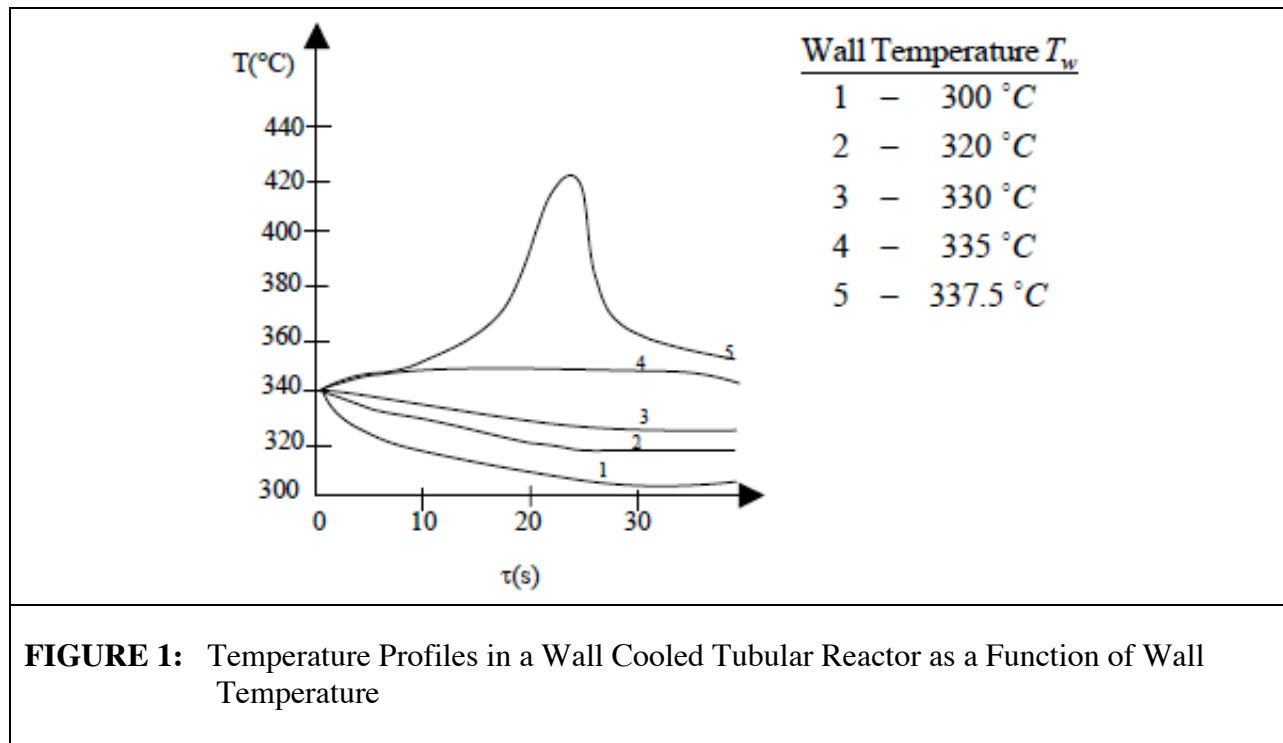


### WALL COOLED TUBULAR REACTORS: AVOIDANCE OF HOT SPOTS

The pioneering work of Bilous and Amundsen (AIChE J. 2, 117, 1956) showed that a plug flow reactor (PFR) cooled from the wall can exhibit extreme parametric sensitivity to small changes in the wall temperature or heat transfer parameters. Their observation is sketched in Figure 1 below:



Clearly a small variation in the wall temperature of 2.5 °C (from 335°C to 337.5 °C) caused an 80°C local rise in reactor temperature! This 'hot spot' generation can lead to reactor runaway for many reasons. Undesirable reactions of high activation energy can take off at this elevated temperature, vapor formation can cause increased pressure, rate of reaction may reach extreme values, etc. Therefore, it is imperative to operate the wall cooled tubular reactor in such a manner that it does not exhibit such extreme parametric sensitivity and, hence, is not prone to runaway.

