

On the divergence criterion for runaway detection: Application to complex controlled systems

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1. Introduction

Fast and highly exothermic chemical processes are very difficult to be optimized and scaled-up from laboratory to full plant scale because of the possible triggering of a reactor temperature loss of control, occurring whenever the rate of heat evolution becomes greater than the rate of heat removal provided by the installed cooling equipment. Such an unwanted phenomenon, called "thermal explosion" or "runaway", can take place into every type of reactor (both continuous and discontinuous), operated in whatever temperature control mode (isothermal, isoperibolic, polytropic, etc.) and fed by the most disparate dosing strategies (linear, ramp, etc.), because of a great number of operating and human factors, such as: control system failure, stirrer breakdown, refrigerating system inefficiency, maintenance, reactants loading errors, dead times enlarging or shortening, etc.

In fine chemical and pharmaceutical industries, potentially runaway reactions are usually carried out in semibatch reactors (SBRs), where one or more reactants (called co-reactants) are dosed on an already loaded mixture in order to control the rate of heat

generation by the dosing rate. However, if the process is operated under high accumulation conditions (that is, a large amount of unreacted co-reactants accumulates in the reactor during the dosing period), the desired reaction thermal control may be lost and the reactor temperature may increase up to values at which secondary undesired reactions or, worse, decompositions of the reacting mixture can be triggered. Such reactions, apart from a reduction of the selectivity with respect to the desired product, may lead to a further and ultimate system thermal loss of control, since they are usually much more fast and exothermic than the desired reaction. Moreover, if a decomposition event arises because of the system thermal loss of control, the consequent release of incoercible gases will pressurize the reactor leading to its physical explosion if the venting system cannot deal with such a phenomenon.

According to statistics, in a typical European country more than 100 runaways are expected to occur annually (Benuzzi & Zaldivar, 1991). However, despite only a little amount of these accidents hurts the workers or the inhabitants of the neighborhood of the damaged factory, when strong runaways occur the consequences can be really serious. This motivates the great amount of work that has been done on runaway phenomena in exothermic chemical batch and semibatch reactors during the previous century and, particularly, in the last thirty years. As a matter of fact, many

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different studies on the detection of the so-called “runaway boundary” or “marginal ignition line” (that is, the system operating parameters in correspondence of which runaway phenomena are triggered) have been conducted (Alós, Nomen, Sempere, Strozzi, & Zaldívar, 1998; Bosch, Strozzi, Zbilut, & Zaldívar, 2004; Hugo & Steinbach, 1985; Maestri & Rota, 2005a, 2005b; Morbidelli & Varma, 1982, 1985, 1988; Steensma & Westerterp, 1988, 1990, 1991; Steinbach, 1999; Strozzi, Zaldívar, Kronberg, & Westerterp, 1999; Varma, Morbidelli, & Wu, 1999; van Woezik & Westerterp, 2000, 2001; Wu, Morbidelli, & Varma, 1998a, 1998b; Zaldívar, Bosch, Strozzi, & Zbilut, 2005; Zaldívar et al., 2003).

The first rigorous approach for isoperibolic SBRs was developed by Hugo and Steinbach (1985). Their work, based on homogeneous systems, introduced the accumulation criterion for the analysis of a SBR thermal behavior: co-reactant accumulation into the system, which arises from a not negligible characteristic time of the chemical reaction with respect to that one of the co-reactant supply, must be kept at sufficiently low values to avoid the reactor thermal loss of control (runaway). If co-reactant accumulates into the reactor, the system switches from semibatch to batch-like conditions and the cooling system might not control the heat evolution anymore. According to this criterion, operating conditions characterized by a sufficiently low co-reactant accumulation are considered not only safe but also productive.

Steensma and Westerterp (1988, 1990, 1991) extended the results obtained by Hugo and Steinbach (1985) to heterogeneous (liquid–liquid) SBRs, introducing the concept of target temperature and producing the so-called boundary diagrams (BDs) for single reactions of (1,1) reaction order kinetics. Particularly, such diagrams are generated in a suitable dimensionless space (i.e., Reactivity, R_y , versus Exothermicity, E_x) that allows end users to easily discriminate between safe (referred to as “Quick onset, Fair conversion, Smooth temperature profile”, QFS) and excessive accumulation operating conditions without solving the mathematical model of the reactor.

