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Some Aspects of the Constant-Conversion Policy Dealing with Catalyst Deactivation[1]

TEH CHUNG HO

Corporate Research Laboratories, Exxon Research and Engineering Company,
Annandale, New Jersey 08801

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Some practical aspects of the constant-conversion rising-temperature policy dealing with catalyst deactivation are discussed. Included are the extraction of deactivation kinetics from observables, the selection of optimum operating conditions under various process constraints, and the use of accelerated aging for acquiring information on catalyst life.

INTRODUCTION

In an often quoted paper, Szepe and Levenspiel (*1*) proposed a constitutive equation describing catalyst deactivation which can be used for mechanistic studies of catalyst deactivation or be incorporated into the design equation for reactor sizing. For a single irreversible *m*th order reaction, they introduced the following Arrhenius type equations relating the main reaction (r) to deactivation (r_D)

$$r = KC^m a \equiv A_m \exp(-E/RT) C^m a \quad (1)$$

$$r_D = K_d a^n C^l \equiv A_d \exp(-E_d/RT) a^n C^l \quad (2)$$

where C is the concentration of reactant and a the catalyst activity. Based on the model, they proceeded to solve the optimization problem of choosing the temperature policy in a batch reactor for maximum time-averaged conversion for the case of concentration independent deactivation ($l = 0$). The principal result is that so long as deactivation is more sensitive to temperature than the main reaction, the temperature should be continuously raised to maintain Ka at constant. This condition, when applied to flow reactors, means a policy of maintaining a constant exit conversion through temperature adjustment. In the case of concentration dependent deactivation, it was shown by other workers that the policy of maintaining constant Ka, while no longer optimum in batch reactor operation (*2*), can still be an optimum policy for flow reactors under quasi-steady-state conditions (*3, 4*). (The deactivation time scale is much larger than the characteristic time scales of the main reaction and flow.) Besides providing optimality, the constant-conversion policy avoids the difficulty of designing and controlling separation and recycle units with varying feed composition. This policy has in fact been the most commonly used operation mode in petroleum and chemical process industries. Accordingly, in practice catalyst life tests in the bench or pilot stage are commonly conducted at constant conversion.

Krishnaswamy and Kittrell (*5*) integrated Eqs. (1) and (2) analytically to obtain the temperature vs time trajectory in isoconversional operation and then used the results to analyze their pilot plant hydrocracking and reforming data. However, the analytical properties of the constant-conversion rising-temperature policy have not been fully exploited. Here we examine the problem in more detail. Included in the discussion are the extraction of deactivation kinetics from observables, the selection of optimum operating conditions under vari-

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ous process constraints, and the use of accelerated aging for acquiring information on catalyst life

CONSTANT-CONVERSION RISING-TEMPERATURE POLICY

In a plug-flow reactor at quasi-steady state, the conversion x at any time t is

$m \neq 1$

$$x(t) = 1 - \left[1 - (1 - m)C_0^{m-1}\frac{K(t)a(t)}{S}\right]^{\frac{1}{1-m}} \tag{3}$$

$m = 1$

$$x(t) = 1 - e^{-K(t)a(t)/S} \tag{4}$$

where S is the space velocity and C_0 the inlet concentration Suppose that we raise reactor temperature to maintain constant conversion, then this should be done in such a way that Ka remains constant, i e ,

$$K(t)a(t) = K(0)a(0) = K_0, \qquad K_0 \equiv A_{\mathrm{m}}e^{-E/RT(0)} \tag{5}$$

Moreover, the concentration term in r_{D} can be removed from the problem (i e , $l = 0$) without loss of generality because it is kept constant Denoting T_0 as the start-of-run (SOR) temperature, $T(0)$, we obtain

$$\frac{T_0}{T(t)} = 1 + \frac{RT_0}{E}\ln a(t) \tag{6}$$

It can be shown that the progressions of activity and temperature are

$n - q \neq 1$

$$a(t) = [1 + K_{\mathrm{do}}(n - q - 1)t]^{-\frac{1}{(n-q-1)}}, \tag{7}$$

$$\frac{T_0}{T(t)} = 1 - \frac{RT_0}{E}\frac{1}{(n - q - 1)}\ln[1 + K_{\mathrm{do}}(n - q - 1)t] \tag{8}$$

