Safe Operation of Stirred-Tank Semibatch Reactors Subject to Risk of Thermal Hazard

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In this work, the behavior of exothermic chemical reactions conducted in a wall-cooled, semibatch stirred-tank reactor is studied, with particular attention to conditions that lead to a thermal accident. The dimensionless heat and mass conservation equations for a semicontinuous tank were solved using second-order irreversible kinetics and a number of selected dimensionless numbers, for both the feed period and the late batch stage. The criterion implemented is based on the nonaccumulation of the dosed reactant, and the safest operating mode is based on the values of the reactor parameters that lead to an instantaneous consumption of the dosed feed. The criterion is implemented into an algorithm that runs in parallel with the integration of the model equations. Its applicability is shown using a few examples that show that the computer implementation of our methods works well in hazard prediction. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 3570–3582, 2006

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Introduction

The operation of exothermic reactors in chemical synthesis always involves a potential hazard resulting from a faulty operation, wrong heat transfer assumptions, or related human errors. For instance, if the cooling capacity of the reactor vessel is low compared with the heat generated by the reaction, the temperature of the mixture will rise. For a given reaction system, this could unleash an exponential evolution of heat that will increase temperature still higher, leading to an uncontrolled temperature feedback cycle and resulting in a thermal runaway. Knowledge of the chemical process characteristics and the circumstances that could bring about this situation are essential factors in achieving an intrinsically safe operation. The kinetic and thermodynamic parameters such as the ratio of heat transfer area to volume of the vessel and a sufficiently high heat transfer coefficient available are key factors to avoid the occurrence of a runaway.

Traditionally, the Semenov theory[1] has been used to assess the thermal safety of a chemical reactor or an unstable chemical in liquid form. This theory is based on the assumptions that the reaction is zero-order, the reactant is unconsumed, and the vessel is well mixed. To avoid a runaway, the Semenov's parameter (Ψ) should be below its critical value Ψ_{crit}—thus, $\Psi < \Psi_{\mathrm{crit}} = e^{-1}$.[2] In some cases, this approach proves too conservative given that reactant consumption is not taken into account.[3,4] In fact, if reactant consumption is allowed for, the Ψ_{crit} is two- or threefold larger than that based on the Semenov theory. In general, the risk of a runaway for a given reactor is attributed to a high parametric sensitivity of the reaction-vessel system.[5] Bilous and Amundsen[6] were the first authors to describe that phenomenon in tubular reactors. Contributions in this field are ascribed to Dente and Collina,[7] Hlavacek et al.,[8] Van Welsenaere and Froment,[9] Morbidelli and Varma,[10] Hugo,[11] and Balakotaiah and Luss[12] among others.

In a previous work, Velo et al.[4] established a critical set of parameters that characterize a thermal runaway in a stirred-tank reactor or a storage tank with wall cooling for first- and second-order reactions. The runaway conditions were identified as a function of the temperature–conversion trajectories

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near complete conversion using a so-called CAPSA methodology. Some authors[10,13] used the plane of parameter N vs. S to define the runaway to the nonrunaway semiplanes, where N is the cooling capacity of the reactor and S is the reaction sensitivity.[14-16] (See definitions under Theory below.) This type of safety maps is useful for assessing safety as shown by Velo et al.[4] in batch cases. In a recent work, Fortuin et al.[17] give a procedure that allows determining the safety of the operation. It is based on the consideration of the initial concentration values, the cooling onset temperature, and the Newtonian-cooling time. The emphasis here, however, is in semicontinuous and batch reactors because this type of reactor affects the processes where more runaway incidents occur as shown by historical records.[18] One such frequent accident is related to polycondensations and vinyl polyadditions in emulsion processes.

Processes that operate in the batch mode [batch reactor (BR)] are generally faster than those operated in a semibatch reactor (SBR), but the former present a higher thermal risk at the start-up. In some cases, when the reaction has a strong parametric sensitivity, the risk in a BR can be so great that the reactant must be added slowly. In the so-called SBR operating mode, the runaway risk is avoided by slowly adding one or more reactants over a delayed period of time. If the feed stream reacts as soon as it reaches the agitated fluid (thus with no delay) it is possible to control the balance between the heat generation arising from reaction and the heat absorbed by the cooling system. Because the heat generation rate depends on the dosed reactant flow rate, it should always be possible to make a slow enough addition. The rules set by Hugo[19] can be used to decide when the use of an SBR is recommended. These rules are based on the fraction of heat necessary to reach the maximum allowable temperature of the reacting mixture. In general, a BR operation will be possible if the reactor temperature is kept below acceptable limits, that is, $T_{\max}$, where $T_{\max}$ is the upper allowable temperature at which the heat of reaction can still be absorbed from the vessel by the cooling system available. In terms of the adiabatic temperature rise (ΔT_{ad}), the conditions for using a batch reactor are[11]

$$\frac{T_{\max} - T_0}{\Delta T_{ad}} \geq 1 \tag{1}$$

together with a heat generation potential S, evaluated at $T_{\max}$, below the critical, S_{crit}. In Eq. 1, $T_{\max}$ is a practical upper temperature limit imposed by the available cooling power (not to be confused with the autothermal or adiabatic final temperature). A conservative value is $S_{\text{crit}} = 3$.[11]

Conversely, if the above ratio is too small, say <0.25, and if S exceeds S_{crit}, the reactor cannot operate safely in batch mode because a large excess of the heat load must be imposed to the cooling system. In this case, a batch can be operated by choosing a lower start-up T_0 or in semibatch mode.

Early theoretical work on SBRs is ascribed to Hugo and Steinbach[20] as well as Westerterp.[21] Hugo and Vlassis[22] established two empirical correlations that predict the distinction between runaway, intrinsically safe operation, and a third one where a process is possibly safe provided that certain limits are avoided. These limits were observed by analysis of a few thousand simulations performed under different operation conditions with parameters varied over the range of industrial significance and then correlating the simulated results with those obtained empirically. A striking conclusion from that study is that, although in a BR the reactor temperature should be kept *below* a certain limit, in an SBR, in contrast, the reaction temperature must be kept *above* a certain temperature to avoid a hazardous reactant accumulation, provided that a parallel, higher activation energy reaction is not unleashed.[23]

Steinbach[24] evaluated the system response to a regular variation in the process variables for an SBR operation. He established that in an SBR if the initial reaction rate is too low with respect to the addition rate, because either the reference temperature chosen is too low or the feed rate is too high, the system will experience reactant accumulation that can bring about a dangerous overheating. By many simulation runs of the operating conditions in the range of industrial significance, Steinbach proposed an empirical safety criterion for SBRs (see below).

According to Steensma and Westerterp,[21,25,26] SBR is safe if a sudden temperature excursion is prevented and if reactant accumulation is avoided. Because of the difficulties of formulating an appropriate accumulation criterion, these authors based safety on the evolution of temperature of the reacting mixture. Here the concept of the so-called *target temperature* was introduced. The calculation of the target temperature is based on a quasi-steady-state heat balance without reactant accumulation. The target temperature is a controlled, stable, and feasible temperature target that can be achieved during safe operation under quasi-steady-state conditions with regard to the maximum reaction rate. Under conditions of constant heat transfer area during the feed period, the target temperature is constant. In industrial reactors, however, the available heat transfer area will increase somewhat during the dosing period so that the target temperature vs. time profile will be a slightly declining curve. Four possible scenarios will be observed for the target temperature in a given SBR:

(1) *No ignition* (that is, the reactor temperature never reaches the target temperature during the dosing period or thereafter).

(2) *Marginal ignition* (that is, reactor temperature approaches the target temperature at any time).

(3) *Temperature runaway* (that is, target temperature is largely exceeded).

(4) *Smooth reaction* (that is, target temperature is approached all over the dosing period).

Authors have shown the thermal response of an SBR using the exothermicity and reactivity as parameters.

Safety issues related to SBR were also examined by Stoessel[23] and coworkers, based on the thermal behavior. Using simulation they showed that in an SBR, the temperature excursion and the addition feed rate can meet a compromise to satisfy safety constraints as well as production needs. Thus the cooling capacity and the degree of accumulation can be controlled at a certain optimum temperature.[27] Ubrich et al.[28] developed the control algorithms later implemented in the case of the reaction of propionic anhydride with butanol[29] in the experiments. These researchers showed with an example that it is possible to modulate the reactant feed rate to attain a safety objective with feedback control on the estimated accumulation.

