

SAFE OPERATION OF TUBULAR (PFR) ADIABATIC REACTORS

In an exothermic reaction the temperature will continue to rise as one moves along a plug flow reactor until all of the limiting reactant is exhausted. Schematically the adiabatic temperature rise as a function of space time, measured from the reactor entrance, takes the form shown in Figure 1.

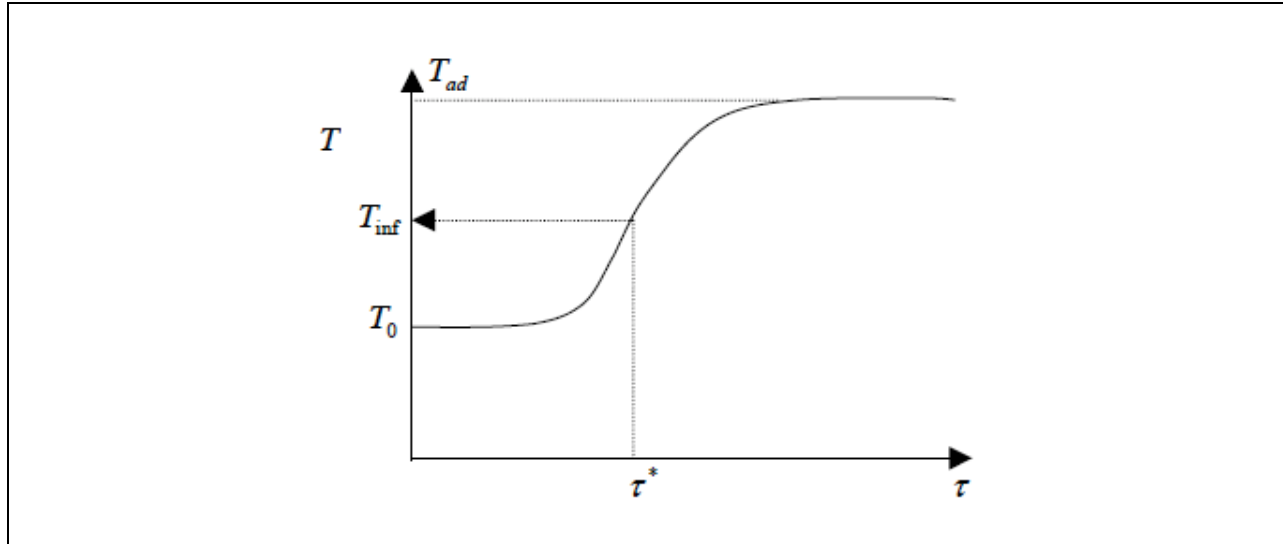


FIGURE 1: Temperature as a function of space time in an adiabatic PFR with exothermic reaction.

The final adiabatic temperature T_{ad} :

$$T_{ad} = T_o \left[1 + \frac{(-\Delta H_{r_A}) C_{A_o}}{\rho C_p T_o} \right] = T_o [1 + \beta] \quad (1)$$

is often excessive for highly exothermic systems (β large) and needs to be avoided. In such situations the old rule of thumb suggests that we should operate in such a way that the inflection point, i.e. the point of maximum temperature rise $\left(\frac{dT}{d\tau} \right)_{\max}$, is never reached. This implies that we operate with $\tau < \tau^*$ where τ^* is the value of space time at which the inflection point $\left(\frac{d^2T}{d\tau^2} = 0 \right)$ occurs.