To identify the parameter space for safe operation one starts with the mass and energy balance for the reactor. Assuming for simplicity, constant volumetric flow rate,  $Q = \text{const.}$ , and a single simple irreversible reaction,  $A \rightarrow \text{products}$ , the governing equations are:

Mass balance on species A:

$$\frac{dx_A}{d\tau} = \frac{(-R_A)}{C_{A0}} \quad (1)$$

Energy balance (assuming constant average physical properties and constant heat of reaction):

$$\rho C_p \frac{dT}{d\tau} = (-\Delta H_{r_A})(-R_A) - U a_v (T - T_w) \quad (2)$$

The initial conditions are:

$$\tau = 0 \quad x_A = 0, \quad T = T_o \quad (2a)$$

In the above equations:

$\tau = \frac{V}{Q}$  (min) is the space time measured from the reactor entrance as reactor internal volume V is also measured from the entrance.

$C_{Ao} \left( \frac{\text{mol}}{\text{m}^3} \right)$	=	molar feed concentration of A
$\rho \left( \text{kg}/\text{m}^3 \right)$	=	fluid density
$C_p \left( \text{J}/\text{kg}^\circ\text{K} \right)$	=	mean specific heat of the reaction fluid
$\Delta H_{r_A} \left( \frac{\text{J}}{\text{mol A}} \right)$	=	heat of reaction per mole of A
$-R_A \left( \frac{\text{mol A}}{\text{m}^3 \text{min}} \right)$	=	rate of reaction of A
T(°K)	=	temperature in kelvin
$x_A$	=	conversion of A
$U \left( \frac{\text{J}}{\text{m}^2 \text{K min}} \right)$	=	overall heat transfer coefficient
$a_v \left( \text{m}^2/\text{m}^3 \right) = \frac{4}{d_t}$	=	area for heat transfer per unit internal reactor volume
$T_w$ (°K)	=	coolant (wall) temperature
$T_o$ (°K)	=	inlet feed temperature
$d_t$ (m)	=	tube (reactor) diameter

To simplify the algebra, but without loss of generality of the result to be derived, we will take  $T_o = T_w$  thus assuming the inlet and wall temperature to be the same.

We can now divide eq (2) by eq (1) and rearrange the result to get:

$$\frac{dT}{dx_A} = \frac{-\Delta H_{r_A} C_{Ao}}{\rho C_p} - \frac{4U(T - T_o)}{d_t \rho C_p (-R_A)/C_{Ao}} \quad (3)$$

Let us define the characteristic reaction time based on the value of the reaction rate at the feed conditions of concentration and temperature:

$$\tau_R = \frac{C_{A_o}}{(-R_A)_o} = \frac{C_{A_o}}{k_o e^{-E/RT_o} C_{A_o}^n} \quad (4)$$

Here we have assumed for simplicity an n-th order irreversible reaction and  $(-R_A)_o$  means that we evaluate the rate at feed conditions of concentrations and temperature.

We also have a characteristic heat transfer time:

$$\tau_h = \frac{d_t \rho C_p}{4U} \quad (5)$$

Based on these, two dimensionless groups arise naturally:

$$\kappa = N = \frac{\tau_R}{\tau_h} = \frac{4U C_{A_o}}{(-R_A)_o d_t \rho C_p} \quad (6)$$

and

$$\beta = \frac{(-\Delta H_{r_A}) C_{A_o}}{\rho C_p T_o} \quad (7)$$

Equation (3) now becomes (recall we assumed  $T_o = T_w$ )

$$\frac{dT}{dx_A} = \beta T_o - \kappa \frac{T - T_o}{(-R_A)/(-R_A)_o} \quad (8)$$

This last expression contains the dimensionless rate of reaction,  $(-R_A)/(-R_A)_o$ , which for an n-th order irreversible reaction can be written as:

$$\frac{(-R_A)}{(-R_A)_o} = \frac{k_o e^{-E/RT} C_A^n}{k_o e^{-E/RT_o} C_{A_o}^n} = e^{\frac{E}{RT_o} \left(1 - \frac{T_o}{T}\right)} (1 - x_A)^n \quad (9)$$