$n - q = 1$

$$a(t) = e^{-K_{\mathrm{do}}t}, \tag{9}$$

$$\frac{T_0}{T(t)} = 1 - \frac{RT_0}{E}K_{\mathrm{do}}t \tag{10}$$

where $K_{\mathrm{do}} \equiv A_{\mathrm{d}}\exp(-E_{\mathrm{d}}/RT_0)$ and $q \equiv E_{\mathrm{d}}/E$ It may be noted that in isoconversional operation $n - q$ may be referred to as the "effective" order of deactivation [2]

ESTIMATION OF DEACTIVATION PARAMETERS

It should be emphasized that the above results are based on the assumption that the time constants for the main reaction and flow are much smaller than that for deactivation (quasi-steady-state approximation) A corollary of this is to state that the parameters E, m, and A_{m}, for practical purposes, may be determined from experiments essentially free of catalyst deactivation And Eqs (8) and (10) can be used for the determination of the deactivation parameters K_{do}, q, and n from life experiments This is easily done by choosing the deactivation parameters to minimize the following objective function J, i e ,

$$J = \sum_{j=1}^{N}\left(\frac{T_0}{T_j} - \frac{T_0}{\hat{T}_j}\right)^2 = \text{minimum} \tag{11}$$

where T_j and $\hat{T}_j$ are the observed and calculated temperatures, respectively, and N is the total number of measurements For $n - q = 1$, the determination of deactivation parameters is even simpler, for the plot of $1/T$ vs onstream time will be linear with slope $-RK_{\mathrm{do}}/E$, thus allowing K_{do} to be extracted Moreover, if one conducts several constant-conversion runs with different SOR temperatures, then E_{d} can be determined

A few remarks on the practical use of the above method may be in order The constant-conversion rising-temperature policy can be easily implemented in practice because the deactivation rate we are dealing with is rather slow in comparison with the rates of the main reaction and flow This is in fact a primary reason why in industrial practice this policy is so commonly used for continuous reactors subject to slow deactivation The deactivation kinetic parameters

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[2] It can be shown that at constant conversion, $a(t)$ is governed by $da/dt = -K_{\mathrm{do}}a^{n-q}$, $a(0) = 1$

determined by the above method may be used to predict catalyst lifetime (see an example in Ref (*6*)) and optimum operating conditions Also, as can be seen from the development, the method can be conveniently used for determining the deactivation parameters in situations involving concentration-dependent deactivation, an advantage over the constant-temperature method (*7*)

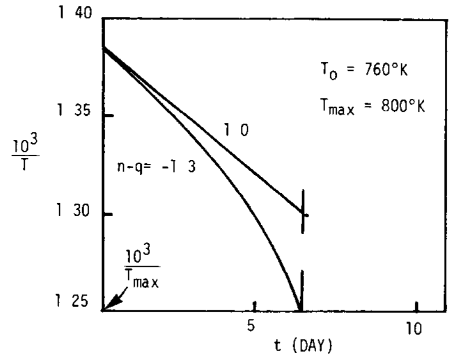

FIG 1 $1/T$ vs time-on-stream at constant conversion

PSEUDO-FIRST-ORDER APPROXIMATION

For small times, expanding the logarithmic function in Eq (8) into the Taylor series and keeping only the first term gives

$$\frac{T_0}{T(t)} \approx 1 - \frac{RT_0}{E} K_{do} t \qquad (12)$$

We see that the case where $n - q = 1$ represents the asymptote of the general case where $n - q \neq 1$ at small times (An analogy in this respect may be made with the pseudo-first order approximation used in conventional kinetic studies)