Let us now develop a convenient and simple formula for use by practicing engineers which would guarantee safe operation. Consider an n-th order irreversible reaction:

$$-R_A = k_o e^{-E/RT} C_{Ao}^n (1 - x_A)^n \quad (2)$$

At adiabatic conditions temperature and conversion are related by the adiabatic line equation

$$T = T_o (1 + \beta x_A) \quad (3)$$

If we define, as in the case of wall cooled reactors, the dimensionless temperature by

$$\theta = \gamma \frac{T - T_o}{T_o} \quad (4)$$

then conversion in Eq. (3) can be expressed in terms of dimensionless temperature as:

$$x_A = \frac{\theta}{\delta} \quad (5)$$

where

$$\delta = \beta \gamma \quad (6)$$

with

$$\gamma = E/RT_o \quad (7)$$

The rate of reaction evaluated at adiabatic conditions in terms of dimensionless temperature is obtained by using the adiabatic line eq (5) to replace conversion. The result is:

$$(-R_A)_{ad} = (-R_A)_o e^{\gamma\theta/(\theta + \gamma)} \left(1 - \frac{\theta}{\delta}\right)^n \quad (8)$$

where the rate evaluated at the feed condition is:

$$(-R_A)_o = k_o e^{E/RT_o} C_{Ao}^n \quad (9)$$

The energy balance for adiabatic PFR operation is:

$$\rho C_p \frac{dT}{d\tau} = (-\Delta H_{rA}) (-R_A)_{ad} \quad (10)$$

Written in terms of dimensionless temperature it becomes:

$$\frac{d\theta}{d\tau} = \frac{\delta}{\tau_R} e^{\gamma\theta/(\theta + \gamma)} \left(1 - \frac{\theta}{\delta}\right)^n \quad (11)$$

where the characteristic reaction time is:

$$\tau_R = \frac{C_{A_0}}{(-R_A)_0} \quad (12)$$

The initial condition is

$$\tau = \theta = 0 \quad (13)$$

We can rewrite Eq. (11) in the most compact way by defining the Damkohler number as the ratio of characteristic process time and reaction time, i.e.

$$Da = \frac{\tau}{\tau_R} = \frac{(-R_A)_0 \tau}{C_{A_0}} \quad (14)$$

Equation (11) and initial condition (13) become:

$$\frac{d\theta}{d(Da\delta)} = e^{\gamma\theta/(\theta+\gamma)} \left(1 - \frac{\theta}{\delta}\right)^n \quad (15)$$

$$\text{At } Da\delta = 0 \quad \theta = 0 \quad (16)$$

Now we want to have the reactor “short” enough (limit the conversion achievable) so that we can keep the inflection point $\frac{d^2\theta}{d\tau^2} = 0$ out of the reactor i.e. we do not let it occur in the reactor.

The critical temperature at inflection point, θ_{inf} , is obtained by setting

$$\frac{d^2\theta}{d(Da\delta)^2} = 0 \quad (17)$$

which results in an equation for $\theta = \theta_{\text{inf}}$ yielding:

$$\theta_{\text{inf}} = \frac{\gamma}{2n} \left[\sqrt{\gamma^2 + 4n(\gamma + \delta)} - 2n - \gamma \right]; n \neq 0 \quad (18a)$$

$$\theta_{\text{inf}} = \delta, \quad n = 0 \quad (18b)$$

The result for the zeroth order reaction, eq (18b), can be obtained by applying the L'Hospital rule to eq (18a). A better approach is to notice that for $n = 0$ equation 15 indicates that $d\theta/d(Da\delta) > 0$ always, so that there is no inflection point as the rate of temperature rise keeps rising until all reactant is depleted. Then at $x_A = 1$, from eq (5) it follows that $\theta_{\text{max}} = \delta$ and therefore $T_{\text{max}} = T_{ad}$.

We can integrate the differential equation (15) by separating the variables to obtain the critical value of $Da\delta^*$ and, hence, of τ^*

$$Da\delta^* = \int_0^{Da\delta^*} d(Da\delta) = \int_0^{\theta_{\text{inf}}} \frac{e^{-\gamma\theta/(\theta+\gamma)}}{\left(1-\frac{\theta}{\delta}\right)^n} d\theta \quad (19)$$

Clearly for given values of parameters $\gamma, \beta, \delta = \beta\gamma$, and reaction order n , we can evaluate θ_{inf} from eq (18a) and then calculate the value of $Da\delta^*$ by numerically evaluating the integral in eq (19).