Dimensionless activation energy is:

$$\gamma = \frac{E}{RT_o} \quad (10)$$

and dimensionless temperature is conveniently defined by:

$$\theta = \gamma \frac{T - T_o}{T_o} \quad (11)$$

Upon substitution of eqs (9), (10), (11) into equation (8) we get:

$$\frac{d\theta}{dx_A} = \beta\gamma - \frac{\kappa\theta}{e^{\theta/(1+\theta/\gamma)}(1-x_A)^n} \quad (12)$$

The product  $\beta\gamma$  in the literature is often denoted by  $\delta$  or  $S$ :

$$S = \delta = \beta\gamma \quad (13)$$

We can rewrite eq (12) as:

$$\frac{d\theta}{dx_A} = \delta e^{-\theta/(1+\theta/\gamma)}(1-x_A)^{-n} \left[ e^{\theta/(1+\theta/\gamma)}(1-x_A)^n - \frac{\kappa}{\delta}\theta \right] \quad (14)$$

Since the term on the right hand side of eq (14) that multiplies the term in the brackets is always positive the sign of the derivative of the dimensionless temperature with respect to conversion,

i.e the sign of  $\frac{d\theta}{dx_A}$ , depends on the terms in the brackets in eq (14). By taking the coolant

temperature  $T_c$  to be equal to the feed temperature  $T_o$ , we have assured that  $\frac{d\theta}{dx_A} > 0$  and

temperature rises with conversion. This is obvious by observing and plotting the terms in the brackets in eq (14). Physically this tells us that if we try to cool an exothermic reaction with the coolant at feed temperature, unless the characteristic heat transfer time is infinitesimal in comparison to characteristic reaction time, i.e  $\kappa \rightarrow \infty$ , or stated differently the heat removal rate is infinitely faster than the heat generation rate by reaction at the feed (wall) temperature, then the reactor temperature must rise with conversion. We can allow for this but we want to know what values of parameters  $\delta, \kappa, \gamma$  will keep that temperature rise within safe limits.

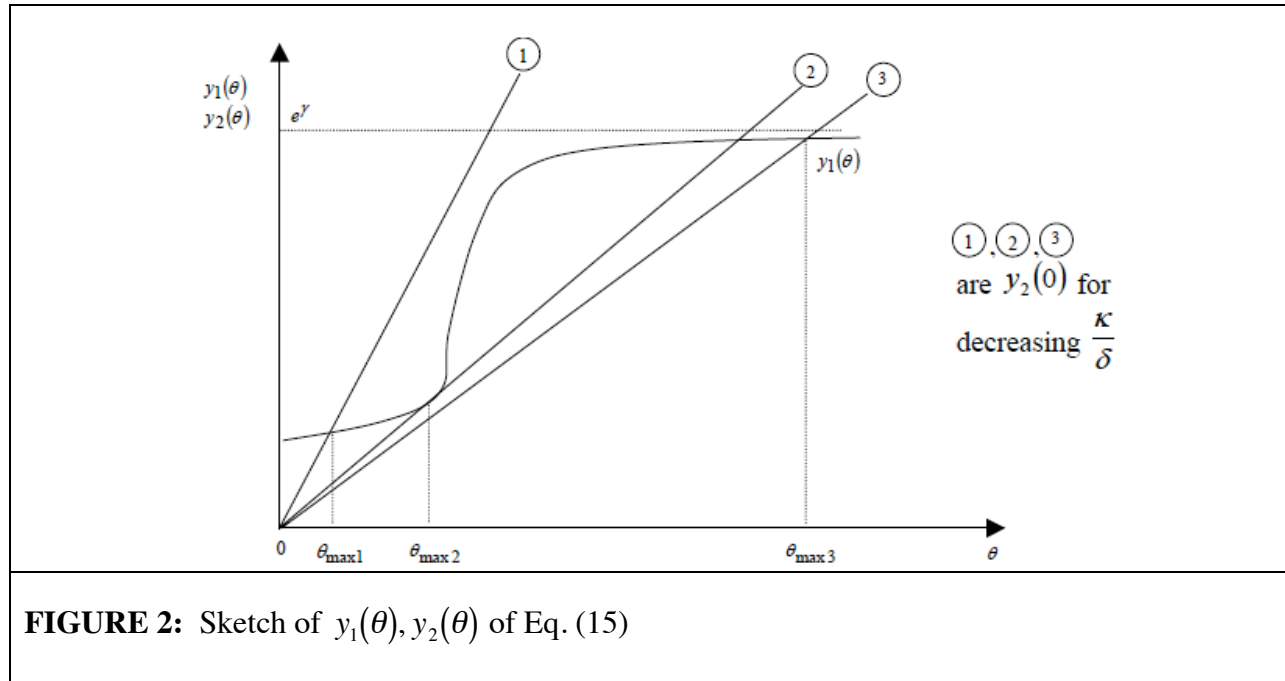
We can think of the first exponential term in the brackets of eq (14) as the heat generation term by reaction and the second as the heat removal rate. Indeed heat generation term has an Arrhenius dependence on temperature, heat removal rate is linear in temperature. Now the heat generation term is difficult to plot as a function of dimensionless temperature  $\theta$  because of the presence of the  $(1-x_A)^n$  conversion dependent term. We would need to integrate eq (14), save values of  $x_A$  vs  $\theta$  and then we could plot the terms in brackets of eq (14) against  $\theta$ . However, since we are interested in preventing excessive maximum temperatures in the reactor, we can take a conservative approach by assuming the worst possible scenario. In the  $n$ -th order reaction ( $n > 0$ ) the rate of heat generation is being slowed down as conversion increases with  $\theta$  as the  $(1-x_A)^n$  term becomes smaller and smaller at increased conversion. The worst possible scenario is then if the heat generation rate (and hence the rate of temperature rise) is not affected by increased conversion. This is the case of zeroth order reaction.