Recently, Van Woezik[30,31] carried out the oxidation of 2-octanol with nitric acid. To avoid runaway, the accumulation of the dosed reactant should be controlled. To determine the safety of the operation, Van Woezik used the Steensma approach by applying an extension of the model to the multiple reaction case. The conclusion of the study is that operation is safe for high values of the dosing time or for high values of the system cooling capacity, that is, in general, for a small, rather than a large, reactor vessel.

From the findings in SBR operation it can be concluded that safe operation in an SBR implies such conditions where the reactant accumulation is under control, either because the overcooling originated by an excessive heat removal is avoided or because a too rapid dosing rate is prevented. All the approaches available so far for the assessment of the safe operation of an SBR have been obtained empirically or are based on the study of the reactor temperature evolution.

It will be evident that the nonaccumulation criterion for SBR operation is a sufficient condition for safety, but it is not a necessary condition. For very strongly exothermic processes, however, it is desirable to adhere strictly to nonaccumulation, although it might prove too conservative, leading to lower production rates. The compromise is subject to optimization provided that reliable detectors are available.[32]

In this work, an approach to assess the safe operation for an SBR-based process is presented for a single exothermic reaction. The method is based on the implementation of the accumulation criteria graphically or implemented in computer programs. Species accumulation and conversion and reactor temperature values are determined as functions of time by simulation, and relationships between these values are obtained. These values establish a new approach to determine the range of safe operating conditions. This allowed us a simplified classification of the operation in three different clear-cut scenarios: *safe behavior*, *runaway behavior*, and *nonignition behavior*. The last case is the most unfavorable one because it produces a total accumulation of the reactant fed, which can lead to a thermal runaway once the feeding period is over and the system operates to completion in the batch mode. Therefore, to assess the safe operation of a nonignition case in an SBR it is also necessary to assess the safe operation once the feeding is over and the reactor operates in batch mode.[4] Finally, for the SBR case, our method is used to calculate a few generalized safety maps and to solve some industrial cases of operation and safe scale-up relevant to chemical production.

Theory

To study the thermal safety of an SBR, the reaction behavior both during the feeding period ($t \leq t_D$) and during the late batch period, after feeding is over ($t > t_D$), should be examined. If conversion at the end of the dosing period is large, the late batch can be disregarded. In such cases, the risk of runaway will be of concern only during the first stage.

SBR equations for the feed stage ($t \leq t_D$)

To establish a mathematical model for this stage, the following assumptions will be made. (1) Reaction is a liquid-phase, homogeneous, second-order, irreversible process, without phase change. (2) A is the reactant initially loaded and B is the reactant delayed over a dosing time t_D. (3) Stoichiometry is one to one. (4) Equimolar quantities of A and B will be fed at $t = t_D$. (5) The wall-cooling is isoperibolic (constant coolant temperature $= T_C$). (6) The total volume fed relative to the initial volume V_0 is large; thus the heat transfer capacity available (UA) will change with time and is taken to be proportional to the total liquid volume in the tank. (7) The feed stream temperature T_f is different from the reactor temperature and close to ambient.

Model equations are obtained by writing the mass and energy balance equations, for well mixed reactants and, considering that volumes are additive, the mass conservation and the mass and energy balance equations are as follows:

$$\frac{d(V\rho)}{dt} = v\rho_f \tag{2}$$

$$\frac{dT}{dt} = \frac{(-\Delta H)}{\rho c_p} kC_A C_B - \frac{v(T - T_f)}{V} - \frac{UA(T - T_c)}{V\rho c_p} \tag{3}$$

$$\frac{dC_A}{dt} = -kC_A C_B - \frac{C_A}{V} v \tag{4}$$

$$\frac{dC_B}{dt} = v\frac{C_{Bf}}{V} - kC_A C_B - \frac{C_B}{V} v \tag{5}$$

With the following initial conditions: $V = V_0$, $C_A = C_{A0}$, $C_{B0} = 0$, $T = T_0$, and $A = A_0$ at $t = 0$ for time $t < t_D$. The following explicit relationship between V and A is

$$A = A_0 + \frac{4(V - V_0)}{D_t} \tag{6}$$

where D_t is the tank diameter and V_0 is the volume of the initial charge. It is thus assumed that the added volume fills only a cylindrical portion above the bottom. Thus V_0 is at least equal to the bottom contents of the reactor, whose area is A_0. Critical conditions for runaway are defined in terms of the usual dimensionless parameters.[4] The governing equations then are

$$\frac{dX}{d\tau} = \mathrm{Da}\frac{(1 - X)(\tau - X)}{(1 + \varepsilon\tau)} \exp\left(\frac{\theta}{1 + \frac{\theta}{\gamma}}\right) \tag{7a}$$

$$\frac{d\theta}{d\tau} = S\ Da\ \frac{(1 - X)(\tau - X)}{(1 + \varepsilon\ \tau)^2} \exp\left(\frac{\theta}{1 + \frac{\theta}{\gamma}}\right) - \frac{Da[(N1 + \varepsilon\tau) + N_f)\theta - N_f\theta_f]}{(1 + \varepsilon\ \tau)} \tag{7b}$$

valid for $0 < \tau < 1$, with $X(0) = 0$ and $\theta(0) = \theta_0$. In the above equations, the dimensionless temperature of the reactor θ is defined as

$$\theta = \gamma\left(\frac{T - T_C}{T_C}\right) \tag{8}$$

with γ defined as

$$\gamma = \frac{E}{RT} \tag{9}$$

The usual value for the Arrhenius number γ is between 10 and 100, of which 40 is a standard value in industrial operations. The initial conditions for the governing equations are $X(0) = 0$, $\theta(0) = \theta_0$. The numerical parameters for the above system of equations are defined as follows.

The heat generation potential for the reaction is

$$S = \frac{E}{RT_C^2}\,\Delta T_{ad} \tag{10}$$

so that the ratio S/γ represents the reduced adiabatic temperature rise, that is,

$$S/\gamma = \frac{\Delta T_{ad}}{T_C} \tag{11}$$

The heat transfer capacity of the reactor (at $t = 0$) is defined as

$$N = \frac{UA_0}{V_0 \rho c_p k_c C_{A0}} \tag{12}$$

and the cooling capacity arising from the inlet stream, colder in general than the reacting mixture, is

$$N_f = \frac{(\rho c_p)_f v}{(\rho c_p)_0 k_c N_{A0}} \tag{13}$$

The dosing time t_D appears in the Damköhler number (Da), calculated at the coolant temperature:

$$\mathrm{Da} = k_c C_{A0} t_D \tag{14}$$

Da represents the ratio between the dosing time and the characteristic reaction time at T_C. For the case of an SBR, the ratio of the dosing time to the characteristic cooling time is the Stanton number (St) and thus

$$\mathrm{St} = \frac{UA_0 t_D}{V_0 \rho c_p} = N\mathrm{Da} \tag{15}$$

In the above equations, it is known that the heat generation potential S increases linearly with the adiabatic temperature rise for the reaction and it is a direct expression of reaction sensitivity to temperature through the group $E/(RT_C^2)$.[33] The cooling intensity N defines the nominal heat absorption capacity of the cooling system. For an adiabatic reaction $N = 0$, the cooling intensity N decreases for vessels of increasing size, so that this quantity can be used to rank reactor vessel sizes.[34]

After solving the system of equations it is possible to know the temperature of the reacting mixture and both the conversion and the accumulation of unreacted species. The accumulation α is defined as the moles of B remaining relative to the moles of A initially charged. A zero accumulation ratio means an instantaneous reaction of the moles of B added with some moles of A present in the reactor. On the other hand, when accumulation increases, the rate of conversion decreases accordingly. Therefore, the function α allows following the fate of the reactant fed. The accumulation function is

$$\alpha = \frac{N_B}{N_{A0}} \tag{16}$$

that can be written as

$$\alpha = \varepsilon Ch\tau - X \tag{17}$$

$$Ch = \frac{C_{Bf}}{C_{A0}} \tag{18}$$

As seen above, during a reaction run the accumulation function can be readily calculated from the current values of time and conversion.