Using then the definitions of Da and δ we get the criterion for safe operation $Da\delta < Da\delta^*$ which can be expressed as:

$$\frac{k_o e^{-E/RT_o} C_{Ao}^n (-\Delta H_{rA}) E \tau^*}{R \rho C_p T_o^2} \leq Da\delta^* \quad (20)$$

To get a convenient, easy to remember value of $Da\delta^*$, the following approximations are often made. First, the Arrhenius dependence of the rate constant on temperature is replaced by an exponential dependence, in effect

$$e^{\gamma\theta/(\theta+\gamma)} \approx e^\theta \quad (21)$$

Substituting this approximation in eq (15) yields via eq (17) to a new approximate value of the temperature at inflection point

$$(\theta_{\text{inf}})_{\text{app}} = \delta - n \quad (22)$$

Substituting eq (21) and eq (22) into eq (19) yields

$$(Da\delta^*)_{\text{app}} = \int_0^{\delta-n} \frac{e^{-\theta}}{\left(1-\frac{\theta}{\delta}\right)^n} d\theta = \delta^n e^{-\delta} \int_n^\delta \frac{e^u}{u^n} du \quad (23)$$

The final approximation (which is conservative in nature as it assumes the worst possible case of zeroth order reaction) ignores the slowdown of the temperature rise due to the consumption of the reactant, which is the same as taking $n = 0$ in eq (23).

This yields

$$\begin{aligned} (Da\delta^*)_{app,0} &= e^{-\delta} \int_0^{\delta} e^u du = e^{-\delta} (e^u)_0^{\delta} \\ &= e^{-\delta} [e^{\delta} - 1] = 1 - e^{-\delta} = 1 \quad (\text{for large enough } \delta) \end{aligned} \quad (24)$$

For highly exothermic reactions $\delta \geq 10$ and clearly $(Da\delta^*)_{app,0} = 1$.

Substituting this into eq (20) gives the conservative criterion for safe operation.

It is constructive to note that this same equation (20a) with time t replacing τ

$$\frac{k_o e^{-E/RT_o} C_{A_o}^n (-\Delta H_{r_A}) E t^*}{R \rho C_p T_o^2} < 1 \quad (20a)$$

is used to determine the so called “time of no return” or time to explosion in batch systems. This time to inflection point t^* may be very long for low T_o but becomes quite short if the system of high activation energy is exposed to higher T_o . Hence, chemicals that may be safe to store at 25°C may be explosion prone if exposed to 40 – 50°C!

SAFE OPERATION OF ADIABATIC CSTR

The mass balance for an irreversible n-th order reaction is:

$$C_{A_o} x_A = (-R_A) \tau \quad (25)$$

The adiabatic equation relates conversion and temperature

$$x_A = \frac{T - T_o}{(-\Delta H_{r_A}) C_{A_o} / \rho C_p} \quad (26)$$

Upon substitution of dimensionless temperature we get from eq (25)

$$\frac{1}{Da_n \delta} \theta = e^{\gamma\theta/(\theta + \gamma)} \left(1 - \frac{\theta}{\delta}\right)^n \quad (27)$$