Since in practice the constant-conversion rising-temperature run ends at the maximum allowable temperature (T_{max}), usually the temperature at which the target conversion can no longer be obtained, we may define catalyst lifetime θ as the time span between the start and the end of the run (EOR) The above development suggests that with a limited amount of initial temperature-time data, θ may be predicted or estimated For $n - q = 1$ (first order), θ can be predicted by a linear extrapolation of the initial $1/T - t$ data to $1/T_{max}$ If $n - q \neq 1$, the same procedure may be used to obtain a rough estimate of θ This is illustrated in Fig 1 as a dotted line with the same values of the parameters (E, A, E_d, A_d, and T_{max}) as Levenspiel and Sadana (*8*) and in addition with T_0 = 760°K, and $n - q = -1$ 3 As seen, the pseudo-first-order approach gives an upper bound for θ because here $n - q <$ 1 In lack of anything better, this approach may be used for comparative screening of catalyst lives

PROPERTIES OF TEMPERATURE RISE

Denoting a_f as the activity at T_{max}, a_f can then be calculated as

$$a_f = e^{-\gamma(1-\beta)} \qquad (13)$$

with $\beta \equiv T_0/T_{max}$ and $\gamma \equiv E/RT_0$ It is convenient to nondimensionalize time with respect to $1/K_d(T_{max})$ Using the overbar to denote dimensionless quantities, the dimensionless catalyst lifetime $\bar{\theta}$ can be calculated

$n - q \neq 1$

$$\bar{\theta} = \frac{1}{(n-q-1)}[e^{\gamma(n-q-1)(1-\beta)} - 1]e^{\gamma_d(1-\beta)} \qquad (14)$$

$n - q = 1$

$$\bar{\theta} = \gamma(1 - \beta)e^{\gamma_d(1-\beta)} \qquad (15)$$

with $\gamma_d \equiv E_d/RT_0$ Equations (7)–(10) can also be rephrased in dimensionless form, i e ,

$n - q \neq 1$

$$\bar{T} = \beta\left\{1 - \frac{1}{\gamma(n-q-1)} \ln[1 + (n-q-1)e^{-\gamma_d(1-\beta)}\bar{t}]\right\}^{-1} \qquad (16)$$

$$a = [1 + (n-q-1)e^{-\gamma_d(1-\beta)}\bar{t}]^{\frac{-1}{n-q-1}} \qquad (17)$$

$n - q = 1$

$$\bar{T} = \beta\left[1 - \frac{e^{-\gamma_d(1-\beta)}}{\gamma}\bar{t}\right]^{-1} \qquad (18)$$

$$a = \exp(-\bar{t}e^{-\gamma_d(1-\beta)}) \qquad (19)$$

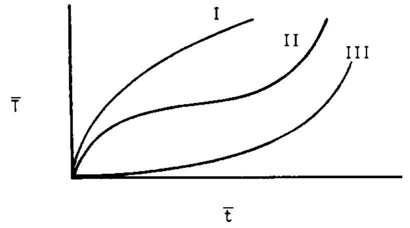

FIG. 2. Properties of temperature-rise history at constant conversion.

where $\bar{t} = tK_d(T_{max})$ and $\bar{T} = T(t)/T_{max}$. It is easy to verify that the temperature rise can exhibit three distinct types of behavior, depending on the effective order $n - q$, as depicted in Fig. 2.

1. Decelerating (Type I); this is to be found for $n - q \geq 1 + 2/\gamma\beta$.

2. Combined decelerating and accelerating (Type II); there is an inflection point within the interval $(0,\bar{\theta})$ whenever $1 + 2/\gamma < n - q < 1 + 2/\gamma\beta$.

3. Accelerating (Type III); this type of behavior occurs for $n - q \leq 1 + 2/\gamma$.

Thus, the shape of the temperature rise would allow one to infer a priori the general character of the deactivation kinetics. Moreover, it can be used as a guide for parameter estimation. Physically, Type I behavior might be suggestive of plugging of fine pores in situations where coke deposition is the cause of deactivation. That poisons may become less strongly chemisorbed on the catalyst as temperature increases also concurs with Type I behavior. Type II behavior is of common occurrence in hydroprocessing in which catalyst deactivation is caused by both coke and metal deposition. Type III behavior could be caused by changes in catalyst structure, which usually is a highly activated process characterized by an initial slow period of deactivation (*6*). Experimental examples of the above three types of behavior can be found in Refs. (*9–11*).

