Design Procedure for Safe Operations in Agitated Batch Reactors

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An application-oriented design procedure is presented for completely mixed liquid reacting systems in batch reactors. These systems can safely be operated by neglecting the heat capacity of the vessel and attributing suitable values to three scale-independent control parameters: the initial concentration (c_0); the inlet coolant temperature ($T_{c,i}$); and the Newtonian cooling time (t_N). For given dimensionless values of the reaction order n, heat-transfer capacity β_n, and inlet coolant temperature ϵ, the design value α^* of the dimensionless adiabatic temperature rise must satisfy $\alpha_c > \alpha^* < \alpha_{m,a}$. This can help avoid both runaways ($\alpha^* < \alpha_c$) and oversteps of the maximum allowable temperature rise ($\alpha^* < \alpha_{m,a}$). A model is derived to calculate α_c and $\alpha_{m,a}$ for three different reaction orders. Simulated relationships are verified with experimental results concerning the hydration of 2,3-epoxypropanol in a 0.27-L agitated batch reactor.

Introduction

Generally, the temperature-conversion profile (TCP) $\theta = \theta(\xi)$ of a reacting system can be predicted by a numerical integration procedure applied to the differential equation $d\theta/d\xi = f(\theta,\xi)$, which has been derived from an energy balance and a component balance. Since Semenov (1928) investigated zeroth-order reaction systems, many articles regarding the safety of batch reactors have been published. Among them, Adler and Enig (1964) defined a runaway as the behavior of a reacting system of which the TCP has a region of positive second-order derivatives before the maximum temperature rise is reached. For a first-order reaction system, the critical TCP, which bounds the region where no runaways occur, has a unique inflection point. In the definition of Morbidelli and Varma (1982, 1988), the sensitivity of the maximum temperature θ_m with respect to any model parameter reaches its maximum at criticality.

In the process industry, the temperature of a liquid reacting system in a batch reactor generally may not exceed a maximum allowable value. Examples are the bubble point or decomposition temperature of the system, the temperature at which undesired parallel or sequential reactions occur, or the maximum allowable pressure in the system is reached. Exceeding the maximum allowable temperature can lead to explosion of reacting systems, loss of reactor content, destruction of vessels, and dangerous situations for the environment. These situations may occur as a result of mischarging, impurities, inadequate cooling, agitator failure, or unreliable kinetic data. The maximum temperature rise of a liquid reacting system is affected by the physical and chemical properties of the system. It can be controlled by three scale-independent parameters: the initial concentration c_0 of the key component, the inlet temperature $T_{c,i}$ of the coolant, and the Newtonian cooling time t_N of the system; or, equivalently, by three dimensionless parameters: the adiabatic temperature rise (α), the inlet coolant temperature (ϵ), and the heat-transfer capacity (β_n).

In this article, it will be shown that, for a safe operation, the design of batch reactors must also fulfill a no-overstep criterion, in addition to the well-known no-runaway condition. More precisely, the Alder and Enig criterion $\alpha < \alpha_c$ can only result in a safe operation of a batch reactor if the maximum temperature rise $\theta_{m,c}$ of the critical TCP does not exceed the maximum allowable one $\theta_{m,a}$. If $\theta_{m,c} > \theta_{m,a}$, a smaller value $\alpha < \alpha_{m,a}$ has to be applied, where $\alpha_{m,a}$ refers to a TCP with maximum value $\theta_m = \theta_{m,a}$.

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During the last few years, runaways of reacting systems have been investigated in batch reactors of different sizes, for example, hydration of 2,3-epoxypropanol in a 0.5-L reactor (Vleeschhouwer, 1991), hydrolysis of acetic anhydride in a 1.0-L reactor (Haldar and Phaneswara Rao, 1992), and in a 1.2-L reactor (Shukla and Pushpavanam, 1994), esterification of propionic anhydride with 2-butanol in a 2-L bench-scale reactor and in a 100-L pilot-plant reactor (Strozzi et al., 1994). In most of these articles, the data necessary for simulation of the behavior of the reacting system are not complete, so a good comparison of simulated and observed temperature-conversion profiles is not possible.

In the present article, a quantitative comparison between the simulated and observed behaviors of reacting systems in a batch reactor are given. It is shown that runaways are possible under conditions that are thought to be subcritical. This can be explained by the inaccurate values of physical and kinetic parameters, the optimistic value $Le > 1$ used in simulation, or insufficient mixing of the reaction system. For these reasons, inclusion of a safety factor κ in the Adler and Enig criterion is recommended. Based on experimental results, this article concludes that a safe operation can only be expected if the liquid system is well-mixed and the design value α^* satisfies the conditions $\kappa \cdot \alpha_c > \alpha^* < \alpha_{m,a}$, where the no-runaway and no-overstep conditions are calculated considering $Le = 1$.

This article is organized as follows: the first two sections present the batch-reactor model and computation of the α_c and $\alpha_{m,a}$ values. Then, simulation results are used (1) to illustrate the high sensitivity of the maximum temperature rise in the vicinity of the critical TCP, and (2) to present the runaway and overstep boundaries of zeroth-, first-, and second-order reacting systems in diagrams that can be used by design engineers. Next, a design procedure is briefly described. Afterwards, experimental work concerning the acid-catalyzed hydration of 2,3-epoxypropanol is discussed in detail. The article ends with conclusions where four conditions for safe operation of batch reactors are summarized.

Batch-Reactor Model

The behavior of an agitated, completely mixed exothermic liquid reacting system in a batch reactor can be simulated with a model consisting of the energy and component balance equations. The model contains variables (c; T; t), control parameters (c_0; $T_{c,i}$; t_N), and the remaining physical quantities ($C_{p,w}$; k_n; m_w; n; ΔQ; T_A), which are all defined in the Notation section. The model can be written in the following dimensionless form:

$$\frac{d\theta}{d\tau_n} = -\beta_n \cdot \theta + \alpha \cdot (1-\xi)^n \cdot \exp\left(\frac{\theta}{1+\epsilon \cdot \theta}\right) \equiv f_1 \qquad \text{(Energy balance)} \qquad (1)$$

$$\frac{d\xi}{d\tau_n} = (1-\xi)^n \cdot \exp\left(\frac{\theta}{1+\epsilon \cdot \theta}\right) \equiv f_2 \qquad \text{(Component balance)}, \qquad (2)$$

with $\xi = 0$ and $\theta = 0$ at $\tau_n = 0$.