SBR equations for the late batch reactor stage ($t > t_D$)

When dosing is finished, the conservation equation in terms of kinetics and heat transfer can be written in terms of dimensionless parameters, as[4,14]

$$\frac{d\theta}{dX} = S - \frac{N\theta \exp[-\theta/(1 + \theta/\gamma)]}{g(X)} \tag{19}$$

with initial conditions, $\theta(X = X_D) = \theta_D$. In the above model, $g(X) = 1$, $g(X) = 1 - X$, and $g(X) = (1 - X)(M - X)$, for zero-, first-, and second-order reaction kinetics, respectively.[14]

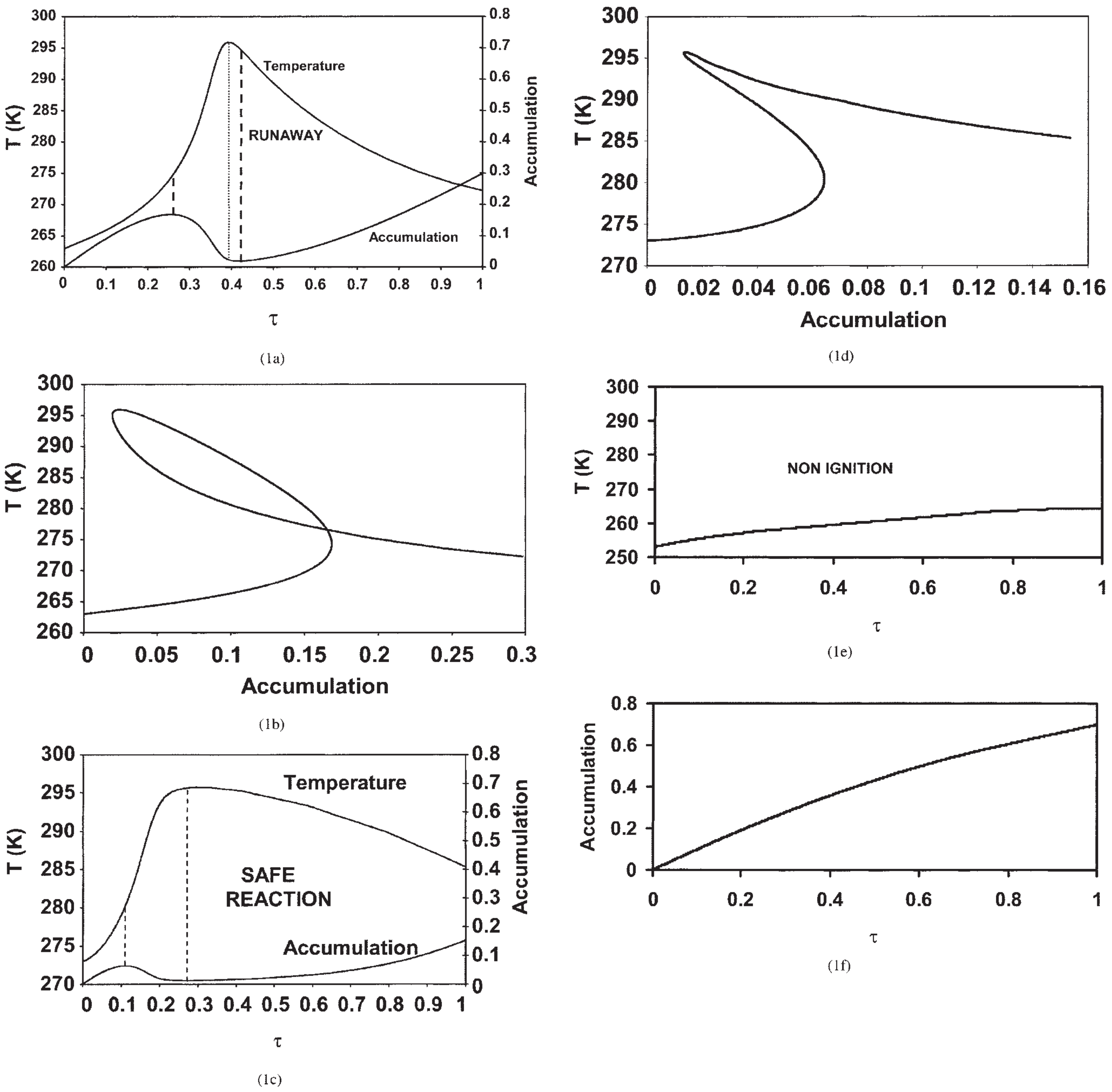
Accumulation–temperature phase plane

For each system, the values of temperature and accumulation vs. time are obtained by the numerical integration of the ordinary differential equations (ODEs) during the dosing stage. Temperature vs. accumulation plots for different values of ΔT_{ad} show a correlation between the temperature peaks and the values of ΔT_{ad}. The T vs. t profiles for the proposed model are in agreement with the results reported by Steinbach.[24]

Thermal Classification Algorithm: Recognizing the Hazard

The proposed safety criterion is based on analysis of the accumulation and temperature changes with time. Model equations are integrated from the beginning of the dosing period up to $\tau = 1$, where the late batch process starts. The accumulation and temperature are followed. After carrying out a considerable number of simulation runs, it was observed that an isoperibolic SBR presents three possible stages.

In the first stage, the operation is started at a low temperature (close to the coolant temperature), so the global reaction rate is less than the feeding rate. Therefore, accumulation increases, with a very slight increase in temperature (Figures 1a and 1c). This causes an increase in the reaction rate, up to the point



(1a)

(1d)

(1b)

(1e)

(1c)

(1f)

Figure 1. Typical temperature–time and accumulation profiles on the T–τ plane and the T–α plane.

(a) and (b) Runaway behavior; (c) and (d) controlled or ignited reaction behavior; (e) and (f) nonignition behavior with complete accumulation.

where more reactant is consumed, together with a decrease in accumulation. Depending on the temperature history during this stage, the reactor will exhibit either a controlled, *safe*, steady behavior (Figure 1c) or an uncontrolled or *runaway* behavior (Figure 1a). Finally, there is a third stage, where almost all the reactant has been consumed and temperature starts to decline, with an increase in accumulation.

Also based in a number of simulation runs there is another type of operation where accumulation is increasing continuously from the start all over the end of the dosing period (Figure 1e). From there the reaction is completely stopped. In other words, a *nonignition* behavior is observed, with a nonsignificant reactant conversion. As explained later, the program CAPSA+ implements classification of these reaction types.

Characterizing the runaway behavior

In Figures 1a and 1b, a typical runaway reaction is shown in terms of the reactor temperature and the accumulation function. Accumulation initially increases as a result of the low temperature, but after the temperature has increased slightly, it suddenly decreases as a result of the acceleration in reactant consumption. A sudden self-heating occurs over a short time interval, where a maximum in temperature is seen. During the

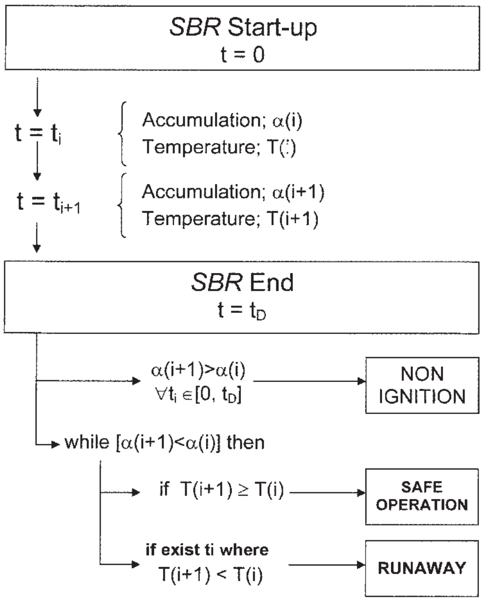


Figure 2. CAPSA+ algorithm for the classification of the thermal behavior for a semibatch reactor.

peak, most of the reactant is consumed. Then temperature decreases because of the reactor cooling system. A typical runaway in an SBR is characterized by an uncontrolled temperature excursion over a short time interval.