OPTIMUM OPERATING CONDITIONS

The objective function considered here, which is to be maximized for optimality, is usually referred to as the "space conversion," SC,

$$SC = \int_0^\theta C_0 Sx\,dt = C_0 Sx\theta \qquad (20)$$

which measures the total product produced per unit volume (or weight) of catalyst. We may call C_0Sx the production rate. In dimensionless form, SC becomes $\overline{SC} = \bar{S}x\bar{\theta}$ with $\bar{S} = S/K(T_{max})C_0^{m-1}$. We see that the control variables for maximization of $\overline{SC}$ are β and $\bar{S}$. The following examples illustrates how β and $\bar{S}$ should be chosen under different process constraints.

Example. We use the same parameters as before and, in addition, consider the case of $m = 1$, $n = 0$, and $S = 0.6498\ s^{-1}$. The space conversions as a function of space velocity at several constant production rates are plotted in Fig. 3. Also plotted are the loci of constant β (dotted curves). These plots show the following.

(1) A gain in space conversion can be obtained by increasing space velocity at

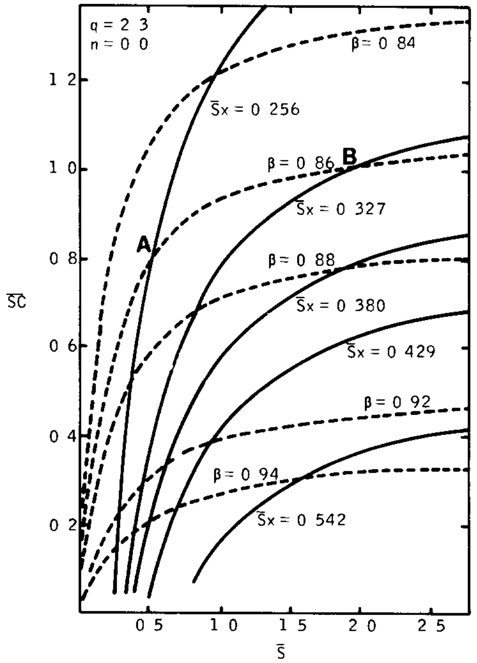

FIG. 3. Space conversion as a function of space velocity at constant production rates or constant starting temperatures.

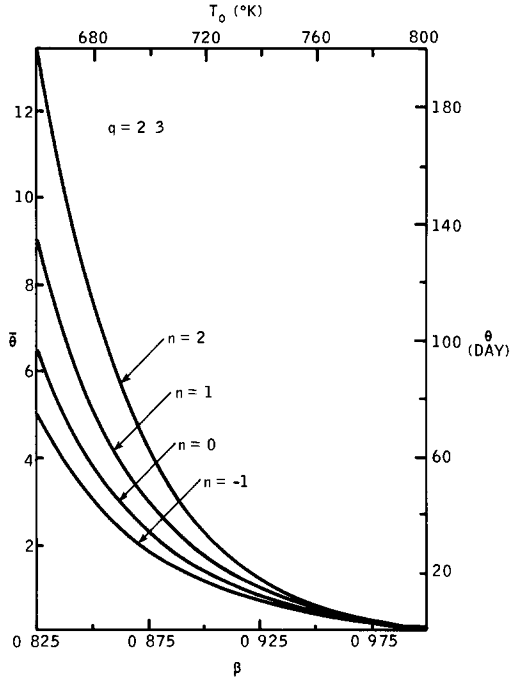

FIG 4 Effect of starting temperature on catalyst life for different orders of deactivation

a constant production rate This is because an increase in space velocity, while maintaining constant production rate, allows the catalyst to be operated at a lower temperature (this is true provided that the order of the main reaction is positive) Thus, if production rate is the only concern, then one should run the catalyst at the highest permissible space velocity For example, taking the curve for $\overline{Sx}$ = 0 327, increasing $\bar{S}$ from 0 4 to 0 6 results in a threefold increase in $\overline{SC}$