These equations contain:

- The dimensionless variables:

$$\theta = \frac{T - T_{mc}}{\epsilon \cdot T_{mc}}; \qquad \xi = 1 - \frac{c}{c_0};$$
$$\tau_n = t \cdot c_0^{n-1} \cdot k_n \cdot \exp(-\epsilon^{-1}). \qquad (3)$$

- The dimensionless parameters:

$$\alpha = \frac{(-\Delta H) \cdot c_0}{Le \cdot C_p \cdot T_{mc} \cdot \epsilon}; \qquad \beta_n = \frac{\exp(\epsilon^{-1})}{Le \cdot t_N \cdot k_n \cdot c_0^{n-1}};$$
$$\epsilon = \frac{T_{mc}}{T_A}; \qquad Le = \frac{m \cdot C_p + m_w \cdot C_{p,w}}{m \cdot C_p}, \qquad (4)$$

in which

$$T_{mc} = T_{c,i} + \frac{\Delta Q}{\varphi \cdot U \cdot S} \qquad \text{(Modified coolant temperature)}$$

$$t_N = \frac{m \cdot C_p}{\varphi \cdot U \cdot S} \qquad \text{(Newtonian cooling time)}.$$

Equations 1 and 2 lead to $\theta_\xi = f_1/f_2$ or

$$\theta_\xi = \alpha - \frac{\beta_n \cdot \theta}{(1-\xi)^n} \cdot \exp\left(-\frac{\theta}{1+\epsilon \cdot \theta}\right) \qquad \text{(slope of TCP)} \qquad (5)$$

with $\theta = 0$ at $\xi = 0$.

In Eq. 5, $\theta_\xi = \alpha$ at $\theta = 0$ and $\theta = \alpha_{ad} \cdot \xi$ if $\beta_n = 0$; further,

$$\theta_{n\xi} \equiv \frac{d^n\theta}{d\xi^n}. \qquad (6)$$

A completely mixed reacting system in a batch reactor can be operated safety if, for fixed values of n, ϵ, and β_n, the value of α is chosen in such a way that there is no runaway and no overstep of the maximum allowable temperature rise of the system. A runaway is assumed to occur if the TCP has a region of positive second-order derivatives before the maximum temperature rise of the TCP is reached. In order to avoid a runaway, the adiabatic temperature rise α of the reacting system should be lower than the value α_c of the well-defined *critical* TCP. The critical TCP bounds the region where no runaways occur and has a maximum temperature rise, $\theta_{m,c}$. For safe operation, a design value $\alpha^* < \alpha_c$ is necessary. This condition is only sufficient, if $\theta_{m,c} < \theta_{m,a}$. If $\theta_{m,c} > \theta_{m,a}$, the design value has also to satisfy $\alpha^* < \alpha_{m,a}$ in which $\alpha_{m,a}$ is the maximum allowable adiabatic temperature rise that yields a TCP with a maximum temperature rise $\theta_m = \theta_{m,a}$. Summarizing, it may be stated that safe operations of completely mixed systems in a batch reactor can be expected, if the following necessary and sufficient conditions hold:

$$\alpha_c > \alpha^* < \alpha_{m,a}, \qquad (7)$$

where α_c and $\alpha_{m,a}$ are calculated assuming $Le = 1$. Then, no runaway and no overstep of the maximum allowable temperature rise can occur.

When the kinetics of the completely mixed reacting systems are unknown, a safe batchwise operation can be performed, if the adiabatic temperature rise is smaller than the maximum allowable one, neglecting the heat capacity of the vessel ($\alpha_{ad} < \theta_{m,a}$, where $Le = 1$).

Parameters α_c and $\alpha_{m,a}$

Critical TCPs pass through the characteristic point $C(\xi_c;\theta_c)$ defined by:

$$\theta_\xi = 0 \quad \text{and} \quad \theta_{2\xi} = 0, \quad \text{if } n = 0 \tag{8}$$

$$\theta_{2\xi} = 0 \quad \text{and} \quad \theta_{3\xi} = 0, \quad \text{if } n \geq 1. \tag{9}$$

Moreover, the point $O(0;0)$ belongs to each TCP. For given values of n, β_n, and ϵ, the solution of Eqs. 5 and 8 or 9 gives the critical adiabatic temperature rise α_c and the coordinates of the characteristic point $C(\xi_c;\theta_c)$.

If n = 0, Eqs. 5 and 8 lead to:

$$\theta_c = \frac{(1-2\cdot\epsilon)-(1-4\cdot\epsilon)^{0.5}}{2\cdot\epsilon^2} \approx 1+2\cdot\epsilon+5\cdot\epsilon^2+14\cdot\epsilon^3+\cdots;$$

$$(\theta_c)_{\epsilon\to 0} = 1 \tag{10}$$

$$\alpha_c = \beta_0\cdot\theta_c\cdot\exp\left(-\theta_c^{0.5}\right) \tag{11}$$

$$\theta_\xi = \alpha - \beta_0\cdot\theta\cdot\exp\left(-\frac{\theta}{1+\epsilon\cdot\theta}\right); \qquad \theta = 0 \quad \text{at} \quad \xi = 0. \tag{12}$$

For zeroth-order reactions, the maximum temperature rise of a TCP is given by:

$$\theta_m = \theta(\xi = 1). \tag{13}$$

To find the value $\alpha_{m,a}$ that gives the maximum allowable temperature rise $\theta_{m,a}$, an initial guess is proposed. Afterwards, Eq. 12 is numerically integrated, the maximum temperature rise is checked (Eq. 13), and the value $\alpha_{m,a}$ updated, until convergence is obtained.