For a conservative approach assume  $n = 0$  and now consider the term in the brackets of eq (14)

$$F(\theta) = e^{\theta/(1+\theta/\gamma)} - \frac{\kappa}{\delta}\theta = y_1(\theta) - y_2(\theta) \quad (15)$$

Clearly, as  $\theta = 0$ ,  $y_1(0) = 1$ ; and as  $\theta \rightarrow \infty$ ,  $y_1 \rightarrow e^{\gamma}$  and  $y_1$  is bounded. At the same time, as  $\theta = 0$ ,  $y_2(0) = 0$ ; and as  $\theta \rightarrow \infty$ ,  $y_2$  is unbounded. Thus,  $y_1(\theta)$  is a sigmoidal (S-shape) curve and  $y_2(\theta)$  is a straight line through the origin as shown in Figure 2.

Depending on the value of the ratio of the two dimensionless groups  $\kappa/\delta$  the three scenarios depicted in Figure 2 may occur.



**FIGURE 2:** Sketch of  $y_1(\theta), y_2(\theta)$  of Eq. (15)

The three straight lines in Figure 2 represent  $y_2(\theta)$  at three different values of the parameter  $\kappa/\delta$ . Please, recall that at  $\kappa/\delta \rightarrow \infty$  our  $y_2(\theta)$  would be a vertical line guaranteeing  $\theta = 0$ , i.e.  $T = T_o = T_w$ . For the three scenarios depicted above

$$\left(\frac{\kappa}{\delta}\right)_1 > \left(\frac{\kappa}{\delta}\right)_2 > \left(\frac{\kappa}{\delta}\right)_3 \quad (16)$$

and the rate of cooling decreases as we go from case 1 to case 3. Also remember that the value of  $\theta$  at which  $y_1(\theta) = y_2(\theta)$  signifies  $F(\theta) = 0$  i.e.  $\frac{d\theta}{dx_A} = 0$  and yields the maximum temperature that is observed in the reactor at such conditions. So, in case of rapid heat removal rate (Case 1) the maximum temperature  $\theta_{\max 1}$  is relatively small and of no concern. At the certain lower value of heat transfer rate than in case 1,  $y_2(\theta)$  not only intersects but is a tangent of  $y_1(\theta)$  (Case 2). In this case the maximum temperature  $\theta_{\max 2}$  is still tolerable but any further, even very small, decrease in  $\kappa/\delta$  would lead to an excessive maximum temperature as depicted in Case 3 where clearly  $\theta_{\max 3}$  is a hot spot to be avoided.