Characterizing the safe behavior

A safe reactor behavior is shown in Figures 1c and 1d. After a short time interval where the dosed reactant accumulation takes place, reaction starts and accumulation smoothly decreases. Temperature is more or less constant as long as the accumulated reactant is consumed. The typical *safe reaction* is characterized by a slight decrease in accumulation, whereas the temperature is almost constant, without any sudden peaks.

A runaway condition can also be recognized graphically in the phase plane of temperature vs. accumulation over the dosing stage.

The *runaway behavior* is characterized by the appearance of a loop in the phase plane, caused by a simultaneous decrease in temperature and in accumulation. *Safe reaction behavior*, on the other hand, is characterized by the absence of a loop in the phase plane (see Figures 1b and 1d), which implies that during the decrease in accumulation, temperature has been either constant or increasing, but with no sudden maximum. The occurrence of the loops on the temperature–accumulation phase plane allows a fast and direct method to the classification of reactor behavior. Once the simulation is complete, retrieval of the temperature–accumulation data set allows recognizing a runaway behavior in simple terms.

Characterizing the nonignition behavior

In this kind of operations, accumulation increases steadily over the dosing stage. Conversion is practically zero and temperature is kept close to that at the start. Figures 1e and 1f show the temperature–accumulation curve for a nonignition reaction. To confirm the safety of a nonignition reaction, an analysis of the late batch reactor (which follows) is required. Safety assessment of the late batch reaction is made using the previous CAPSA program,[35] except that the initial conditions for the batch are those prevailing after the feed period at time $\tau = 1$. To apply CAPSA, neither the initial temperature nor the conversion is zero for the analysis of the batch reactor.

Thermal safety classification algorithm

In summary, the safety criterion implemented in the CAPSA+ program is shown in Figure 2. As seen, the algorithm classifies the type of thermal behavior using an off-line examination of the accumulation–temperature data collection after integration of the equation system. In the nonignition case, the batch CAPSA algorithm[35] would be required because runaway can occur later on.

Validation of the CAPSA+ Accumulation Algorithm

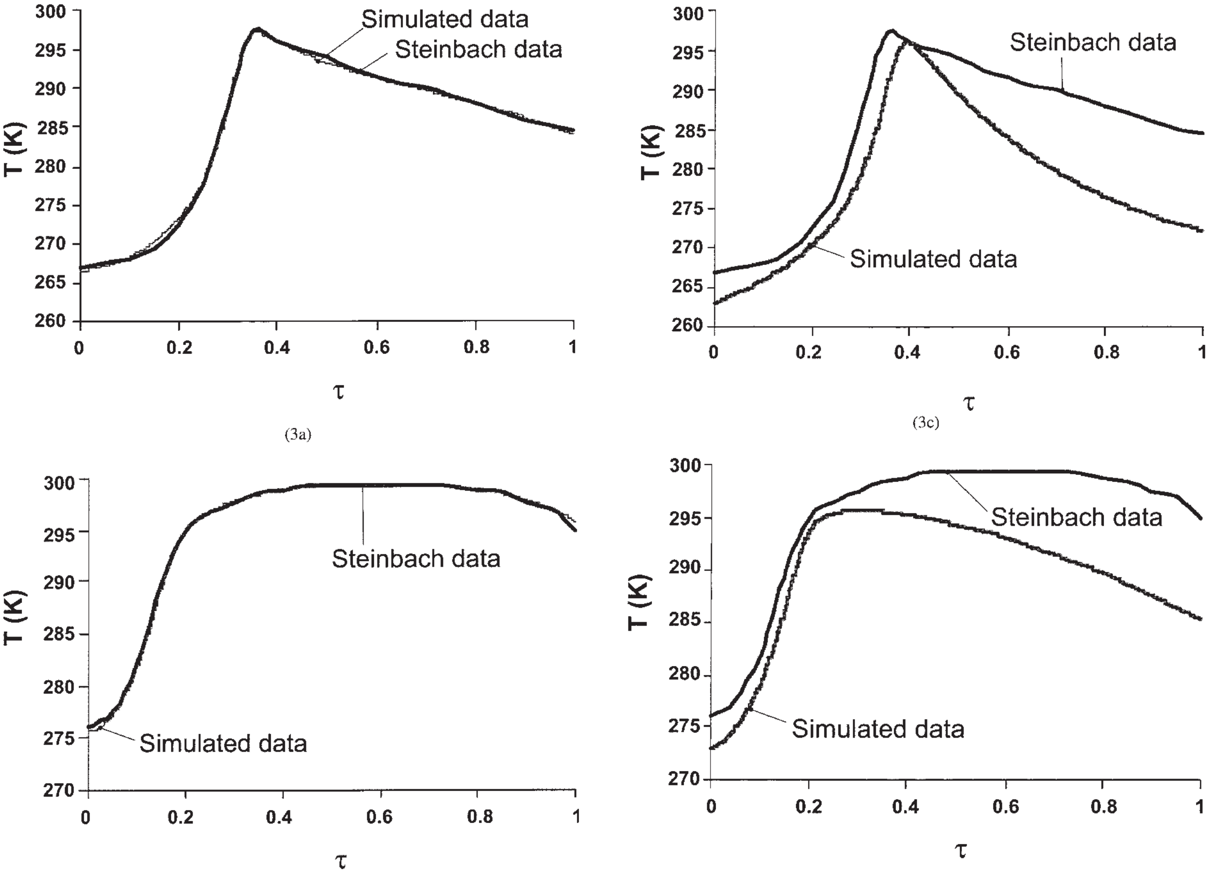
To verify the safety algorithm, the case study proposed by Steinbach[24] will be examined. In an example given by this author, a large reactor is analyzed for safety during semibatch operation. Reaction is second order, irreversible, and is carried out under isoperibolic conditions in a 20-m^3 reactor. All the reactant *A* is charged initially after which a stoichiometric amount of *B* is dosed at a constant flow rate. The recipe and reactor characteristics are given in Table 1. To check our model, the conditions should be adapted to meet the Steinbach hypothesis. These are: (1) *UA* is assumed to be constant all over the process, irrespective of the liquid volume change; and (2) the initial temperature T_0 is different from the temperature of the coolant, but will be taken as an average between the coolant temperature and that of the feed stream (T_f). That is,

$$T_0 = \frac{T_f + \dfrac{1+\varepsilon}{\varepsilon}\mathrm{St}_s T_C}{1 + \dfrac{1+\varepsilon}{\varepsilon}\mathrm{St}_s} \tag{20}$$

Table 1. Data for the Reaction A + B = Products*

Parameter	Symbol	Value	Unit
Activation energy	E	86,881.3	J mol^{-1}
Frequency factor	k_0	4.43×10^9	m^3 mol^{-1} s^{-1}
Reaction enthalpy	ΔH	85,000	J mol^{-1}
Volumetric heat capacity	ρc_p	1700×10^3	J m^{-3} K^{-1}
Feed temperature	T_f	298	K
Conc. *B* in feed	C_{Bf}	4860	mol m^{-3}
Conc. in initial charge	C_{A0}	3400	mol m^{-3}
Dosing time	t_D	18,000	s
Initial charge volume	V_0	10.43	m^3
Initial mols of *A*	N_{A0}	35,462	mols *A*
Stoichiometric excess		1	—
Moles of *B* dosed up to *t*	N_{Bt}	35,462	mols *B*
Molar flow rate		4.0537×10^{-4}	mol m^{-3}
Dosed volume		7.3	m^3
Final volume		17.73	m^3
Heat transfer factor	UA_0	6000	W K^{-1}
Reactor volume	V	20	m^3

*Dosing of *B* from Steinbach.[24]



(3a) (3c)

(3b) (3d)

Figure 3. Comparison of the Steinbach model with our model.