If n = 1, Eqs. 5 and 9 yield:

$$\theta_c = \frac{2}{1-2\cdot\epsilon}; \qquad (\theta_c)_{\epsilon\to 0} = 2 \tag{14}$$

$$\xi_c = 1 - \frac{\theta_c}{\alpha_c}\cdot\left(\frac{1}{1-4\cdot\epsilon}+\frac{\beta_1}{e^2}\right) \tag{15}$$

$$\theta_\xi = \alpha - \frac{\beta_1\cdot\theta}{1-\xi}\cdot\exp\left(-\frac{\theta}{1+\epsilon\cdot\theta}\right); \qquad \theta = 0 \quad \text{at} \quad \xi = 0. \tag{16}$$

For given values of β_1 and ϵ, an initial value α_c is proposed, ξ_c is calculated from Eq. 15, and Eq. 16 is integrated from $O(0;0)$ to $C(\xi_c;\,\theta_c)$. Then, condition 14 is checked and the α_c value updated until convergence. Setting $\alpha = \alpha_c$ in Eq. 16, the maximum temperature rise $\theta_{m,c}$ is found. If $\theta_{m,c} < \theta_{m,a}$, the second safety condition also holds. If $\theta_{m,c} > \theta_{m,a}$, the value $\alpha_{m,a} < \alpha_c$ should be numerically calculated. The same algorithm can be applied, with condition $\theta_m = \theta_{m,a}$ replacing Eq. 14.

If n = 2, Eqs. 5 and 9 lead to

$$\theta_c^2 - 2\cdot\left\{1-(\epsilon\cdot\theta_c)^2\right\}\cdot\theta_c - (1+\epsilon\cdot\theta_c)^4 = 0;$$

$$(\theta_c)_{\epsilon\to 0} = 1+\sqrt{2} \approx 2.4142 \tag{17}$$

$$\alpha_c\cdot(1\text{-}\xi_c)^2 - 2\cdot\left\{\frac{1}{(1+\epsilon\cdot\theta_c)^2}-\frac{1}{\theta_c}\right\}^{-1}\cdot(1-\xi_c)$$

$$-\beta_2\cdot\theta_c\cdot\exp\left(-\frac{\theta_c}{1+\epsilon\cdot\theta_c}\right) = 0 \tag{18}$$

$$\theta_\xi = \alpha - \frac{\beta_2\cdot\theta}{(1-\xi)^2}\cdot\exp\left(-\frac{\theta}{1+\epsilon\cdot\theta}\right); \qquad \theta = 0 \quad \text{at} \quad \xi = 0. \tag{19}$$

For given values of β_2 and ϵ, the numerical solution of Eq. 17 gives the critical temperature rise θ_c. Subsequently, estimated values α_c and ξ_c are proposed and Eq. 19 is numerically integrated from $O(0;0)$ to $C(\xi_c;\,\theta_c)$. Then, θ_c and Eq. 18 are checked and the guess $(\alpha_c;\xi_c)$ is updated, until convergence is obtained. In this way, α_c was determined with the desired accuracy. The value $\theta_{m,c}$ of the critical TCP is calculated by setting $\alpha = \alpha_c$ in Eq. 19, followed by numerical integration. If $\theta_{m,c} < \theta_{m,a}$, the second safety condition also holds. If $\theta_{m,c} > \theta_{m,a}$, the value $\alpha_{m,a} < \alpha_c$ should be numerically calculated. The algorithm is similar to the one previously described, but the condition $\theta_m = \theta_{m,a}$ replaces Eq. 17.

Simulations

Profiles

The maps of Figure 1 show subcritical, critical, and supercritical simulated temperature-conversion profiles referring to reacting systems of zeroth order (Eqs. 10 to 12), first order (Eqs. 14 to 16), and second order (Eqs. 17 to 19). From Figure 1 it can be obtained that a 5% overstep of α_c yields about a 35% increase of θ_m for $n = 0$ and about a 350% increase of θ_m for $n = 1$ and $n = 2$. It is evident that in the vicinity of the critical TCP, the value θ_m is extremely sensitive to small deviations of α_c.

Operation regions

No-Runaway Regions. The adiabatic temperature rise, α_c, of the critical TCP has been numerically calculated as a function of β_n and ϵ for zeroth-, first-, and second-order reaction systems, as mentioned in the previous section. In Figure 2 these simulated relationships have been plotted for different values of n and ϵ. Each isotherm, ϵ, divides a map into two regions. The lower region refers to desired subcritical conditions, the higher one to undesired supercritical conditions. If $n = 0$, 1, or 2, and β_n and ϵ are known, Figure 2 yields regions of $\alpha < \alpha_c$ where no runaways occur.

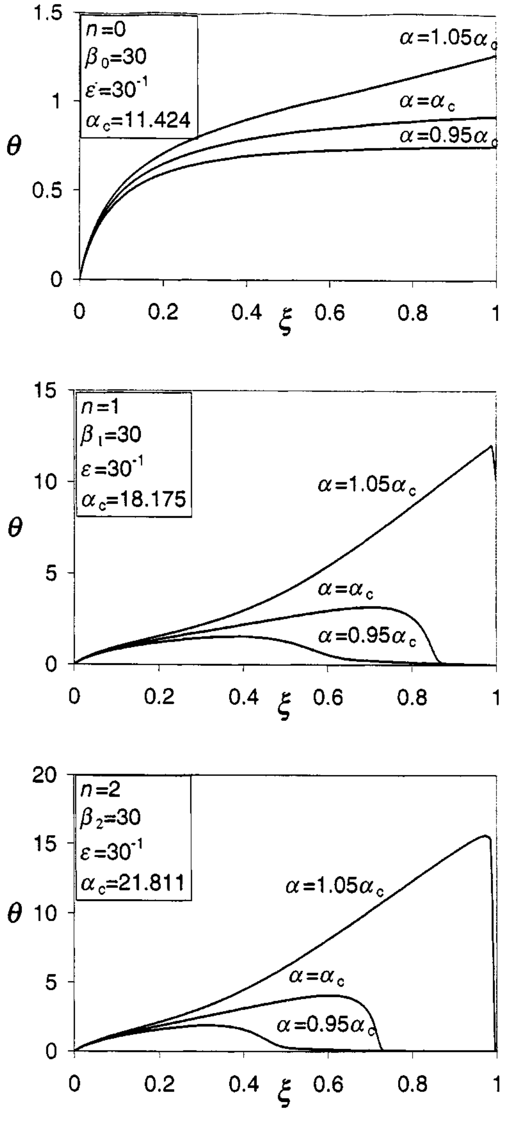

Figure 1. Simulated TCPs of reacting systems of three different orders in batch reactors at subcritical, critical and supercritical runaway conditions.