Maestri and Rota (2005a, 2005b, 2006), analyzing the role that estimated kinetic parameters play on conclusions drawn through boundary diagrams calculated for reaction orders different from (1,1), prove that unjustified assumptions on the reaction kinetics cannot be accepted for a reliable application of the BDs method: such a conclusion has been found to be true for both heterogeneous and homogeneous reaction systems (with or without autocatalytic behavior), and it makes a kinetic investigation (usually performed through calorimetric techniques) of great importance. Moreover, van Woezik and Westerterp (2000, 2001) tried to extend the concepts introduced by Steensma and Westerterp (1988, 1990, 1991) for single reaction systems to the case of consecutive reactions with autocatalytic behavior, studying both theoretically and experimentally the nitric acid oxidation of 2-octanol to 2-octanone (first reaction) with further oxidation of the desired product to carboxylic acids (second reaction). These studies proposed to use boundary diagrams generated for single reactions to characterize the thermal behavior of such a system. Such an approach was refined by Copelli, Derudi, and Rota (2010b), who developed a rigorous method to generate boundary diagrams for consecutive reactions with autocatalytic behavior and used the same experimental data provided by van Woezik and Westerterp to validate it.

For what concern the identification of the marginal ignition line only, the first general criterion able to handle multiple reactions systems and different reactor typologies was the generalized parametric sensitivity criterion (Morbidelli and Varma, 1982, 1985, 1988; Varma et al., 1999; Wu et al., 1998a, 1998b). This criterion, with the shortcoming of being implicit (that is, it is not able to establish if the system operates under runaway conditions only by evaluating its constitutive parameters), identifies the runaway boundary looking for the maximum of a suitable objective sensitivity coefficient

(Varma & Morbidelli, 1997): the normalized sensitivity coefficient of the maximum reactor temperature with respect to any operating parameter, $s_{T_{MAX},\phi} = \phi/T_{MAX} \cdot \partial T_{MAX}/\partial \phi$. The criterion shows the advantage of being applied both theoretically (through the use of a mathematical model describing the analyzed reacting system) and experimentally (through the monitoring of the maximum reactor temperature evolution by varying any system operating parameter).

Actually, the most general criterion for the detection of the runaway boundary, able to operate with multiple reactions, different temperature control modes and reactor typologies (e.g., batch reactor (BR), continuous stirred tank reactor (CSTR), plug-flow reactor (PFR), etc.), is the divergence criterion (Bosch et al., 2004; Strozzi et al., 1999; Zaldívar et al., 2003, 2005). This criterion, originally developed by Zaldívar and co-workers, states that if the system of ordinary differential equations (ODEs) that describes the analyzed process exhibits positive divergence (that is the trace of the corresponding Jacobian matrix), the synthesis is operating under runaway conditions. Such a criterion shows the relevant advantage of being usable both on-line (the divergence can be easily reconstructed, at any time during the process, through temperature measures provided by four thermocouples located into the reactor) and off-line (the runaway boundary is individuated by keeping constant the values of all the constitutive parameters except one and, then, by setting the divergence expression with respect to the variable model parameter to zero). Moreover, since a fast reaction that does not produce or consume heat can generate a strong volume contraction in the N-dimensional state space that is not related to runaway phenomena, the term related to the extent-of-reaction of such a reaction must be disregarded into the divergence calculation in order to obtain predictions in agreement with the experimental evidences (Zaldívar et al., 2003).

In this work, it has been shown that, when controlled reacting systems are involved, also other state variables (apart from the extent-of-reaction related to a fast reaction that does not produce or consume heat) can generate a strong volume contraction in the N-dimensional state space that is not related to runaway phenomena, therefore leading the divergence criterion to fail in predicting runaway phenomena. As a consequence, a modified version of the divergence criterion for runaway detection has been developed. Such a modified version is capable of treating whatever type of controlled reacting system (taking into account not only temperature control but also dosing strategies) and its reliability has been demonstrated for isoperibolic semibatch reactors using literature experimental data (Maestri et al., 2009a, 2009b; van Woezik & Westerterp, 2000, 2001).