(2) If there exists a lower limit on the SOR temperature, then the optimal policy would be to operate at that limiting temperature and the highest permissible space velocity In other words, the optimum trajectory along a constant β curve points to the direction of increasing production rate, as shown in Fig 3 from A to B for β = 0 86 The range over which increasing space velocity is effective is rather narrow, however

(3) If space velocity has to be fixed, then lowering production rate to the least permissible level is optimum, e g , at $\bar{S}$ = 1 0 a decrease in production rate from 0 429 to 0 327 causing $\overline{SC}$ to go up by about a factor of 2

The above results are hardly surprising, for catalyst life is exponentially dependent upon temperature Figure 4 shows the dependency of catalyst lifetime on the SOR temperature for different deactivation orders at an identical set of flow and kinetic parameters As seen, the effect of deactivation order becomes greater as the SOR temperature is lowered Also, catalysts with high-order deactivation give longer service than those with low-order deactivation

ACCELERATED AGING

A most difficult step in catalyst development is to obtain reliable information on catalyst life, which may require several months or even years In practice, accelerated aging is often used as an expedient technique for both screening and prediction purposes However, experiments of this sort have to be carefully formulated and interpreted because a change in the deactivation mechanism at the accelerated conditions may result in totally misleading conclusions

Depending upon the dominant deactivation mechanism, there are many ways of formulating accelerated aging For example, hydrogen starvation may be used to intensify coking Oxygen starvation may be used in hydrocarbon selective oxidations on metal oxide catalysts Runs with spiked feed or at high space velocities may be made to accelerate metal deposition Also, use of high mass velocity has been found to be very effective in some cases because a particular catalyst constituent may be relatively more volatile (*12*)

If the deactivation mechanism is thermal in nature, then exposing the catalyst to a more severe thermal environment may be used to generate accelerated aging This can be best illustrated in the plane of ln S vs

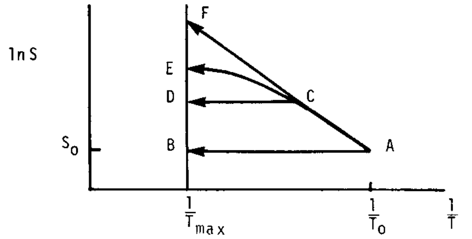

FIG 5 Methods of accelerated aging described in the plane of ln S vs $1/T$

$1/T$ shown in Fig 5 (S_0 is the SOR space velocity) With no deactivation, the trajectories of isoconversionals in this plane under most circumstances are straight lines with a slope proportional to the activation energy of the reaction (line AF in Fig 5) At design conditions, the SOR temperature and space velocity are chosen to give the design conversion (point A in Fig 5) As catalyst ages, the constant-conversion rising-temperature policy causes point A to move progressively toward the left until the EOR temperature is reached (path AB) A simple way of generating rapid aging would be to run the catalyst at design conversion along path CD which is at a higher-than-design space velocity

Alternatively, the isoconversional run may be performed at design conversion by raising both temperature and space velocity along path AE One practical way to implement this is to raise temperature linearly and adjust space velocity accordingly, that is, an isoconversional operation consists of

$$T = T_0 + \alpha t \tag{21}$$

$$\frac{d}{dt}\left(\frac{Ka}{S}\right) = 0 \tag{22}$$

It can be shown that, on invoking the following approximation, for large E_d/RT,

$$\int_{T_0}^{T} e^{-E_d/RT}\,dT \approx \int_{0}^{T} e^{-E_d/RT}\,dT \approx \frac{RT^2}{E_d}\left(1 - \frac{2RT}{E_d}\right)e^{-E_d/RT} \tag{23}$$

one can obtain for $n = 1$ an approximate analytic form for the space velocity vs temperature relationship, i e ,

$$\ln\frac{S}{S_0} \approx \frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) - \frac{A_d}{\alpha}\frac{RT^2}{E_d}\left(1 - \frac{2RT}{E_d}\right)e^{-E_d/RT} \qquad \left(\frac{E_d}{RT} \gg 1\right) \tag{24}$$