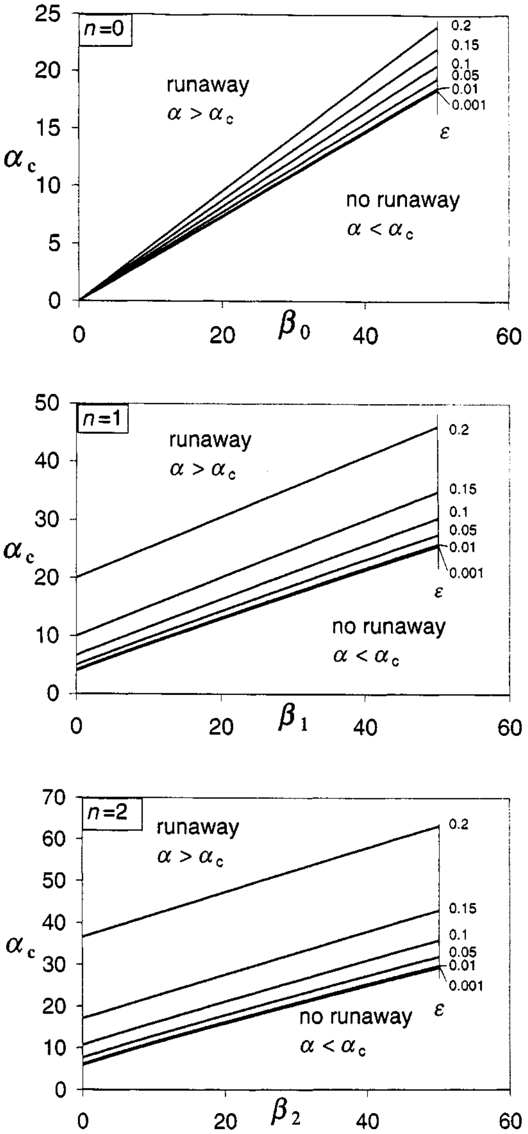

Figure 2. Simulated runaway boundaries of reacting systems of three different orders in batch reactors.

Each isotherm ϵ bounds a no-runaway region.

In the vicinity of the boundary, the sensitivity of the maximum temperature, T_m, of the reacting system is extremely large for small deviations in values, p, of both the system and the control parameters. Morbidelli and Varma (1988) have described this phenomenon by the *normalized objective sensitivity*:

$$S_p = \frac{p}{T_m}\frac{\partial T_m}{\partial p} \qquad \text{where } p = \alpha,\ \beta,\ \epsilon. \tag{20}$$

In a previous article (Heiszwolf and Fortuin, 1996), it has been shown that for fixed values of α and ϵ, the sensitivity S_β of Morbidelli and Varma is maximal at the β value that is next to β_c based on the Adler and Enig criterion presented in Figure 2.

No-Overstep Regions. The value $\alpha = \alpha_{m,a}$ that leads to a TCP with $\theta_m = \theta_{m,a}$ was obtained as described in an earlier section. In Figure 3, simulated values of $\alpha_{m,a}$ have been plotted against β_n, with $\theta_{m,a}$ as the parameter for $n = 0$, 1, and 2, and $\epsilon = 0.01$ and 0.05. In a similar way, isotherms $\theta_{m,a}$ can be calculated for other values of ϵ. Each isotherm $\theta_{m,a}$ divides a map into two regions. The lower region refers to the desired conditions $\alpha < \alpha_{m,a}$, which result in maximum temperature rises $\theta_m < \theta_{m,a}$. The upper region refers to undesired conditions $\alpha > \alpha_{m,a}$, which result in maximum temperature rises $\theta_m > \theta_{m,a}$.

In Figure 4, a combination of the boundaries of Figures 2 and 3 is presented for a first-order reaction system ($n = 1$) and $\epsilon = 30^{-1}$. From this figure, it can be obtained that, if $\theta_{m,a} \geq 5$, then $\theta_{m,c} < \theta_{m,a}$. This means that in this case, the

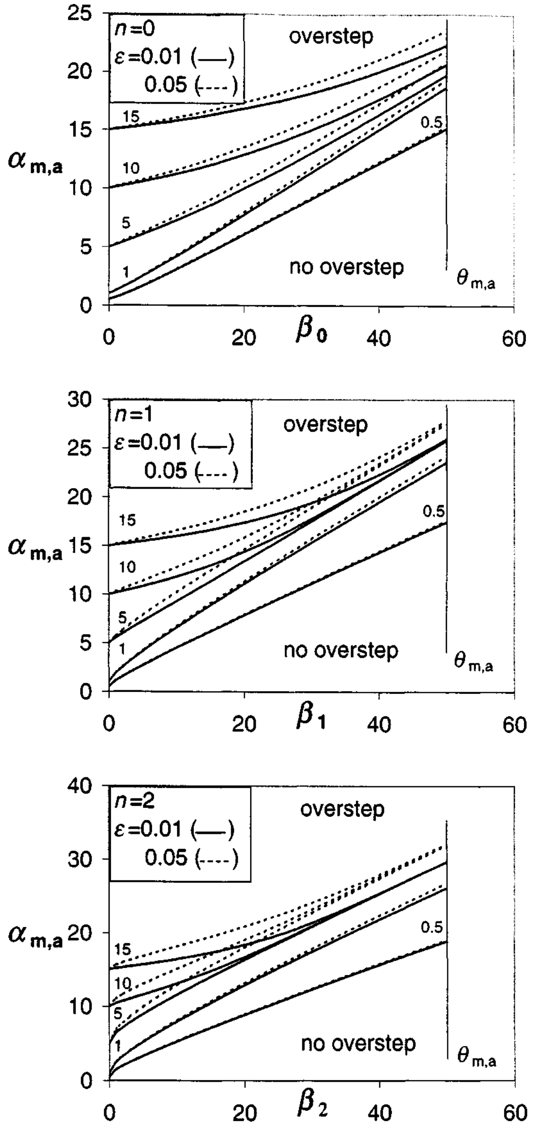

Figure 3. Simulated overstep boundaries of reacting systems of three different orders in batch reactors.

Each isotherm $\theta_{m,a}$ bounds a region yielding $\theta_m < \theta_{m,a}$.

condition $\alpha^* < \alpha_c$ includes the condition $\alpha^* < \alpha_{m,a}$. Figure 4 also shows the high sensitivity of the maximum temperature rise at large values of β_1. When $\beta_1 = 40$ and $\epsilon = 30^{-1}$, θ_m increases from 2 to 12.5, if α increases 5%. In addition, it can be seen that, in this region, the runaway boundary practically coincides with the no-overstep boundaries of a wide range of the maximum allowable temperature rise.