2. Modified divergence criterion

The divergence criterion was originally developed by Zaldívar and co-workers (Strozzi et al., 1999) and it is based on the concepts of state space (that is, the geometric space where the set of all possible states of a dynamical system – namely, the solution or trajectory – is represented) and phase portraits (that is, the representation of the trajectories of a dynamical system in the phase space when an initial condition or a constitutive model parameter is varied in a suitable range) as key instruments that can be used for the complete description of whatever reacting system thermal behavior. As the matter of fact, the dynamics of a reacting system can be always represented by a system of ordinary differential equations (ODEs), that suitably describes material and energy balances, temperature and dosing control strategies, mixing rules, etc. in the general form: $dx_i/dt = F_i[\bar{x}(t)]$. Particularly, to each state of the reacting system corresponds a unique point onto the state space, which is called state point, and the system state time evolution is represented as a motion along a trajectory. According to the Liouville's theorem (Zaldívar et al., 2003) there is a relation

between the state space volume of a N-dimensional dynamical system and its divergence. This relation can be expressed as:

$$V(t) = V(0) \cdot \exp \left[\int_0^t \text{div}\{F[\bar{x}(t)]\} dt \right] \quad (1)$$

where:

$$\text{div}\{F[\bar{x}(t)]\} = \sum_{i=1}^N \frac{\partial F_i[\bar{x}(t)]}{\partial x_i} \quad (2)$$

Hence for a dynamical system the rate of change of an infinitesimal volume $V(t)$, following an orbit $\bar{x}(t)$, is given by the divergence of the flow, which is locally equivalent to the trace of the $F[\bar{x}(t)]$ Jacobian. Even though for dissipative systems, as chemical reactors are, the divergence unavoidably decreases as time approaches ∞ , it has been observed (Strozzi et al., 1999) that when the system is operated under potentially runaway conditions it exhibits, during a certain period of time, a state space volume expansion. This means that trajectories originating from nearby starting points will diverge and such a feature can be correlated with the parametric sensitivity of the reactor temperature with respect to the system constitutive parameters or initial conditions. Therefore, taking into account such a correlation between parametric sensitivity and the divergence of nearby trajectories, Strozzi et al. (1999) defined a general criterion for runaway detection. Particularly, a reactor is operating under runaway conditions when the divergence of the ODEs system describing its thermal behavior becomes positive on a segment of the reaction path.

$$\text{div}\{F[\bar{x}(t)]\} > 0 \quad (3)$$

This criterion is so general that can be easily applied to both controlled (there are suitable equations expressing temperature control strategy, e.g. isothermal) and uncontrolled (typically, when the reactor operates in the isoperibolic temperature control mode, coolant temperature is assumed to be constant for all process duration) systems independently on the reactor type (CSTR, PFR, BR, SBR).

Nevertheless, such a general criterion needs to be subjected to a single constraint in order to be in accordance with both theoretical and experimental evidences on runaway detection. This constraint takes into account the presence of a fast reaction that does not

produce directly heat (Zaldívar et al., 2003). For describing the kinetics of the reacting systems of interest, usually the minimum number of global reactions (NR) is utilized; therefore, thanks to the stoichiometric constraint, the NC number of moles of each species can be computed from the NR extent-of-reactions, which are easily related to the conversion of some reactants or to the yield of some products/intermediates. Consequently, the NC material balances can be recast in NR balance equations for the NR extent-of-reactions, one of these being that of the fast reaction that does not produce or consume heat.

Particularly, such an extent-of-reaction can generate a strong volume contraction (synthesized in a no runaway condition according to the divergence criterion) in the N-dimensional state space arising by considering that extent-of-reaction in the divergence computation, but a global expansion (runaway) in the (N-1)-dimensional space arising by not considering that extent-of-reaction into the divergence computation. Therefore, as a general constraint for the runaway criterion based on divergence, all contributions arising from extent-of-reactions that are not related to heat evolutions must be disregarded into the divergence calculation. Such an expedient is necessary in order to avoid evaluation errors due to the presence of strongly negative terms (the divergence is a sum with sign) that are not related to the runaway phenomenon and could lead to underpredict the chance of runaway.

As will be shown in the following "Results" section, this is a particular case of a more general behavior of the divergence criterion: when controlled reacting systems are involved, also other state variables (apart from the extent-of-reaction related to a fast reaction that does not produce or consume heat) can generate a strong volume contraction in the complete N-dimensional state space that is not related to runaway phenomena, therefore leading the divergence criterion to fail in predicting runaway phenomena.