For curves (a) and (b) no allowance is made for changes in *UA* with *V*, and coolant temperature (see text). For curves (c) and (d) *UA* is not constant. (a) $T_C = -10°\text{C}$, $T_0 = -6°\text{C}$; (b) $T_C = 0°\text{C}$, $T_0 = 2°\text{C}$; (c) $T_0 = T_C = -10°\text{C}$, (d) $T_0 = T_C = 0°\text{C}$. Reaction data from Steinbach.[24]

The results of Steinbach and those of our model were compared for two coolant temperatures: −10 and 0°C. It was clearly observed that the proposed model fits exactly to the author's model (not shown). Figure 3, however, shows a large departure between the Steinbach results with respect to those obtained with the model without making the above hypothesis. That is, (1) variable *UA* with reactor volume contents and (2) the initial temperature is the same as that of the coolant (Figures 3c and 3d).

In summary, if the Steinbach hypotheses are considered in our accumulation algorithm, the results of Steinbach and those of our model agree almost exactly, as expected; however, we think that the above hypothesis (variable heat exchange area, variable coolant temperature) should be embodied in the model (see Eq. 7).

Validation of the CAPSA+ criterion

To verify whether CAPSA+ performs well, we use the above simulation runs, for the two coolant temperatures: −10 and 0°C. The Steinbach and Steensma–Westerterp criteria are further considered.

The data from Table 1 are used for the reaction and reactor vessel. Application of the CAPSA+ program shows that a *thermal runaway* is predicted, according to our methodology.

For the following values: $T_C = -10°\text{C}$; $\text{St}_s = 3.6$; $\varepsilon = 0.7$; $T_0 = -6.5°\text{C}$; and $\text{Da}(T_0) = \text{Da}_\infty \exp(-E/RT_0) = 1.5$ (see other data in Table 1), the Steinbach criterion gives

$$\frac{1.45\text{Da}(T_0)}{\dfrac{\varepsilon}{1+\varepsilon} + \text{St}_s} = 0.55 < 1 \tag{21}$$

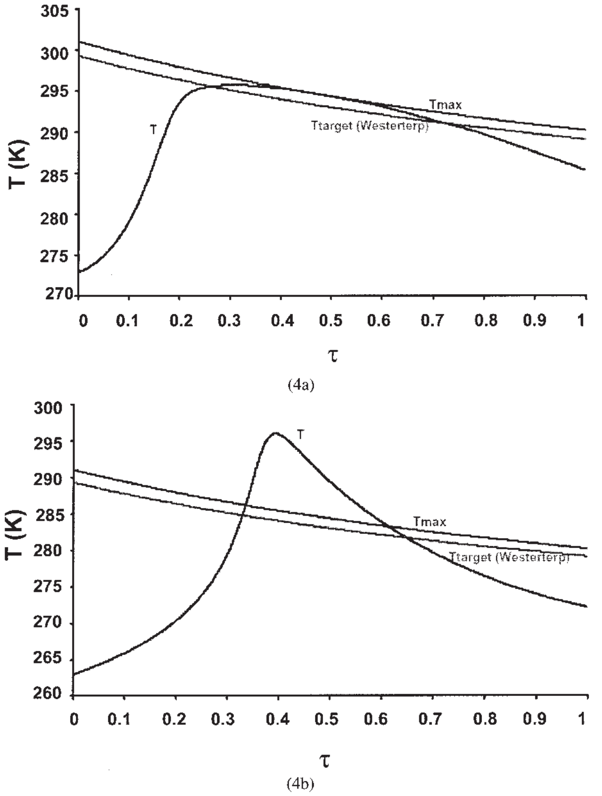
Therefore, a *thermal runaway* is indeed expected. Runaway is also predicted by CAPSA+.

Similar calculations with higher coolant temperature provide a safer operation, as expected. Thus $T_C = 0°\text{C}$ gives $T_0 = 2.5°\text{C}$, $\text{Da}(T_0) = 5.36$, and

$$\frac{1.45\text{Da}(T_0)}{\dfrac{\varepsilon}{1+\varepsilon} + \text{St}_s} = 1.94 > 1 \tag{22}$$

Therefore, the reactor is safe according to the Steinbach criterion. Safety is predicted by CAPSA+ as well.

Now, let us examine the Steensma–Westerterp criterion for the same operating conditions. In this case the target temperature should not be overcome. In terms of the reaction/vessel



(4a)

(4b)

Figure 4. Shape of the target temperature vs. τ for Westerterp's target temperature and our temperature T_{max} vs. τ as calculated with CAPSA+, using the same reaction recipe.

(a) $T_C = 0$°C; (b) $T_C = -10$°C.

parameters, the target temperature can be calculated as a function of time as[26,36]

$$T_{\text{target}} = T_C + \frac{1.05\Delta T_{ad}}{\varepsilon R_h + \text{St}(1 + \varepsilon\tau)} \tag{23}$$

This expression is an approximation and represents the maximum steady-state temperature that can be obtained by dosing with full cooling when the reaction is almost instantaneous (allowing for only a 5% accumulation of the dosed reactant). Obviously, the target temperature provides a safety degree slightly higher than necessary; in other words, it should be regarded as a sufficient but not necessary condition for safety. In Figures 4a and 4b, the evolution of the target T vs. time for reaction conditions $T_C = -10$°C and also $T_C = 0$°C is shown. The T_{target}, as calculated by the Steensma–Westerterp equation, and the peak temperature of our model or $T_{\max}$, as evaluated by CAPSA+, are plotted together in Figures 4a and 4b, providing a very close approach. The two criteria agree well with each other in that runaway occurs as predicted by both.

Once the validity of our methodology, CAPSA+—against both the Hugo–Steinbach and Steensma–Westerterp criteria—is proved, we proceed to define the critical values of the parameters. These will allow safe operation or scale-up of semibatch processes.

Table 2. Nature of the Parameters Analyzed in a Hazardous Semibatch Reaction

	Dimensional Parameter	Dimensionless Number
Reaction-specific parameters	Activation energy*	$S/\gamma = \Delta T_{ad}/T_C$
	Kinetic constant*	$\gamma = -E/RT_C$
	Heat of reaction	
Cooling system parameters	Coolant intensity	N
	Initial reactor temp.	θ_0
	Reactor size/HTArea	St
Operation-specific parameters	Dosing time	Da
	Reactant-concentration levels	

*E and k_0 require experimental determination. The rest of parameters can be estimated.

Reactor Behavior and Critical Parameters

Effects of the various parameters on the safe SBR operation are analyzed. Their general effect on safety is described in Table 2 in a qualitative way. The characteristic semibatch safety parameters are ΔT_{ad}, γ, N, θ_0, St, and Da, which presume only the knowledge of the intrinsic rate constant and its activation energy and both thermochemical and heat transfer data. Our purpose here is to establish safety operation and safe scale-up maps that allow recognizing hazardous situations from reaction parameters. These maps are derived from CAPSA+ using appropriate values of the parameters, so they are not general because they are given for restricted values of the latter. In the following section, a few industrial operation cases are solved.

The first important parameter is the increase in adiabatic temperature ΔT_{ad}, which measures the severity of the energy release of a process. For liquid-phase reactions operated in batch, an increase of about 50°C is not quite significant. It is known from practice that values $>$ 100°C are of concern, and $>$200°C are very dangerous for batch liquid-phase operation. To see the influence of this parameter, several simulations revealed the effect of ΔT_{ad} for several possible values of the heat of reaction for a given reaction. In Figure 5, the temperature profiles for three simulations allow us to characterize the three safety behaviors. For a $\Delta T_{ad} > 106$°C, there is a temper-

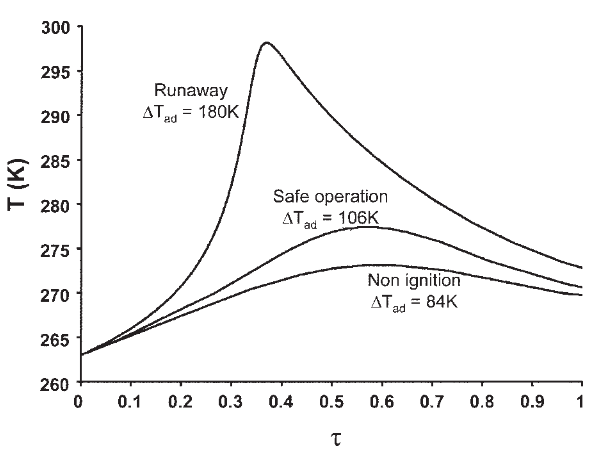


Figure 5. Effect of ΔT_{ad} on the three safety scenarios.