Design Procedure

Conditions for safe operations in batch reactors can now easily be obtained from Figures 2 and 3. After collecting the values of 13 physical quantities (C_p; $C_{p,w}$; k_n; m; m_w; n; T_A; $T_{c,i}$; S; φ; U; $-\Delta H$; ΔQ), the values β_n and ϵ are calculated with Eq. 4. For a conservative design of a batch reactor, the value $Le = 1$ has to be preferred, as will be shown with our experimental results.

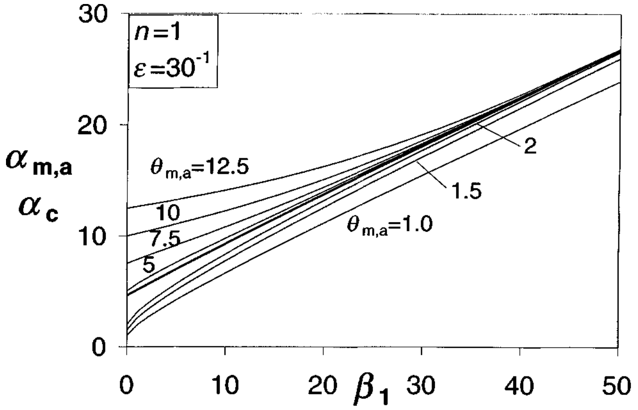

Figure 4. Combination of simulated boundaries of first-order reaction systems ($n = 1$).

The value $\epsilon = 30^{-1}$ agrees with the value applied in the experiments represented in Figure 7. The bold line bounds the no-runaway region; the isotherms $\theta_{m,a}$ bound regions yielding $\theta_m < \theta_{m,a}$.

From Figure 2, the value α_c can be obtained, if β_n, ϵ, and n are known. Figure 3 yields the value $\alpha_{m,a}$ in a similar way, if

$$\theta_{m,a} = \frac{T_{m,a} - T_{mc}}{\epsilon \cdot T_{mc}}$$

is given. Then, the design value α^* has to be chosen in such a way that $\alpha_c > \alpha^* < \alpha_{m,a}$.

Experimental Studies

Reaction system

The reaction system used for investigating runaways is the acid-catalyzed hydration of 2,3-epoxypropanol (EP) to glycerol in an aqueous solution:

$$C_3H_6O_2\ (l) + H_2O\ (l) = C_3H_8O_3\ (l);$$
$$-\Delta H\ (298\ K) = 88.17 \times 10^3\ J/mol.$$

The reaction-rate equation of this system is given by

$$r = m \cdot k_2 \cdot c_H \cdot c \cdot \exp(-T_A/T)$$
$$= m \cdot k_1 \cdot c \cdot \exp(-T_A/T), \quad (21)$$

with, for example, $k_1 = 1.40 \times 10^{10}\ s^{-1}$; $T_A = 8{,}822$ K.

In Eq. 21, c_H is assumed to be constant in the time domain, because sulfuric acid is a catalyst. This reaction system is suitable for studying bench-scale runaway experiments, because the reaction is moderately exothermic, can be performed in the vicinity of room temperature, takes place in a single-phase aqueous solution, can be cooled with tap water, and can be considered first order. In addition, the reacting system has a suitable bubble point and the reaction-rate constant (k_1) can be affected by the acid concentration.

However, the use of EP has also some disadvantages:

- It has to be handled in small amounts; contact with aqueous acid solutions can lead to explosions.

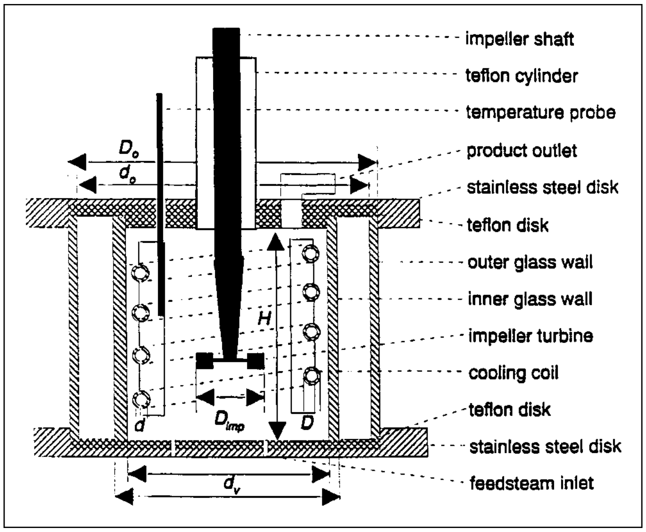

Figure 5. Reactor vessel and its accessories; dimensions are given in Table 1.

- It gradually polymerizes at room temperature and has to be preserved in a refrigerator.
- It decomposes near its boiling point ($\sim 167°C$).
- Purification by distillation is only allowed at low pressures.

Further, EP as a density $\rho = 1114.3\ \mathrm{kg\cdot m^{-3}}$ at 25°C, a refractive index $n = 1.4287$ at 20°C and consists of a racemic mixture of two enantiomers.

The investigations with EP in the university group were inspired by two accidents with epoxy components that occurred in the company where one of the authors (J.F.) spent the main part of his industrial career.

It may be added that the hydration of EP is part of a sequence of reactions used to produce glycerol commercially. The first plant of this glycerol process was built by Shell in Louisiana, in 1958 (Jakobson et al., 1989).

The reactor vessel

The 0.27-L reactor, the geometry and dimensions of which are given in Figure 5 and Table 1, respectively, also has been used for CSTR experiments (Heiszwolf and Fortuin, 1997). It consists of two coaxial glass cylinders that are clamped between two stainless-steel disks (Heiszwolf, 1998). The cylinders and disks are separated by rubber sealing rings followed by Teflon disks, which are partly covered by the steel disks. The inner diameter of the inner cylinder is equal to its height. The space between the cylinders has been evacuated. The reactor is cooled with tap water using a silver-plated (to prevent corrosion caused by sulfuric acid) copper helical cooling coil with four baffles mounted on the coil. The reactor content is agitated by a six-blade Ruston turbine impeller with a stirrer-speed range between 8 and 50 $\mathrm{s^{-1}}$. In case of an overstep of the bubble point, the boiling liquid can be blown off through the annular space between the stirrer shaft and a Teflon cylinder at the top of the reactor. The reactor is surrounded by a removable Plexiglas box equipped with a drain leading to a 50-L stainless-steel catch vessel, partly filled with water. The reactor setup is placed inside a large fume chamber. It was shown that these precautions were adequate, even if a reactor ruptured as a result of a runaway due to a mischarge.