As a consequence, a modified version of the divergence criterion has been developed. Particularly, a more general constraint has been proposed based on the consideration that whatever type of runaway phenomenon is originated by a reactor temperature loss of control, only those terms of the $F[\bar{x}(t)]$ trace that are related to the rate of heat evolution should be considered into the divergence calculation.

Referring for the sake of illustration to a controlled isoperibolic semibatch reactor where NR reactions are carried out in homogeneous phase, the following system of ODEs can be written to describe its thermal behavior:

$$\left\{ \begin{array}{l} \frac{dx_1}{dt} = \frac{dm_{dos}}{dt} = f_{dos}(t) = F_1[\bar{x}(t)] \\ \frac{dx_2}{dt} = \frac{dT_{cool,IN}}{dt} = -K_{pT} \cdot \left[\frac{dT_{cool}}{dt} - \frac{1}{K_{iT}} \cdot (T_{cool,set} - T_{cool}) \right] = F_2[\bar{x}(t)] \\ \frac{dx_3}{dt} = \frac{dV}{dt} = \frac{1}{\rho} \cdot f_{dos}(t) - \frac{V}{\rho} \cdot \frac{d\hat{\rho}}{dt} = F_3[\bar{x}(t)] \\ \frac{dx_4}{dt} = \frac{d\hat{\rho}}{dt} = f_{\rho}(t, T, \vec{n}) = F_4[\bar{x}(t)] \\ \frac{dx_5}{dt} = \frac{dT_{cool}}{dt} = \frac{\hat{\rho}_{cool} \cdot \hat{c}_{p,cool} \cdot \dot{V}_{cool} \cdot (T_{cool,IN} - T_{cool}) + UA \cdot (T - T_{cool})}{\hat{\rho}_{cool} \cdot \hat{c}_{p,cool} \cdot V_{cool}} = F_5[\bar{x}(t)] \\ \frac{dx_{5+j}}{dt} = \frac{d\zeta_j}{dt} = f_{\zeta}(t, T, V, \vec{n}) = F_{5+j}[\bar{x}(t)] \quad j = 1, NR \\ \frac{dx_{6+NR}}{dt} = \frac{dT}{dt} = \frac{f_{dos}(t) \cdot \hat{c}_{p,dos} \cdot (T_{dos} - T) + \sum_{j=1}^{NR} r_j \cdot (-\Delta \hat{H}_{rxn,j}) \cdot V - UA \cdot (T - T_{cool}) - UA_{ext} \cdot (T - T_{ext})}{\rho \cdot V \cdot \hat{c}_{p,mix}} = F_{6+NR}[\bar{x}(t)] \end{array} \right. \quad (4)$$

$$I.C \quad t = 0 \Rightarrow m_{dos} = 0, \quad T_{cool,IN} = T_{cool,IN,0}, \quad V = V_0, \quad \rho = \rho_0, \quad T_{cool} = T_{cool,0}, \quad n_i = n_{i,0}, \quad T = T_0$$

where m_{dos} is the dosing mass (kg), f_{dos} is the dosing stream function, $T_{cool,IN}$ is the inlet coolant temperature (K), T_{cool} is the actual coolant temperature (K), $T_{cool,set}$ is the set-point temperature of the jacket (K), T is the reactor temperature (K), K_{pT} is the proportional gain of the temperature controller (–), K_{iT} is the reset time of the temperature controller (s), V is the total liquid reacting volume (m^3), f_ρ is a function accounting for mixing rules (that can assume a number of different time, temperature and compositions dependent expressions), UA is the global heat transfer coefficient for the cooling system (W/K), ζ_j is the conversion of the j -th reaction (–), f_ζ is the conversion function, T_{dos} is the dosing stream temperature (K), T_{ext} is the ambient temperature (K), UA_{ext} is the global heat transfer coefficient for the ambient (W/K), r_j is the j -th reaction rate ($kmol/(m^3 s)$) according to, e.g., Arrhenius Law and $\Delta\tilde{H}_{rxn,j}$ is the j -th reaction enthalpy (J/kmol). The meaning of other symbols is reported in the “Nomenclature” section.