This tells us that in order to prevent a hot spot we must have:

$$y_1(\theta) = y_2(\theta) \quad \text{which yields } \theta_{\max} \quad (17a)$$

and

$$\left. \frac{dy_1}{d\theta} \right|_{\theta_{\max}} \leq \left. \frac{dy_2}{d\theta} \right|_{\theta_{\max}} \quad \text{for avoiding the hot spot} \quad (17b)$$

This means that at the maximum temperature,  $\theta_{\max}$ , the slope of the heat generation line,  $y_1(\theta)$ , must be less than the slope of the heat removal line,  $y_2(\theta)$ . The condition at which the slopes are equal corresponds to using the equality sign in eq (17b) and is illustrated by line 2 in Figure 2. This defines the maximum allowable maximum temperature  $\theta_{\max 2}$ . Beyond this point excessive hot spots may arise.

We now apply eq (17a) and (17b) to eq (15) to get

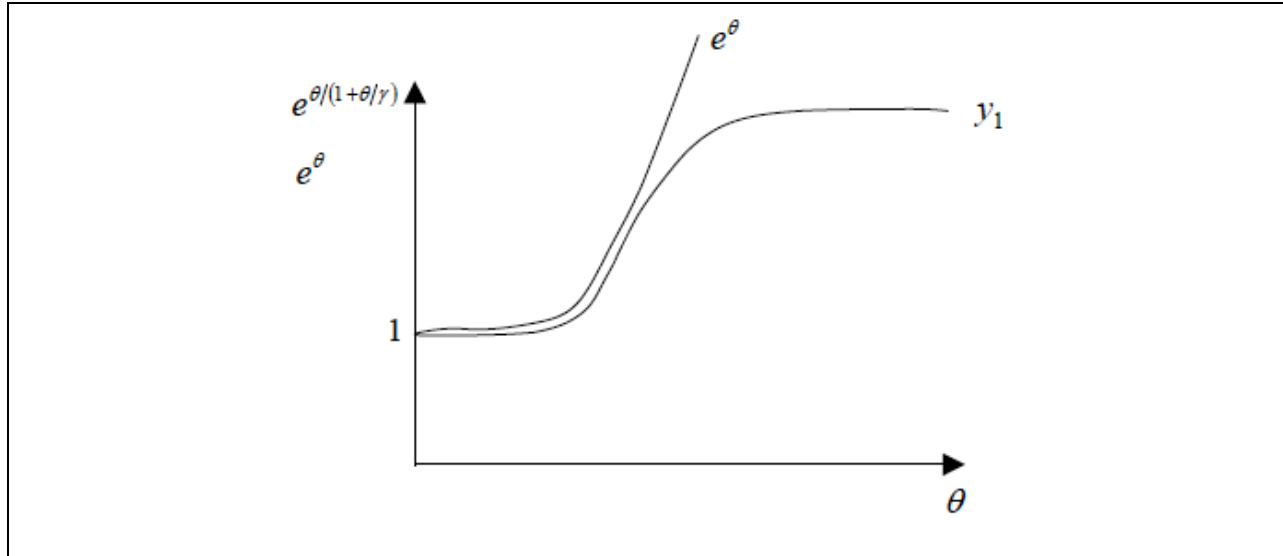
$$e^{\theta/(1+\theta/\gamma)} = \frac{\kappa}{\delta} \theta \quad (18a)$$

and

$$\frac{1}{\left(1 + \frac{\theta}{\delta}\right)^2} e^{\theta/(1+\theta/\gamma)} \leq \frac{\kappa}{\delta} \quad (18b)$$

By eliminating  $e^{\theta/(1+\theta/\gamma)}$  in equation (18b) in terms of  $\frac{\kappa}{\delta} \theta$ , as per eq (18a), and by using the equality sign in eq (18b), we can develop an equation for the maximum permissible temperature. Do that for an exercise by solving the resulting quadratic equation for  $\theta_{\max}$ . Substitution of the result for  $\theta_{\max}$  in the inequality of eq (18b) determines the parameter space that guarantees the absence of hot spots. The result is not pretty looking.