Table 1. Dimensions of the Reactor

Parameter	Description	Value	
d	Internal pipe diameter of cooling coil	0.0042	m
D	External pipe diameter of cooling coil	0.0064	m
D_{coil}	Coil diameter	0.0686	m
d_v	Internal diameter inner glass wall	0.0714	m
D_v	External diameter inner glass wall	0.0792	m
d_0	Internal diameter outer glass wall	0.1031	m
D_0	External diameter outer glass wall	0.1111	m
D_{imp}	Impeller diameter	0.024	m
H	Height of the reactor	0.0723	m
L_c	Length of cooling coil	0.627	m
S	External surface area of cooling coil	0.0125	$\mathrm{m^2}$

Newtonian cooling time

The local overall heat-transfer coefficient, based on the external surface area S of the cooling coil, is calculated from Eqs. 22–25 (Heiszwolf and Fortuin, 1997):

$$U = \left\{ h_L^{-1} + \frac{D}{2\cdot\lambda_t}\cdot\ln\left(\frac{D}{d}\right) + \frac{D}{h_c\cdot d} \right\}^{-1}; \qquad S = \pi\cdot D\cdot L \tag{22}$$

in which the partial heat-transfer coefficients h_L and h_c follow from

$$\frac{h_L\cdot D}{\lambda_L} = 0.06\cdot\left(\frac{N\cdot D_{\mathrm{imp}}^2}{\nu_L}\right)^{0.7}\cdot\left(\frac{\eta_L\cdot C_{p,L}}{\lambda_L}\right)^{1/3} \tag{23}$$

$$\frac{h_c\cdot d}{\lambda_c} = 0.023\cdot\left(\frac{u\cdot d}{\nu_c}\right)^{0.8}\cdot\left(\frac{\eta_c\cdot C_{p,c}}{\lambda_c}\right)^{1/3}\cdot\left(1+\frac{3.5\cdot d}{D_{\mathrm{coil}}}\right), \tag{24}$$

when $ud/\nu_c > 10^4$; $0.7 < \eta_c C_{p,c}/\lambda_c < 700$; $D_{\mathrm{coil}}/d > 60$, and the effectiveness factor:

$$\varphi = \frac{1-\exp\left(-\dfrac{U\cdot S}{\phi_{m,c}\cdot C_{p,c}}\right)}{\dfrac{U\cdot S}{\phi_{m,c}\cdot C_{p,c}}}. \tag{25}$$

Equation 25 holds, if during the batchwise operation, a quasi-steady-state axial coolant-temperature profile is maintained in the cooling coil. Coefficient h_c at the coolant side was calculated with Eq. 24, and coefficient h_L with Eq. 23. The latter was obtained from experimental data, because no correlation was available for a cooling coil with baffles mounted on the coil. The overall heat-transfer coefficient was derived from experimental results obtained with heated glycerol–water mixtures fed to the agitated and cooled reactor vessel, while the temperatures of the reactor feed and content, and those of the inlet and outlet coolant flows, were recorded and the coolant mass flow rate was measured.

Using Eqs. 22–25, the Newtonian cooling time was calculated from

$$t_N = \frac{m \cdot C_p}{\varphi \cdot U \cdot S}. \tag{26}$$

Reaction time

The characteristic reaction time has been defined by

$$t_R = k^{-1} \exp\left(\epsilon^{-1}\right), \tag{27}$$

which means the reaction time needed for obtaining a concentration $c = e^{-1} c_0$ at a temperature $T = T_{mc}$ in a completely mixed batch reactor.

Mixing time

The concept of complete mixedness can be applied if the mixing time (t_{mix}) is considerably smaller than the characteristic reaction time (t_R). The mixing time of a tracer is defined as the time required for obtaining local concentrations that differ less than 5% from the mean concentration. The mixing time t_{mix} is dependent on the circulation time t_{cir} of the liquid in the vessel. For the geometry of the used reactor vessel, it can be estimated as

$$t_{\text{mix}} \approx 4 t_{\text{cir}}. \tag{28}$$

The value of t_{cir} can be obtained from (Voncken, 1966):

$$Vo = 1.10\, Re_{\text{imp}}^{-0.05}, \qquad Re_{\text{imp}} > 10^3,$$

where

$$Vo = t_c N \left(D_{\text{imp}}/d_v\right)^2, \qquad Re_{\text{imp}} = N D_{\text{imp}}^2 / \nu_L. \tag{29}$$

Equations 27–29 result in the condition

$$t_{\text{mix}}/t_R \ll 1. \tag{30}$$

With respect to the considered reaction system, it may be added that

- The key component has been completely mixed before the reaction started.
- The catalyst, sulfuric acid, was injected into the agitated reactor contents within one second.
- The mixing condition of Eq. 30 holds.

Procedure

A weighted amount of 2,3-epoxypropanol is poured into the reactor. The remaining volume is nearly completely filled with demineralized water, the mass of which is also determined. Then, the reactor content is stirred with the speed necessary for obtaining the required heat-transfer capacity and mixing rate, and the coolant flow is started. After some minutes, the temperature T_{mc} of the content is constant. Further, a syringe is filled with about 4 mL of an aqueous sulfuric acid solution that is weighted accurately. The data acquisition is turned on, and the sulfuric acid solution of temperature T_{mc} is injected into the stirred reactor within one second. The temperature of the reacting system then starts to rise. The fume chamber is closed, the temperature-time profile is recorded, and the temperature-conversion profile calculated.

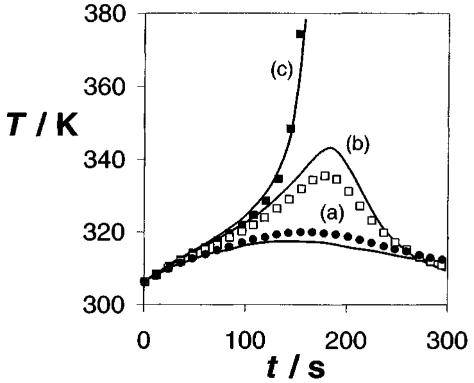

Figure 6. Measured markers and simulated lines (Eqs. 1 and 2; $n = 1$, $\beta_1 = 23.7$, $\epsilon = 28.8^{-1}$) concerning the temperature rise in the time domain of the hydration of 2,3-epoxypropanol in a 0.27-L batch reactor [$t = \tau_1 k_1^{-1} \exp(\epsilon^{-1})$; $T = (1 + \epsilon\theta) \cdot \epsilon T_A$].