In the ODEs system (4), first and second equation express the dosing policy (e.g. constant feeding rate) and the reactor temperature control mode (in this case, isoperibolic), respectively; the third equation is the global material balance onto the reacting mass; the fourth equation synthesizes the mixing rule for density; the fifth one expresses the energy balance for the cooling jacket; the NR equations synthesized in the sixth one represent the balances for the NR extent-of-reactions; the last equation is the energy balance for the reactor.

Looking at the last equation of system (4), it is possible to observe that the term related to heat evolution (power released) is expressed by the following equation:

$$\dot{Q}_{rxn} = \sum_{j=1}^{NR} r_j \cdot (-\Delta\tilde{H}_{rxn,j}) \cdot V \quad (5)$$

If a single reaction of the type:



is assumed to occur, the corresponding reaction rate can be expressed as follows:

$$r = k_\infty \cdot \exp\left(-\frac{E_{att}}{R \cdot T}\right) \cdot f(\zeta, m_{dos}) \quad (7)$$

where k_∞ is the pre-exponential factor and E_{att} is the activation energy.

Therefore, analyzing all the dependent variables involved into Equation (5), it is possible to state that only temperature (T), volume (V), extent-of-reaction (that is, conversion ζ) and dosing policy (m_{dos}) affect the rate of heat evolution. As a consequence, all terms of the $F[\bar{x}(t)]$ trace related to these state variables should be necessary and sufficient to characterize the system thermal behavior (that is, runaway). It is important to note that in this modified divergence criterion all the terms of $F[\bar{x}(t)]$ trace corresponding to temperature control strategy, mixing rules and jacket energy balance are automatically excluded from the divergence calculation. As discussed in the following section, such a difference with respect to the original divergence criterion is effective to correctly detect runaway boundaries for isoperibolic semibatch reactors where one or more exothermic reactions take place.

3. Results

In this section, results concerning the application of both the original divergence criterion for runaway detection and the modified version are presented with reference to the aromatic

nitration of 4-Chlorobenzotrifluoride in mixed acids and the nitric acid oxidation of 2-octanol to 2-octanone and further carboxylic acids. For these systems, no underprediction of the marginal ignition line due to the presence of fast but no exothermic reactions (that can induce strong volume contractions) is expected for the original version of the divergence criterion (that is, no corrections in the divergence calculation must be done) because they involve only exothermic reactions.

3.1. Single non autocatalytic reaction

Since the aromatic nitration of 4-Chlorobenzotrifluoride has been extensively discussed elsewhere (Copelli, Derudi, & Rota, 2011; Maestri et al., 2009a, 2009b), it will be only briefly summarized in the following. The following single non autocatalytic reaction represents the kinetic scheme considered into the 4-Chloro-3-nitrobenzotrifluoride synthesis:



where A represents the species 4-Chlorobenzotrifluoride, B is the nitronium ion (responsible for the nitration reaction), C is the species 4-Chloro-3-nitrobenzotrifluoride (desired product) and D is water.

According to such a kinetic scheme, the reaction rate can be expressed as follows:

$$r = k_\infty \cdot \exp\left(-\frac{E_{att}}{RT}\right) \cdot [A]_c \cdot [B]_c \quad (9)$$

The dynamics of the isoperibolic SBR can be modeled through the following ODEs system expressing, in dimensionless form: isoperibolic temperature PI control loop (first equation), energy balances on both jacket (second equation) and reactor (third equation), extent-of-reaction balance in terms of material balance for the desired product C (forth equation), global material balance

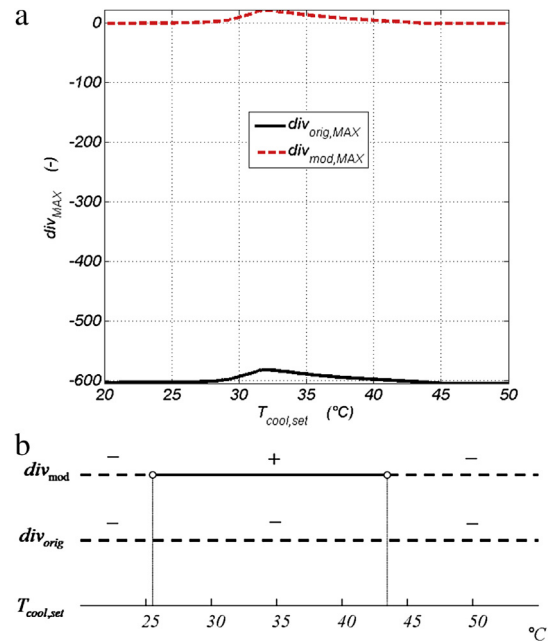


Fig. 1. Comparison between original and modified approach for runaway detection based on the divergence criterion. a) Maximum value of the divergence, and b) sign (positive, +, or negative, –) of the divergence as a function of set point coolant temperature for the aromatic nitration of 4-Chlorobenzotrifluoride in mixed acids.