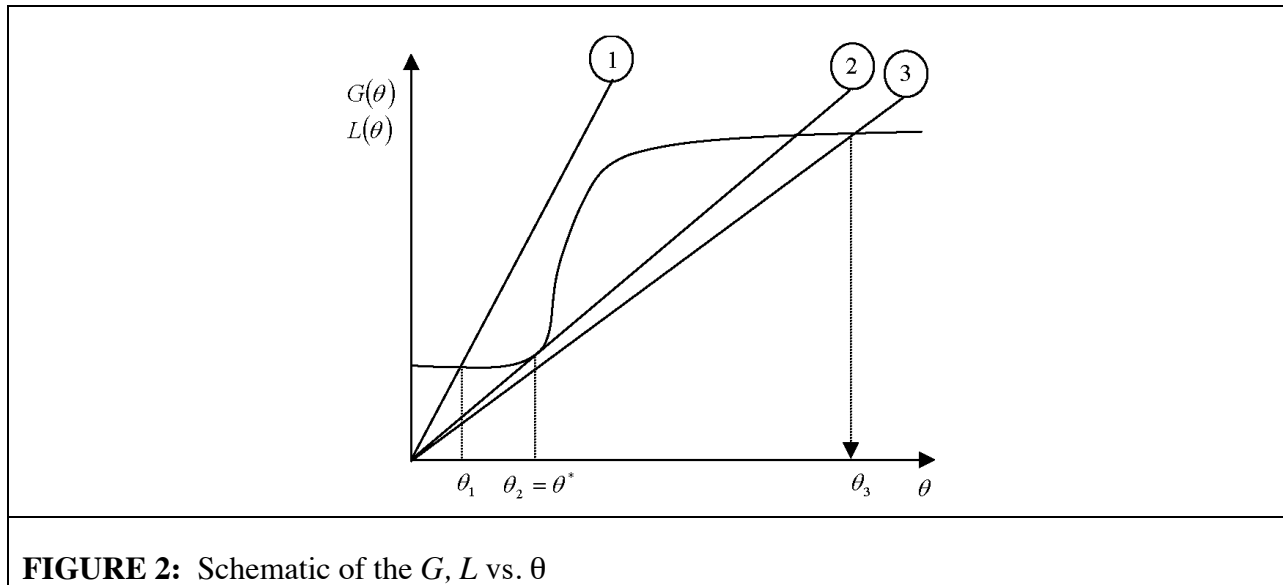
let

$$G(\theta) = e^{\gamma\theta/(\theta + \gamma)} \left(1 - \frac{\theta}{\delta}\right)^n \quad (28a)$$

$$L(\theta) = \frac{1}{Da_n \delta} \theta \quad (28b)$$

We know from before that G is a sigmoidal curve in θ and represents heat generated by reaction. L is the heat removal rate (i.e., heat removed by sensible heat of the fluid that flows through the CSTR).

We know that up to three intersections are possible between G and L lines. To avoid the intersection leading to excessively high temperatures we must assure that intersections at low temperatures are available. The last permissible operating condition is the one when line L is also tangent to curve G as schematically shown in Figure 2.



Clearly as $Da\delta$ increases the slope of the L line decreases so that

$$(Da\delta)_1 < (Da\delta)_2 < (Da\delta)_3 \quad (29)$$

While operating adiabatic temperatures at θ_1 and θ_2 are acceptable, θ_3 represents too large a temperature jump. Hence, we must assure that the L line always intersects the G line at its lower temperature branch. The critical point is reached when L is also tangent to the G line.

For safe adiabatic operation we therefore require

$$L = G \quad (30)$$

$$\frac{dL}{d\theta} \geq \frac{dG}{d\theta} \quad (31)$$

Applying the above to eqs (28a) and (28b), and using the equality sign in eq (31), we get the equation for the maximum permissible temperature $\theta_{\max \text{ perm}} = \theta^*$. The critical value of the space time τ^* can be obtained from the critical value of $Da\delta^*$, which in turn results from substituting the expression for θ^* into eq (30).

To get a simple, easy to remember expression, usually we again replace $e^{\gamma\theta/(\theta+\gamma)}$ with e^θ . This yields

$$\theta^* = \frac{1}{2} \left[\delta - n + 1 - \sqrt{(\delta - n + 1)^2 - 4\delta} \right] \quad (32)$$

The negative sign in front of the square root needs to be taken as we are interested in the lower of the two temperatures at which the L line could be tangent to the curve G . Then equation (30) yields:

$$(Da\delta)_{app}^* = \theta^* \left(1 - \frac{\theta^*}{\delta} \right)^{-n} e^{-\theta^*} \quad (33)$$

A conservative estimate, with $n = 0$, yields $\theta^* = 1$ and

$$Da\delta^* \leq e^{-1} \quad (34)$$

For safe operation then

$$\frac{k_0 e^{-E/RT_o} C_{Ao}^n (-\Delta H_{rA}) E\tau}{R \rho C_p T_o^2} \leq e^{-1} \quad (35)$$