(a) Subcritical operation ($\alpha = 13.1 < \alpha_c = 15.472$; $\theta_m < \theta_{m,a} = \theta_B = 6.4$); (b) operation just above the critical one ($\alpha = 15.5 > \alpha_c = 15.472$; $\theta_m < \theta_{m,a} = \theta_B = 6.4$); (c) runaway and overstep ($\alpha = 15.9 > \alpha_c = 15.472$; $\theta_m > \theta_{m,a} = \theta_B = 6.4$).

Results

Experiments concerning the hydration of EP were performed in the 0.27-L bench-scale reactor described in the previous section. In Figure 6, the markers refer to the experimental results of three temperature–time profiles: (a) a subcritical profile, (b) a profile just above the critical one, and (c) a runaway with an overstep of the bubble point. The solid lines represent simulations obtained with Eqs. 1 and 2, using $n = 1$, $\beta_1 = 23.7$, and $\epsilon = 28.8^{-1}$, with (a) $\alpha = 13.1 < \alpha_c = 15.472$; $\theta_m < \theta_{m,a}$; (b) $\alpha = 15.5 > \alpha_c = 15.472$; $\theta_m < \theta_{m,a}$; and (c) $\alpha = 15.9 > \alpha_c = 15.472$; $\theta_m > \theta_{m,a}$, in which $\theta_{m,a} = \theta_B = 6.4$, the dimensionless bubble point of the reacting system.

In these experiments, the values of α and β_1 were varied by changing the control parameters c_0, $T_{c,i}$ and t_N. Table 2 shows the applied ranges of parameter values in the experiments with the batch reactor.

Table 2. Applied Ranges of Ranges of Parameter Values (batch reactor 0.27 L)

Symbol	Name	Value	
c_H	Proton concentration	0.05–0.20	mol/kg
c_0	Initial concentration EP	2.5–8.6	mol/kg
N	Stirrer speed	8–50	s^{-1}
T_{mc}	Modified coolant temperature	293–315	K
$\phi_{m,c}$	Coolant mass flow rate	0.110–0.130	kg/s

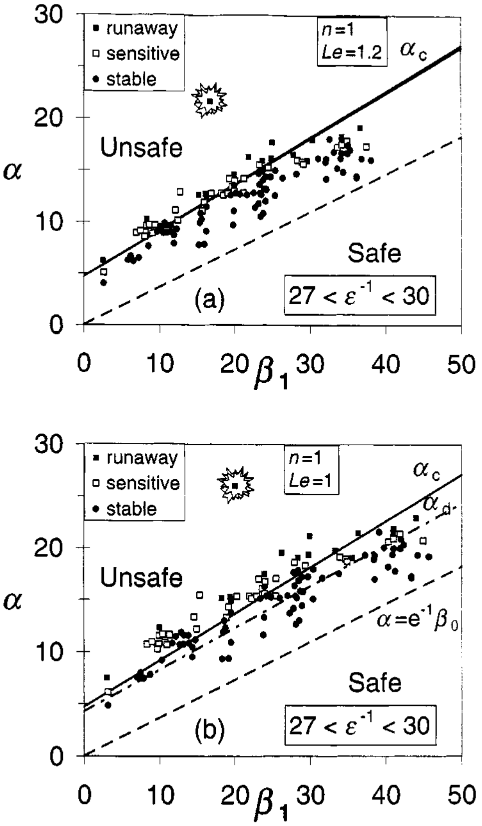

Figure 7. Observed behavior of EP-containing reacting systems in a 0.27-L batch reactor.

(a) $Le = 1.2$; (b) $Le = 1.0$. The bold lines represent the runaway boundaries for $27 < \epsilon^{-1} < 30$. The dashed lines represent $\alpha = e^{-1}\beta_0$ (Semenov, 1928). The dashed-dotted line indicates $0.9\alpha_c$ values. The drawings refer to conditions of a mischarge that resulted in an explosion yielding a destruction of a reaction vessel.

During each experiment, the temperature of the reacting system and the cup-mixed temperatures of the inlet and outlet of the coolant were measured in the time domain. As long as the temperature of the reacting system stays below the bubble point, the TCP was analyzed to detect a region of positive second-order derivatives before the maximum temperature was reached.

Figure 7 shows markers that represent three types of observed behavior of the reacting system: (a) stable, (b) sensitive, and (c) runaway with content loss. The coinciding solid lines in Figure 7a were calculated using Eqs. 14 to 16 and $n = 1$, $\epsilon = 27^{-1}$, and $\epsilon = 30^{-1}$. The markers in Figure 7a refer to $Le = 1.2$. This value was calculated with Eq. 4 and estimated values of m_w and $C_{p,w}$. Further, a point indicating the result of a mischarge is shown deeply situated in the unsafe region. This "experiment" yielded an explosion leading to the complete destruction of the batch reactor. The markers in Figure 7b refer to the same experimental results as the markers in Figure 7a. However, the more conservative value $Le = 1$ has been applied. It is evident that the location of the solid lines in Figure 7 is not affected by the value of Le. However, the markers that represent measured results shift as a result of changing the Lewis number. In Figure 7b, where $Le = 1$, the position of the markers agrees better with the solid runaway boundary than the markers in Figure 7a with $Le = 1.2$, more particularly at high α values. This is due to the fact that the effective value of Le approaches 1, if the temperature rise is very fast. This phenomenon is caused by the restricted heat takeup of the reactor vessel during the rapid temperature rise that results from the very fast reaction rate at a higher temperature.

Figure 7b shows that, at high values of β_1 and α, several runaways occurred in the formal "safe region" of the map, near the runaway boundary. This phenomenon can be caused by (a) insufficiently rapid mixing rate; (b) insufficient accuracy of parameter values, more particularly of the kinetic data; (c) the high sensitivity of θ_m in the vicinity of α_c. Therefore, conditions in the no-runaway region *near* the runaway boundary also have to be avoided, for example, by introducing a safety factor κ, the value of which depends on the accuracy of the design data. Figure 7b shows the dashed-dotted line $\kappa = 0.9$, which excludes all the runaways from the safe region. A very conservative boundary follows from the criterion of Semenov for zeroth-order reaction systems (dashed line).