(fifth equation), mixing rule (sixth equation) and dosing policy (seventh equation).

In the time range $0 \leq \vartheta < 1$:

$$\begin{cases} \frac{dx_1}{dt} = \frac{d\tau_{cool,IN}}{d\vartheta} = -K_{pT} \cdot \left[\frac{d\tau_{cool}}{d\vartheta} - \frac{t_{dos}}{K_{iT}} \cdot (\tau_{set,cool} - \tau_{cool}) \right] = F_1(\bar{x}) \\ \frac{dx_2}{dt} = \frac{d\tau_{cool}}{d\vartheta} = \theta \cdot (\tau_{cool,IN} - \tau_{cool}) + NTU \cdot v \cdot (\tau - \tau_{cool}) = F_2(\bar{x}) \\ \frac{dx_3}{dt} = \frac{d\tau}{d\vartheta} = \frac{dv_{dos}}{d\vartheta} \cdot \frac{\varepsilon}{\rho \cdot v} \cdot R_H \cdot (\tau_{dos} - \tau) + \frac{d\zeta}{d\vartheta} \cdot \frac{\Delta\tau_{ad}}{\rho \cdot v} - \frac{St}{\rho} \cdot (\tau - \tau_{cool}) - \frac{St_{ext}}{\rho \cdot v} \cdot (\tau - \tau_{ext}) = F_3(\bar{x}) \\ \frac{dx_4}{dt} = \frac{d\zeta}{d\vartheta} = Da \cdot RE \cdot \kappa \cdot \varphi = F_4(\bar{x}) \\ \frac{dx_5}{dt} = \frac{dv}{d\vartheta} = \frac{\varepsilon}{\rho} \cdot \frac{dv_{dos}}{d\vartheta} - \frac{d\rho}{d\vartheta} \cdot \frac{v}{\rho} = F_5(\bar{x}) \\ \frac{dx_6}{dt} = \frac{d\rho}{d\vartheta} = \varepsilon \cdot \frac{dv_{dos}}{d\vartheta} \cdot \left(1 - \frac{1}{\rho_{dos}} \right) / \left(1 + \frac{\varepsilon}{\rho_{dos}} \cdot v_{dos} \right)^2 = F_6(\bar{x}) \\ \frac{dx_7}{dt} = \frac{dv_{dos}}{d\vartheta} = 1 = F_7(\bar{x}) \end{cases} \quad (10)$$

with initial conditions:

$$\begin{aligned} \tau_{cool,IN} &= \tau_{cool,IN,0}, \quad \tau_{cool} = \tau_{cool,0}, \quad \tau = \tau_0, \quad \zeta = 0, \\ v &= \rho = 1, \quad v_{dos} = 0 \end{aligned} \quad (11)$$

Some of the equations above changes for $\vartheta \geq 1$ as follows:

$$\begin{cases} \frac{d\rho}{d\vartheta} = 0 \\ \frac{dv_{dos}}{d\vartheta} = 0 \end{cases} \quad (12)$$

Referring to the ODEs system (10) and (12), it is possible to calculate the divergence according to both the original divergence criterion for runaway detection (div_{orig}) and its corresponding modified version (div_{mod}).

$$div_{orig} = \sum_{i=1}^7 \frac{\partial F_i(\bar{x})}{\partial x_i} \quad (13)$$

$$div_{mod} = \frac{\partial F_3(\bar{x})}{\partial x_3} + \frac{\partial F_4(\bar{x})}{\partial x_4} + \frac{\partial F_5(\bar{x})}{\partial x_5} + \frac{\partial F_7(\bar{x})}{\partial x_7} \quad (14)$$

As it can be easily observed, the following terms are always equal to zero and, therefore, they do not contribute to the divergence magnitude.