To get a clear and easy formula to remember an approximate analytical solution is developed via a conservative approach in which one replaces  $e^{\theta/(1+\theta/\gamma)}$  by a rising exponential  $e^\theta$ . This is equivalent to replacing  $k = k_0 e^{-E/RT}$ , i.e. the Arrhenius temperature dependence with  $k' = k'_0 e^{\alpha T}$  and demanding that at  $T = T_0$ ,  $k = k'$  and  $\frac{dk}{dT} = \frac{dk'}{dT}$  at  $T = T_0$  i.e. at that point of  $T = T_0$  both functions are equal and their derivatives are equal. Indeed  $e^\theta$  and  $e^{\theta/(1+\theta/\gamma)}$  have the same value and the same value of the first derivative at  $\theta = 0$ . In Figure 3 we sketch the approximation of  $y_1 = e^{\theta/(1+\theta/\gamma)}$  with  $e^\theta$



**Figure 3:** Approximation of the Arrhenius dependence of the rate constant with an exponential function.

Since we are interested in limiting the  $\theta_{\max}$  the two curves are pretty close for small  $\theta$ . Clearly, if we replaced  $y_1(\theta)$  with  $e^\theta$  in Figure 2 we would lose the intersection with  $y_2(\theta)$  for Case 3 but this is not of concern since we are not interested in  $\theta > \theta_{\max 2}$ , and for Case 2 the intersection of  $y_2(\theta)$  with  $e^\theta$  is close to that of  $y_2(\theta)$  with  $y_1(\theta)$  in Figure 2. The advantage of this approximation is that the criteria of equations (17a) and (17b) applied to

$y_1(\theta) = e^\theta$  and  $y_2(\theta) = \frac{\kappa}{\delta}\theta$  yield

$$e^\theta = \frac{\kappa}{\delta}\theta \quad (19a)$$

and

$$e^\theta \leq \frac{\kappa}{\delta} \quad (19b)$$

From which it follows:

$$\theta_{\max} = 1 \quad (20)$$

Substitution of this into the inequality described by eq (19b) yields the parameter space that guarantees absence of hot spots

$$e \leq \frac{\kappa}{\delta} \quad (21)$$

Replacing the above dimensionless quantities in terms of actual physical variables we get from eq (20) the maximum permissible temperature that can be tolerated in absence of hot spots

$$T_{\max} \leq \left( \frac{1}{\gamma} + 1 \right) T_o \quad (22)$$

From eq (21) we get the conditions that the system parameters must satisfy to guarantee absence of hot spots.

$$\frac{4UR T_o^2}{\left( k_o e^{-E/RT_o} C_{Ao}^n \right) \left( -\Delta H_{rA} \right) E d_t} \geq e \quad (23)$$

where R is the ideal gas constant in proper units.

This equation is usually written in terms of tube diameter that will guarantee absence of hot spots by providing sufficient heat transfer area per unit volume

$$d_t \leq \frac{4UR T_o^2 e^{-1}}{E \left( -\Delta H_{rA} \right) k_o e^{-E/RT_o} C_{Ao}^n} \quad (24)$$

Clearly, other permutations of eq (23) are possible. Given kinetic and reaction parameters, feed temperature and tube diameter one can calculate the maximum permissible feed concentration that guarantees safe operation, etc.

