) to (59). The equations that differ from his due to the correlation between temporary and permanent deactivation are designated with a primed equation number. Otherwise, the numbers correspond to Petersen's.

The mean activity of catalyst entering the reactor, $\overline{A_i}$, is

$$\overline{A_i} = \beta + (1-\beta)\,\overline{K_c} \int_0^\infty F(\theta)\, R(\theta)\, d\theta \qquad (40)$$

where β is the fraction of fresh catalyst entering the reactor, $\overline{K_c}$ is the mean permanent deactivation of recycle catalyst entering the reactor, $F(\theta)$ is the unknown time distribution that yields the temporary activity distribution given, and $R(\theta)$ is the temporary activity by deactivation as a function of time.

The mean activity of catalyst leaving the reactor, $\overline{A_0}$, is

$$\overline{A_0} = \beta \int_0^\infty R(t_r)\, K(t_r)\, T'(t_r)\, dt_r + (1-\beta)\,\overline{K_c} \int_0^\infty F(\theta) \int_0^\infty R(\theta + t_r)\, T'(t_r)\, dt_r\, d\theta \qquad (41')$$

where $K(t)$ is the permanent activity as a function of time and $T'(t_r)$ is the residence time distribution function for the reactor.

The mean activity of the catalyst entering the regenerator is $\overline{A_0}$, which can be represented also by

$$\overline{A_0} = \overline{K_D} \int_0^\infty H(\alpha)\, G(\alpha)\, d\alpha \qquad (42)$$

where $\overline{K_D}$ is the mean permanent activity of all catalyst leaving the reactor, $H(\alpha)$ is the unknown time distribution that yields the temporary activity distribution given, and $G(\alpha)$ the temporary activity by reactivation as a function of time, α.

The mean activity of the stream leaving the regenerator, $\overline{A_i} - \beta$, is given by

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

For the specific example let:

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

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

$$K(t) = e^{-pt} \qquad (47a)$$

After performing substitutions and integrations similar to those in Petersen's article,

$$\overline{A_0} = \overline{A_i}\, t'_R \qquad (50')$$

and

$$\overline{A_i} = \frac{\beta + (1-\beta)\,\overline{K_D}(t'_p - t'_g)}{1-(1-\beta)t'_g\ t'_R} \tag{55'}$$

where, for the case of the CSTR reactor and regenerator of equal size,

$$T'_G(t) = T'_R(t) = \lambda e^{-\lambda t}$$

$$t'_R = \frac{\lambda}{k_r + p + \lambda}$$

$$t'_p = \frac{\lambda}{p + \lambda}$$

$$t'_g = \frac{\lambda}{k_g + p + \lambda}$$

and

$$\overline{K_D} = \frac{\beta\lambda(p+\lambda)}{p^2 + 2p\lambda + \beta\lambda}$$

The approach of Equations (40) and (42) is not exact, but alternate deactivation and reactivation greatly reduces interaction in the second half of a cycle. Thus, a comparison of mean activities calculated from Equations (50′) and (55′) with those from Petersen's equations (50) and (55) showed the latter to be low by about 25% for the once-through makeup catalyst and by about 3% for the total stream (where $p = k_r = k_g = \lambda$, $\beta = 0.1$).

It is worth noting that although the authors, like Petersen, chose to express activity as a function of time, or age, the problem might have been formulated as proposed by Rudd (*Can. J. Chem. Eng.*, **40**, 197, [Oct. 1962]).

Correlation of Liquid Slug Velocity and Frequency in Horizontal Cocurrent Gas-Liquid Slug Flow

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Liquid slug velocities and frequencies have been measured for the system carbon dioxide-water in a ¾ in. diameter tube. The gas and liquid were introduced to the tube using a simple tee mixer, located approximately 300 pipe diameters upstream of the measuring point. This distance was chosen to ensure that fully developed slug flow pattern would be obtained. All runs were performed at essentially atmospheric pressure and 25°C. A detailed description of the complete flow apparatus is given elsewhere (*1, 2*).

SLUG VELOCITY

The slug velocity measuring procedure has been used by Hubbard (*3*) and consisted of measuring the time lag between the pressure pulses for a given slug at two points in the test section. Pressures were measured using high response strain gauge transducers mounted into small wells located on the underside of the test section. The transducer voltage outputs were amplified and recorded on a two channel, high response, strip chart recorder.

The slug velocity values reported each represent the average of about ten determinations for a given set of gas and liquid flow rates. Individual values varied by about ± 18% from the mean. The no-slip velocity is defined as the sum of the gas and liquid superficial velocities. Hence,

$$V_{ns} = V^0{}_L + V^0{}_G \tag{1}$$

Figure 1 shows the measured slug velocity plotted against the no-slip velocity. The line of best fit through the data is given by,

$$V_s = 1.35\ V_{ns} \tag{2}$$

Hubbard (*3*) has obtained the relation

$$V_s = 1.25\ V_{ns} \tag{3}$$

from his slug flow model. However, his data shows better agreement, particularly at the higher slug velocities with Equation (2) than with (3) as shown in Figure 2.

As a consequence of Equation (3), Hubbard's theory also predicts that the true average gas velocity is given by the relation,

$$V_G = 1.11\ V_{ns} \tag{4}$$

Based on the Hughmark correlation (*4*) for slug holdup,

$$V_G = 1.22\ V_{ns} \tag{5}$$

for $N_{ReLs} > 400{,}000$, and for $N_{ReLs} < 400{,}000$, the constant is somewhat larger, being approximately proportional to $(N_{ReLs})^{-1/4}$. [Note: N_{ReLs} = liquid slug Reynolds number $= d\ (V^0{}_L + V^0{}_G)\ \rho_L/\mu_L$]. In addition, Nicklin, et al. (*5*) claim that for horizontal slug flow

$$V_G = 1.20\ V_{ns} \tag{6}$$

With the slug velocity given by Equation (2), Hubbard's theory predicts

$$V_G = 1.19\ V_{ns} \tag{7}$$

which is in better agreement with other published data.

SLUG FREQUENCY

Slug frequencies were measured by two techniques. The first consisted of simply counting, from visual observation, the number of liquid slugs passing a given point in the test section, over a period of time measured with a stopwatch. The second method consisted of counting the number of slug pressure pulses recorded on the strip chart recorder of the pressure measuring system, for a given period of time. Good agreement was obtained between the two methods, and either one is considered satisfactory. The measured slug frequencies, and the corresponding slug velocities are each the average of about 10 individual observations,