The second term on the right-hand side of Eq (24) represents the first-order correction due to catalyst deactivation Depending upon the heating rate α, Eq (24) shows that space velocity can be either increasing or decreasing Thus, one should choose a sufficiently high α so that temperature and space velocity are both rising throughout the run For the same SOR temperature, this would give a set of more severe conditions than does the temperature-rise run

Finally, to make accelerated aging a predictive tool, it is necessary to have information on deactivation kinetics An example to stress this point is given below (see also another example in (*6*))

Example Consider two catalysts A and B of the same nature, both perform identically when they are fresh They are different from each other only in the activation energy for deactivation, say, 23 kcal/mol for A and 20 kcal/mol for B This difference could be attributed to the incorporation of a higher content of stabilizer in A, which

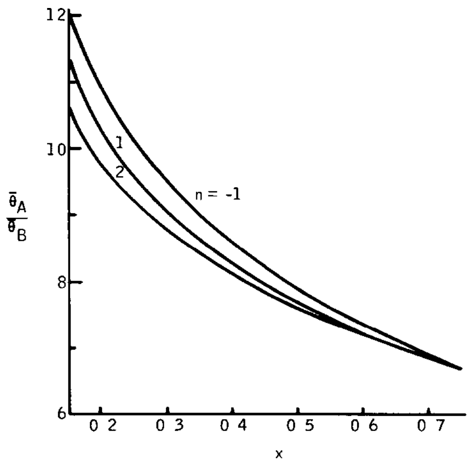

FIG 6 Variation of catalyst life ratio with conversion level for different orders of deactivation

makes A more resistant to thermal aging Suppose that both catalysts are life-tested at a high conversion of 70% through temperature adjustment and the results show that A lives longer than B by a ratio of 7 to 1 One may ask "Does this mean that the same ratio holds at design conversion, say, 30%?" If not, how much does this ratio change? To answer these questions, the ratio of catalyst lifetimes ($\bar{\theta}_A/\bar{\theta}_B$) as a function of conversion is plotted in Fig 6 for different deactivation orders It is seen that, taking $n = 1$, for example, at 30% conversion A lives more than nine times longer than B

CONCLUSIONS

Based on a simple constitutive equation describing catalyst deactivation, we have shown that the deactivation kinetics can be obtained in isoconversional experiments by examining the temperature vs time history, which in general can exhibit three distinct types of behavior We have also shown how the starting temperature and space velocity should be chosen to give the maximum space conversion under various process constraints Accelerated aging may be adequate for screening purposes, but it cannot be used for quantitative extrapolation From the standpoint of catalyst development, it is highly desirable to obtain information on deactivation kinetics from accelerated aging experiments and thus establish a quantitative link between accelerated and natural aging

NOMENCLATURE

A_d	preexponential factor for deactivation
A_m	preexponential factor for main reaction
a	catalyst activity
a_f	final activity
C	concentration of reactant
C_0	feed concentration of reactant
E	activation energy for main reaction
E_d	activation energy for deactivation
J	objective function defined in Eq (11)
K	rate constant of main reaction
K_d	rate constant of deactivation
m	order of main reaction
N	total number of experiments
n	order of deactivation
q	defined as E_d/E
R	gas constant
SC	space conversion
$\overline{SC}$	dimensionless space conversion
S	space velocity
$\bar{S}$	dimensionless space velocity
T	reactor temperature
T_0	starting temperature
T_{max}	maximum allowable temperature
T_j	observed temperature
$\bar{T}$	dimensionless temperature
x	conversion

Greek symbols

β	defined as T_0/T_{max}
γ	defined as E/RT_0
γ_d	defined as E_d/RT_0
θ	catalyst lifetime
$\bar{\theta}$	dimensionless catalyst lifetime

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