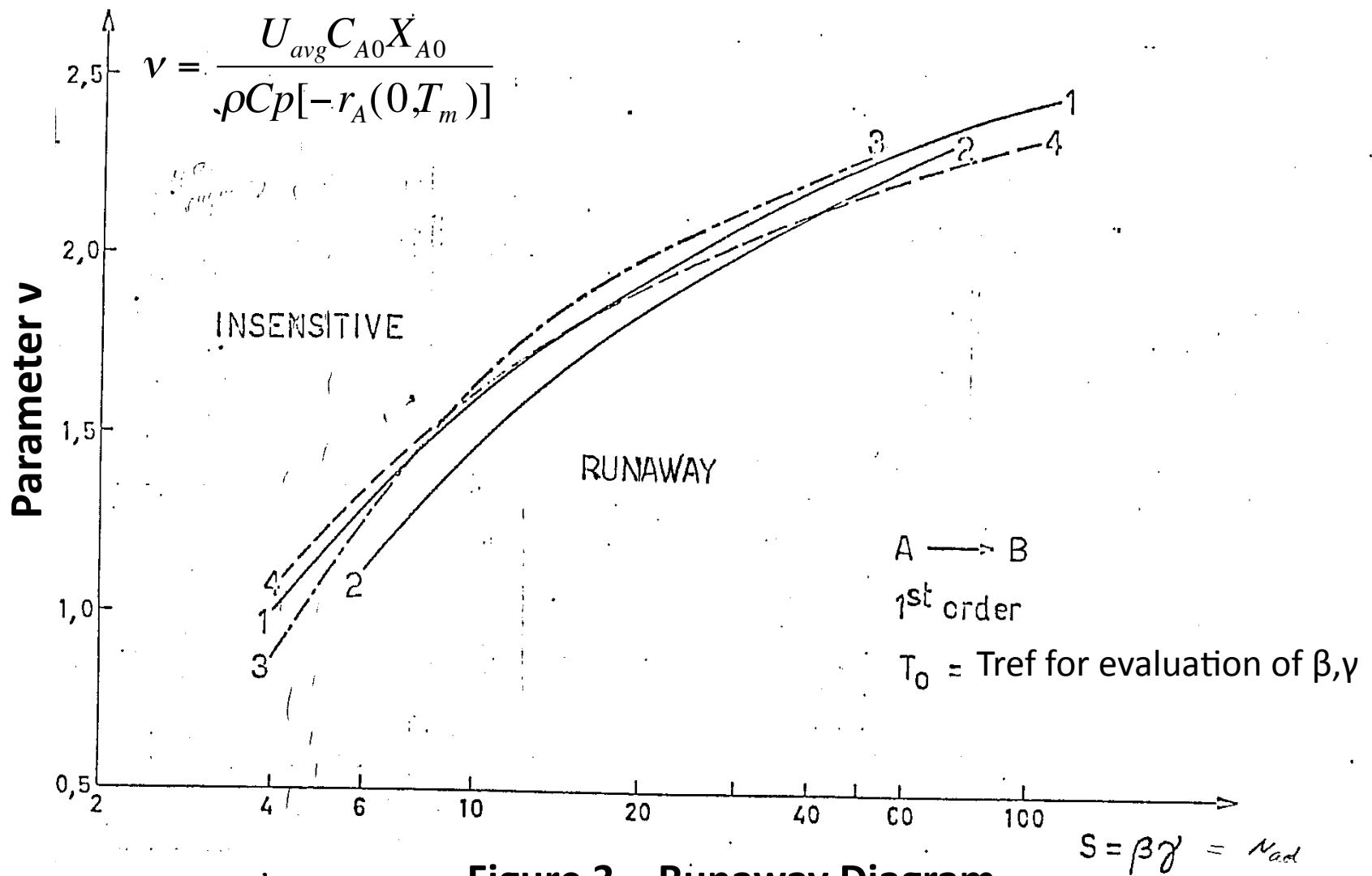
Approximate analysis, using the approximate exponential dependence of the rate constant, but accounting for the effect of reactant depletion, is possible for an n-th order reaction and yields the following result which is a little less conservative than equation (23).

$$\frac{\kappa}{\delta} \geq \frac{e}{1 + 2.703 n^{2/3} \delta^{-2/3}} \quad (25)$$

This result is due to Chandler Barkelew, Chem. Engr. Progress Symp. Ser. No. 25, Vol. 55, p. 37 (1959) and is one of the most useful expressions for nonisothermal tubular or batch reactors.

The graph showing the parameter space that is safe, based on Barkelew's and similar criteria, is appended as Figure 3.





**Figure 3 – Runaway Diagram**

- 1: Barkelew
- 2: Dente & Collina
- 3: Flavacek *et al*
- 4: Van Welsenaere & Fromeut

$$\beta = \frac{(-\Delta H_r) C_{A0}}{\rho C_p T_0} \quad \gamma = \frac{E}{RT_0}$$