Comparing Figures 4 and 7, it can be stated that the condition $\alpha^* < \alpha_c$ in Figure 7b includes $\alpha^* < \alpha_{m,a}$, because $6.4 = \theta_B = \theta_{m,a} > 5.0 > \theta_{m,c}$.

Discussion

In the present article, the behavior of the reacting systems in batch reactors have been simulated with a mathematical model yielding stability maps referring to $\alpha_c = \alpha_c(\beta_n)$ and $\alpha_{m,a} = \alpha_{m,a}(\beta_n)$ of zeroth-, first-, and second-order reaction systems.

These maps respectively contain lines of constant values of the dimensionless inlet coolant temperature ϵ (Figure 2) and lines of constant values of the dimensionless maximum allowable temperature rise $\theta_{m,a}$ (Figure 3). Each line of constant ϵ bounds a no-runaway region. Each line of constant $\theta_{m,a}$ bounds a region where no overstep of $\theta_{m,a}$ occurs. It is evident that for given values of n, ϵ, and β_n, values of α_c and $\alpha_{m,a}$ can be obtained from Figures 2 and 3, or the appropriate equations. As a result, it can be stated that the following four types of behavior can be distinguished, if n, ϵ, and β_n have been fixed, and the design value α^* has to be determined:

- Type 1: $\alpha_c > \alpha^* < \alpha_{m,a}$ stable/safe; curve a, Figure 6.
- Type 2: $\alpha_c < \alpha^* < \alpha_{m,a}$ sensitive; curve b, Figure 6.
- Type 3: $\alpha_c > \alpha^* > \alpha_{m,a}$ unsafe; $\theta_m > \theta_B$.
- Type 4: $\alpha_c < \alpha^* > \alpha_{m,a}$ unsafe; curve c, Figure 6; Figures 7a and 7b.

Further, it has to be taken into account that deviations of β_n and ϵ from nominal values have a profound effect on θ_m near the boundary of the no-runaway region (Figure 2). Consequently, the conditions for safe operations are reduced to $\kappa \cdot \alpha_c > \alpha^* < \alpha_{m,a}$, where, for example, $\kappa = 0.9$ (dashed-dotted line in Figure 7b).

Conclusions

Exothermic, liquid reacting systems in batch reactors can be operated safely if

- The reacting system is completely mixed ($t_{\mathrm{mix}}/t_R \ll 1$).
- The heat capacity of the vessel and its accessories is neglected ($Le = 1$).
- The no-runaway condition holds ($\alpha^* < \kappa\alpha_c$; $\kappa < 1$, for given values of n, ϵ, β_n) to avoid the extreme sensitivity of the maximum temperature for deviations of design parameter values.
- The no-overstep condition holds ($\alpha^* < \alpha_{m,a}$, for given values of n, ϵ, β_n) to prevent exceeding the maximum allowable temperature.

When the kinetics of the reacting system are unknown, safe batchwise operation can be performed, if

- The reaction system is completely mixed.
- The Lewis number is one.
- The adiabatic temperature rise is smaller than the maximal allowed one ($\alpha_{\mathrm{ad}} < \theta_{m,a}$ or $T_{\mathrm{ad}} \equiv T_{mc} + ((-\Delta H)\cdot c_0)/C_p < T_{m,a}$).

Acknowledgment

The authors thank Mrs. R. Hippert for her contribution in the preparation of the present article, and Mr. J. Zoutberg and his colleagues for technical assistance.

Notation

c = concentration of key component, mol/kg
c_0 = initial concentration of key component, mol/kg
c_H = proton concentration, mol/kg
C_p = specific heat of reaction system, J/(kg·K)
$C_{p,w}$ = specific heat of reactor vessel, J/(kg·K)
$C_{p,c}$ = specific heat of coolant, J/(kg·K)
d = internal tube diameter cooling coil, m
D = external tube diameter cooling coil, m
h_c = internal partial heat-transfer coefficient of cooling coil, W/(m^2·K)
h_L = external partial heat-transfer coefficient of cooling coil, W/(m^2·K)
k_n = frequency factor of nth-order reaction, $(\mathrm{kg/mol})^{n-1}\cdot \mathrm{s}^{-1}$
L = length of cooling coil, m
Le = Lewis number (Eq. 4), L
m = mass of reactor content, kg
m_w = mass of reactor vessel and accessories, m
n = reaction order, 1
n = nth order derivative
N = stirrer speed of impeller, s^{-1}
S = external heat-transfer area of cooling coil, m^2
t = time, s
T = temperature of reactor content, K
T_A = Arrhenius temperature of reaction-rate equation, K
T_B = bubble point, K
$T_{c,i}$ = inlet coolant temperature, K
$T_{m,a}$ = maximum allowable temperature of reacting system, K
T_{mc} = modified coolant temperature (Eq. 4), K
U = overall heat-transfer coefficient, based on external surface area of cooling coil, W/(m^2·K)
u = superficial velocity of coolant in coil, m/s

Greek letters

α = adiabatic temperature rise (Eq. 4)
α_c = critical adiabatic temperature rise
β_n = heat-transfer capacity (Eq. 4)
$(-\Delta H)$ = heat of reaction, J/mol
ΔQ = heat flow generated by stirring, minus a constant heat loss to the surroundings, W
ϵ = ratio T_{mc}/T_A
η = dynamic viscosity, Pa·s
θ = dimensionless temperature rise (Eq. 3)
κ = reduction factor ($0 < \kappa < 1$)
λ = thermal conductivity, W/(m·K)
ν = kinematic viscosity, m^2/s
ξ = conversion ($1 - c/c_0$)
ρ = density, $\mathrm{kg/m}^3$
τ_n = dimensionless time (Eq. 3)
φ = heat-transfer effectiveness (Eq. 25)
$\phi_{m,c}$ = mass-flow rate of coolant, kg/s

Indices

ad = adiabatic
B = bubble point
c = coil, coolant, or critical
cir = circulation
L = reaction system
m = maximum value
m,a = maximum allowable value
mc = modified coolant
m,c = maximum of critical TCP
mix = mixing
R = reaction
t = tube

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Manuscript received Jan. 3, 2000, and revision received Aug. 14, 2000.