All data are identical: $T_C = -10$°C, $\varepsilon = 0.7$, Da = 1.5, St = 6.1, $\gamma = 39.7$, $N = 4.0$, $N_f = 0.46$.

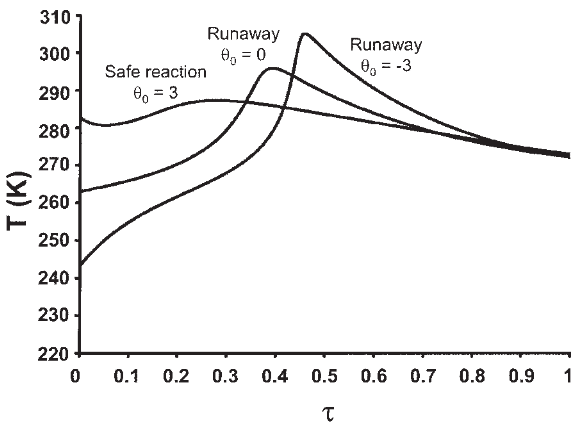


Figure 6. Effect of the initial reactor temperature (θ_0) on the thermal safety scenario.

ature peak followed by a *runaway*. For moderate increments (from 106 to 90°C) a *safe behavior* is observed, whereas for ΔT_{ad} below these values, a *nonignition behavior* is obtained. When all operating parameters are fixed, and ΔT_{ad} cannot be reduced, the only way to limit the occurrence of runaway is to modify the initial conditions, essentially increasing θ_0, to a practical value. To authenticate this (Figure 6) we choose a reaction with a large ΔT_{ad} (=170°C) that exhibits a clear runaway tendency under isoperibolic conditions. A simulation with different increasing initial reaction temperatures ($\theta_0 = -3$ to 3) shows that the temperature peaks are increasingly less pronounced. Finally, for a value of $\theta_0 = 3$, the operation becomes safe. On the other hand, if the initial temperature is made less than the coolant temperature (that is, $\theta_0 < 0$), the runaway tendency is favored. Figure 6 shows the effect of θ_0 on the temperature profiles. This behavior is in contrast with the purely batch reactor, in which low-temperature settings are safer.

Another sensitive parameter is the activation energy, given that the reaction rate increases exponentially with this parameter through an Arrhenius-type of dependency. A small change in activation energy may involve a runaway. A simulation of the activation energy effects (Arrhenius number) is seen in Figure 7 for three cases.

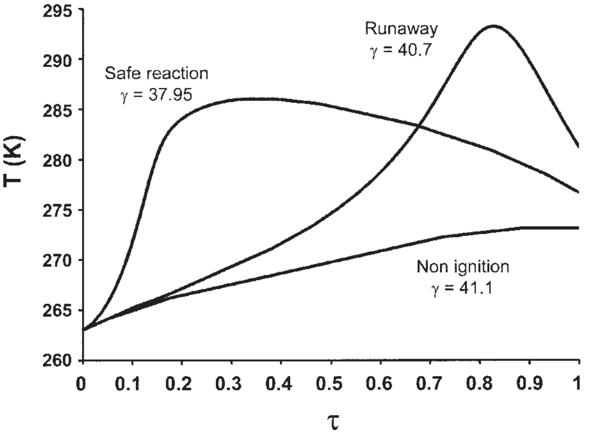
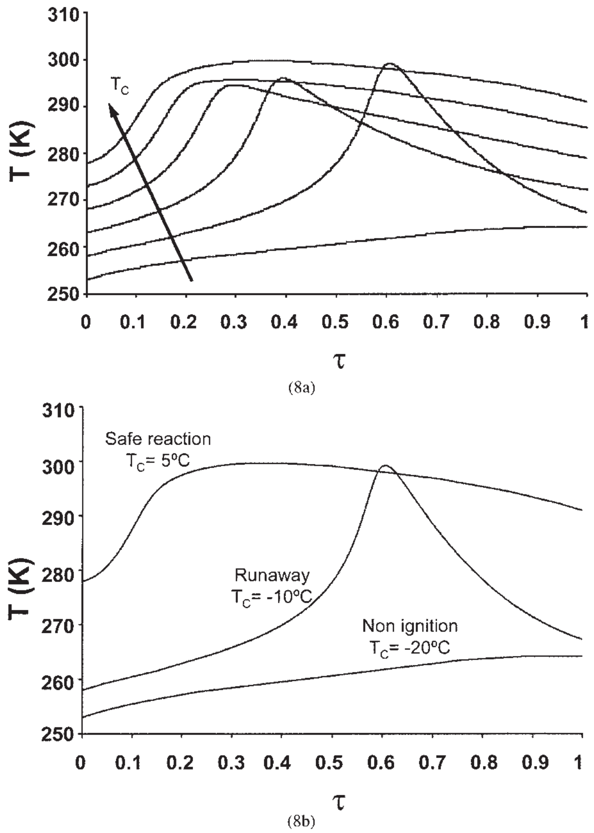


Figure 7. Effect of the Arrhenius number (γ) on determining the safety scenario.



(8a)

(8b)

Figure 8. Effects of the reactor coolant temperature on the safety behavior.

The coolant temperature determines the heat exchange capacity of the refrigeration system. A too large cooling action may involve a dangerous reactant accumulation with a possibility of runaway. For a too low T_C value, a nonignition reaction may result. Figure 8 shows the temperature profiles that are obtained by changing the coolant temperature for the three possible safety regimes. It is observed that safety conditions are achieved only when the T_C takes a sufficiently high value. This again is counterintuitive and opposite to the batch reactor safety.

The other two parameters analyzed are the Damköhler and the Stanton numbers. The Da number is proportional to the ratio of the dosing time and the reaction-characteristic time. A large Da involves a slow addition relative to time for conversion; thus a better distribution of the reaction enthalpy is expected and therefore a lower risk of runaway. If the dosing time increases, the rate of dosing is slower than that of reactant conversion, thus resulting in less accumulation of unreacted material. Low Da gives, in fact, a batch in the limit; thus more thermal risk is involved. It is interesting to study safety in terms of Da. Figure 9 gives the sensitivity of a reaction to Da. For a given reaction, the values of Da that ensure safety according to CAPSA+ can be estimated by running the program.

The cooling intensity (*N*) and the Stanton number (St) are heat transfer parameters that are sensitive to the size of the vessel. The larger the reactor vessel, the larger the volume occupied by the liquid mixture. However, the available heat transfer area will be increased more slowly than the volume, so

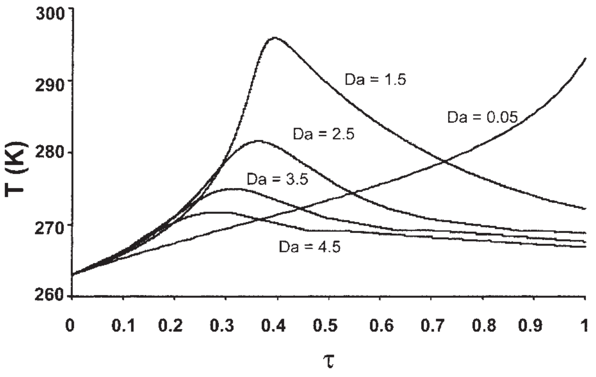


Figure 9. Effect of the Damköhler number (Da) on the operation safety.

that the nominal ratio *A*/*V* decreases with the scale of operation.[34] To summarize the vessel size effects, a parameter designated the characteristic cooling time (C_R) is introduced, defined as the cooling time relative to the feed time:

$$C_R = \frac{\mathrm{St}(1+\varepsilon)}{t_D} \tag{24}$$

By increasing the scale of operation, the system's $1/C_R$ increases, indicating that greater heat transfer capacity is required in larger vessels with the scale-up, given that cooling takes longer. Based on the parameters Da, *N*, and C_R, fairly general safety plots can be prepared, wherein the border between safe and unsafe regions can be seen. These maps allow one to judge the safety of a reactor system for an SBR process and can help one to decide how the operation parameters are chosen for a given process to ensure a safe scale-up. These maps and the conclusions obtained from them are discussed in detail in what follows. Two key maps are presented that are critical to the scale-up of a process.

Critical feed time vs. cooling power available (Da vs. N)

The plot is obtained by simulation of a given reaction for different sizes of stirred reactor, each with different *N* and C_R values. In the process, for a given size, the minimum t_D is determined for which reaction is safe, so that the critical Da is calculated as the minimum Damköhler number above which no runaway can occur. A list of vessels of a few U.S. manufacturers has been published[33] that can then help in the selection. In Figure 10 the safety limit line is seen for different combinations of γ and *S*. In Figure 11 the effect of the initial temperature over the interval $-2 < \theta_0 < 2$ can be seen. From the plot it is observed that the critical Da necessary to achieve safety increases with increasing *N*. Furthermore, for a given value of the intensity *N*, the critical Da necessary is smaller for increasing values of the initial temperature θ_0. Finally, it is concluded that for larger values of γ and *S*, the critical Da is also larger for a given scale of operation.

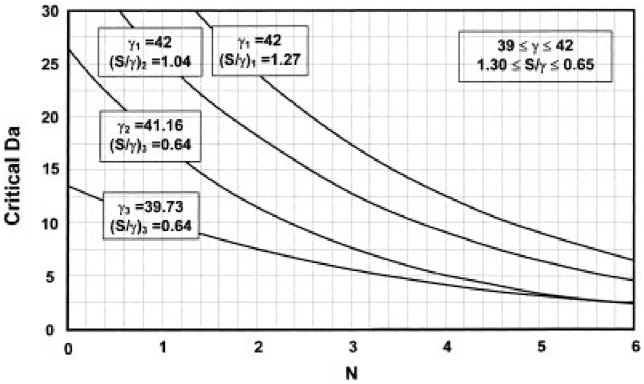


Figure 10. Critical Da numbers vs. *N* for different increases in adiabatic temperature, $S/\gamma = \Delta T_{ad}/T_C$, as a function of reactor size (or *N*).

Safe operation above the line.

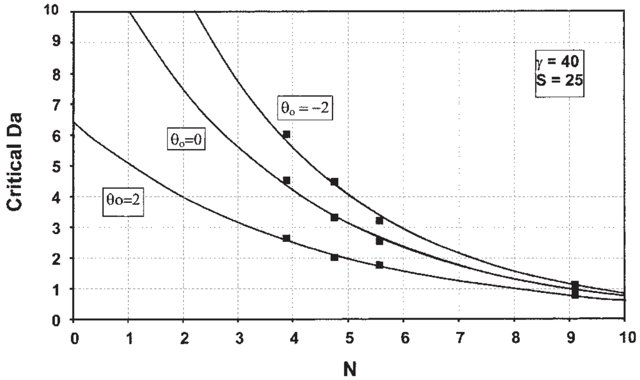


Figure 11. Critical Da numbers for different initial temperatures of reactor (θ_0 from −2 to +2), for a given reaction (γ = 40, *S* = 25).

Safe operation above the line.

Cooling power vs. the heat generation potential (N vs. S)

The procedure consists in finding the critical sensitivity *S* above which reaction is safe for a given reactor scale (that is, for a fixed value of *N*). Shown in Figure 12 is the final plot. It

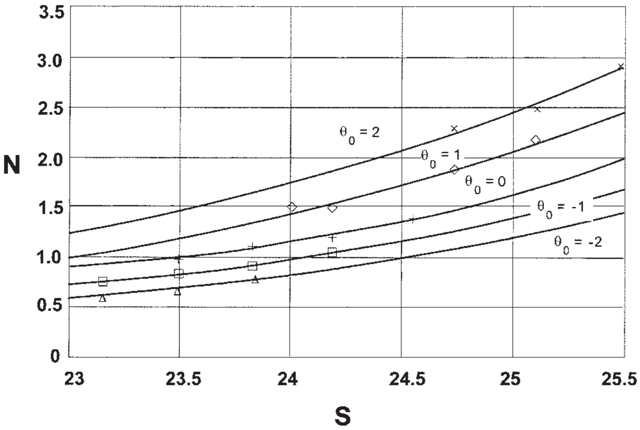


Figure 12. Safety graphs in terms of critical *N* vs. reaction sensitivity *S*, for various initial reactor temperature settings (θ_0= −2 to +2) over a narrow *S* interval.

Controlled reaction below the line, runaway above.

is observed that for an increasing scale of operation (that is, for decreasing values of N), the critical S diminishes, and therefore higher cooling temperatures are required to ensure safety.

Finally, it should be mentioned that in the present study the initial reaction temperature (θ_0) is considered explicitly as the initial condition for the differential equations of the system, so it affects the analysis as a safety parameter in the scale-up (Figures 11 and 12).[24] No previous safety criterion included the effect of the initial temperature.[27]

Application to Process Operation and Reactor Scale-up Problems

The proposed nonaccumulation criterion is now applied to a few problems of industrial significance for the production of fine chemicals or in polymerization processes. The problems or illustrations that follow involve the use of computer implementation of CAPSA+, although some of the cases can be solved with the plots given before.

Illustration 1

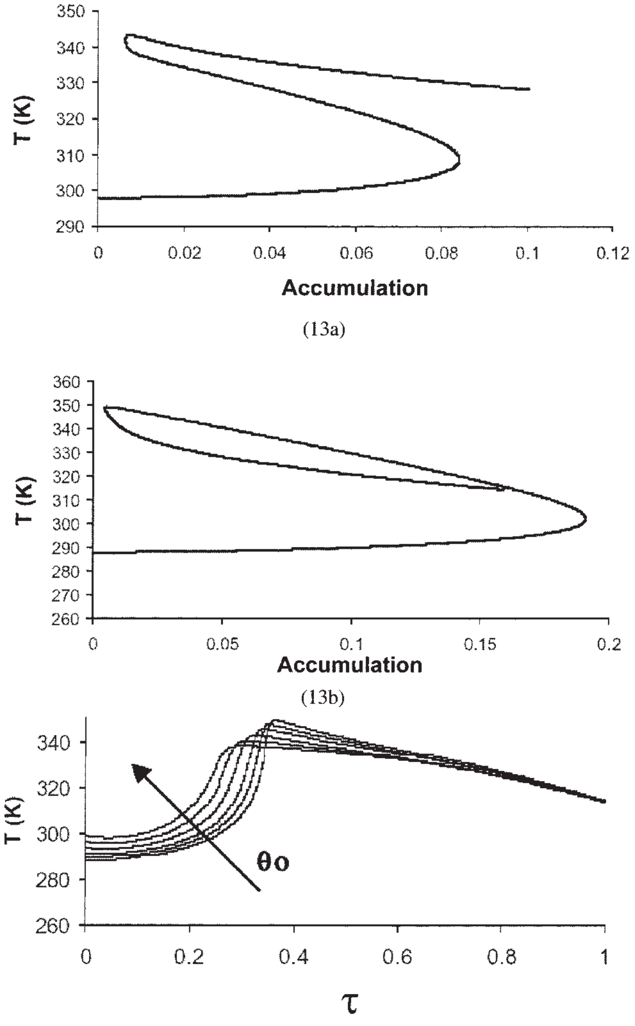
In a process conducted in an SBR an exothermic second-order reaction is carried out in an 8-m^3 reactor. We seek to know the effect of using a refrigerant at lower temperature. The operation was shown to be safe using a coolant temperature of 25°C (in summer). We want to know how reaction safety will be affected if, by mistake, the cooling temperature falls 10°C, that is the new T_C = 15°C (in winter). We will assume that these are isoperibolic temperatures. Other reaction parameters appear in the figure.

To solve the problem, we first apply the CAPSA+ criterion to verify whether the process is stable at 25°C. From CAPSA+ we can retrieve the temperature–accumulation–concentration data sets. Graphically (Figure 13) it is best to see whether unstable loops appear on the temperature–accumulation phase plane (for T_C = 25°C; Figure 13a). Next, the reaction with T_C = 15°C is simulated. However, Figure 13b shows a marked loop on the temperature–accumulation plane, indicating that the reactor becomes unstable, so a runaway at the low coolant temperature is expected. The choice of a coolant temperature set too low can thus be the cause of a runaway arising from accumulation. So if in winter we have a coolant temperature at 15°C it will be difficult to operate the reactor because of too much cooling power. We have the option of finding a new temperature of the initial charge that it is compatible with the colder coolant. This is illustrated next.

Illustration 2

The above reaction presents a runaway behavior when the coolant temperature is T_C = 15°C. For this temperature, find the initial liquid temperature to make it safe.

The SBR is simulated for several increasing values of θ_0 (Figure 13c) and at the same time checking with CAPSA+ until the thermal behavior is safe. In each simulation case, only the initial values of the initial charge are changed. However, the risk of runaway decreases when increasing the initial temperature because this decreases the reactant accumulation. For the reaction, the convergence to a safety behavior is found at θ_0 = 1.3, thus corresponding to an initial temperature of T_0 = 26.2°C and thus 11.2°C above the coolant temperature (15°C).



(13a)

(13b)

(13c)

Figure 13. Different safety scenarios.

Safe operation and runaway: (a) problem 1 with T_C = 25°C, (b) problem 1 with T_C = 15°C, (c) Problem 2: T_C = 15°C, temperature profile for an increasing θ_0.

It is thus concluded that when runaway arises from an abnormally low T_C, the thermal risk can be reduced by heating up the initial charge slightly, thus increasing T_0 to avoid the runaway zone. Figure 13c shows the temperature profile for an increasing θ_0.

Illustration 3

In a polymer plant a semibatch reaction is carried out safely in a 1-m^3 reactor with a coolant temperature of 5°C with a feeding period of 5.8 h. A scale-up to 8 m^3 is intended. It is suspected that for the scale-up the feeding time should be larger. Determine the feed time in the large reactor to avoid a runaway.

The safety of the small reactor will be checked first. After application of the safety criterion it is concluded that under the specified conditions the operation is safe because there is no loop in the accumulation–temperature plane. The next step is to check for a runaway using the same dosing time for the larger reactor. In this case, a loop appears in the accumulation–

temperature plane. Thus, the method will be to progressively increase the dosing times to obtain a final stable accumulation–temperature plane. The safe condition is met for a dosing time of $\geq$14.2 h.

In summary, a significant increase in the scale of operation, for fixed values of the other parameters, can lead to a runaway in an otherwise safe reaction. This trend can be avoided by selecting a longer dosing time in the operation of the larger reactor.

Illustration 4

We want to analyze the safety of a nonignited reaction over the period that follows the late batch.

The typical form of the accumulation–temperature curve is monotonically increasing, and thus a nonignition behavior develops. Reactant conversion during the dosing period is practically zero and temperature remains close to the coolant temperature. In such cases, it is necessary to examine the late batch behavior. According to Bosch and coworkers[4,37] it is necessary to know the initial conditions for the BR at $\tau \geq 1$. The initial conditions for the case analyzed are $\theta_0 = 1.26$; $\alpha = 0.91$; $X = 0.08$; $\Delta T_{ad} = 156$K; $S = 18.0$; and $N = 2.74$. With the above data, use of the CAPSA program provides by the bisection method a critical value for N ($N_{\text{crit}} = 6.68$), thus meaning a larger required heat transfer capacity than that available (available $N = 2.74$). Therefore, the batch will experience runaway as it is subcooled.

Additional industrial problems can be addressed using the CAPSA+ program in the plant operation or in the research development of addition polymers and in manufacturing of fine chemicals. Today, these are better solved by running a computer program on site than graphically because of the ease of iteration. However, the underlying mathematical theory is still lacking.

Conclusions

The thermal hazard involved in the operation of a batch reactor justifies a close control of the risks during operation. The establishment of safety conditions in a chemical reactor supposes the possibility of a runaway, which can unleash a significant amount of energy thus causing an explosion. The occurrence of a runaway is in consequence to sensitivity to either thermodynamic or kinetic and heat transfer parameters associated with the reactor vessel.

In the case of purely batch reactors, Bosch and coworkers[4,37] elaborated an approach to thermal safety based on CAPSA. For this type of reactors they characterized runaway near the end of the temperature jump. In the present work we developed CAPSA+ as an extension of the Bosch et al. algorithm for semicontinuous operations. However, the thermal explosion scenario in a fed-batch reactor is substantially different from the batch case. In the semibatch mode, safe conditions can be exactly the opposite of those required for a safe batch and can be counterintuitive. Thus, a substantially higher operating temperature in a semibatch reactor is safer than a lesser temperature. In a semibatch reactor, a key factor for achieving safety is to control reactant accumulation. Reactor behavior can be classified in three types: runaway mode, well-ignited reaction, and nonignited reaction.

A second-order reaction is characterized with a group of dimensionless numbers: γ, S, N, N_f, Da, St, used by previous authors (Hugo, Steinbach, Steensma, etc.) These facilitate characterization of the state of a system quickly and intuitively and foresee potential risk situations. In this study an analysis on the effect of the above variables has been carried out. Based on simulation runs, the most important parameters to control SBR safety are: the dosing time (t_D, Damköhler number, Da), reactor size (involved indirectly in N, St, C_R), coolant temperature (T_C, S), and the initial temperature of the reacting mixture (T_0). Modification of these parameters allows the generation of safety plots to characterize operation safety for each group of parameters.

A few examples were shown in which the classification of reaction types in safe and unsafe semibatch reactors agreed well using either the Steensma–Westerterp, the Steinbach–Hugo, or our CAPSA+ prediction. This shows that the nonaccumulation criterion is valid for the three authors. Our methodology can thus be implemented into a more general, computer simulation package for indoor use in certain chemical process plants, where different exothermic processes are run every week, on different scales of operation.

Acknowledgments

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Notation

A = reactant A
A = heat transfer area, m^2
A_0 = initial heat transfer area, m^2
B = reactant B, dosed
BR = batch reactor
C_A = concentration of A, = C_B concentration of B, in the reactor, mol m^{-3}
C_{Bf} = concentration of B in the feed stream, mol m^{-3}
c_p = constant pressure heat capacity, J kg^{-1} K^{-1}
Ch = ratio of concentrations, Eq. 18
C_R = reciprocal cooling time, s^{-1}
Da = Damköhler number at T_C, dimensionless
Da$_\infty$ = $k_0 N_{A0} t_D / [V_0(1 + \varepsilon)]$, dimensionless
E = activation energy, J mol^{-1}
k_c = second-order kinetic constant at T_C, m^3 mol^{-1} s^{-1}
k_0 = preexponential factor of the kinetic constant k, m^3 mol^{-1} s^{-1}
M = stoichiometric ratio, dimensionless
N = cooling capacity for a second-order reaction, dimensionless
N_{crit} = critical value of N, dimensionless
N_f = cooling capacity of the feed stream, dimensionless
N_{A0} = initial moles of A, mol
N_B = unreacted moles of B present in reactor, mol
N_{Bf} = moles of B dosed up to t, mol
R = 8314 J K^{-1}·mol^{-1}
R_h = ratio of heat capacities, dimensionless
S = heat generation potential, dimensionless
SBR = semibatch reactor
St = Stanton number, dimensionless
St$_s$ = modified Stanton number, $= UAt_D/[V_0(1 + \varepsilon)]$, dimensionless
t = time, s
t_D = dosing time, s
T = temperature, K
UA = heat transfer factor, at time t, W K^{-1}, UA_f = at end of a run
v = volumetric flow rate of reactant B, m^3 s^{-1}
vC_{B0} = molar reactant B feed rate, mol B s^{-1}
V = liquid volume, m^3
X = conversion of A, dimensionless

Greek letters

α = accumulation of reactant B, Eq. 17, dimensionless
ρ = density, kg m^{-3}
ΔH = enthalpy of reaction, J mol^{-1}
ΔT_{ad} = adiabatic temperature rise, K
Ψ = Semenov's parameter ($=S/N$), dimensionless
τ = reduced time, t/t_D, dimensionless
ε = relative increase in volume on dosing, vt_D/V_0, dimensionless
θ = relative temperature, dimensionless
γ = nondimensional activation energy, dimensionless

Superscripts and subscripts

0 = at zero time
C = coolant
f = feed stream
crit = critical, at runaway
max = maximum

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