$$\frac{\partial F_1(\bar{x})}{\partial x_1} = \frac{\partial F_6(\bar{x})}{\partial x_6} = \frac{\partial F_7(\bar{x})}{\partial x_7} = 0 \quad (15)$$

As a consequence, the only difference between div_{orig} and div_{mod} calculation is the computation of the term $\partial F_2(\bar{x})/\partial x_2$, which is associated to the jacket energy balance. Such a term is expressed by the following equation:

$$\frac{\partial F_2(\bar{x})}{\partial x_2} = -\theta - NTU \cdot v \quad (16)$$

Observing Equation (16) is easy to notice that its contribution to the divergence is always negative and its magnitude depends on the constitutive process parameters.

After this preliminary observation, runaway boundaries can be identified according to the two different criteria. To generate the marginal ignition line, it is necessary to keep constant all constitutive model parameters and initial conditions except one, which

will be varied in a suitably wide range. In this case, for the sake of example, the set point coolant temperature has been chosen as the non-constant parameter. To each value of $T_{cool,set}$ corresponds a unique value of the maximum of the divergence that can be computed with the two different criteria ($div_{orig,MAX}$, computed with Equation (13), or $div_{mod,MAX}$, computed with Equation (14); these are the absolute maxima detected during a single simulation at a current $T_{cool,set}$ value). If such a divergence value is positive, the system is operating under runaway conditions during an interval of its reaction path; if it is negative, the system is always operating under safe conditions; if it is equal to zero, a boundary between safe and runaway conditions (first boundary) or runaway and QFS conditions (second boundary) is detected.

Fig. 1, which has been computed using the recipe reported in Table 1, shows the comparison between the results obtained with the original divergence criterion and the modified one. Particularly, in Fig. 1a, the maximum divergence value vs. time is reported for both the original ($div_{orig,MAX}$) and the modified criterion ($div_{mod,MAX}$), while in Fig. 1b the sign of the maximum divergence is represented. We can note that using the original divergence criterion no runaway boundary is detected in the analyzed range of $T_{cool,set}$ (that is, $20^\circ\text{C} \leq T_{cool,set} \leq 50^\circ\text{C}$). However, it is known that around $25\text{--}30^\circ\text{C}$ a runaway arises, exhibiting an adiabatic temperature rise up to 70°C (Copelli, Derudi, & Rota, 2011; Maestri et al., 2009a, 2009b).

On the contrary, from the same Fig. 1 we can see that the modified divergence criterion identifies a runaway boundary around 25°C , in agreement with the experimental and theoretical behavior previously identified. Moreover, a QFS boundary around 43°C is also identified; such a value is slightly larger than that computed using other methods for QFS detection (Alós et al., 1998; Copelli, Derudi, & Rota, 2011), which predict a QFS boundary at about 38°C . However, this is a well-known feature of the divergence criterion, which usually overpredicts QFS boundary (Strozzi et al., 1999).

The failure of the original divergence criterion in predicting the runaway boundary should be ascribed to the strongly negative magnitude of the term $\partial F_2(\bar{x})/\partial x_2$, which is associated to the jacket energy balance. Such a term is not directly linked to the runaway

Table 1

Process recipe, reactor and cooling system for the aromatic nitration of 4-Chlorobenzotrifluoride in mixed acids.

Initial load		Reactor and cooling system	
30 [g]	HNO ₃	Reactor nominal volume	1.0 × 10 ⁻³ [m ³]
335 [g]	H ₂ SO ₄	Jacket nominal volume	5.0 × 10 ⁻⁴ [m ³]
Dosed stream		Coolant flow rate	5.0 × 10 ⁻⁴ [m ³ /s]
83 [g]	4-Chlorobenzotrifluoride	UA ₀	1.21 [W/K]

behavior; therefore, analogously to what was previously found for a fast reaction that does not produce or consume heat (Zaldívar et al., 2003), it must be disregarded into the divergence calculation to avoid a strong but not meaningful volume contraction in the phase space and to obtain consequently predictions in agreement with the experimental evidences.

$$\begin{cases}
 \frac{dx_1}{dt} = \frac{d\tau_{cool,IN}}{d\vartheta} = -K_{pT} \cdot \left[\frac{d\tau_{cool}}{d\vartheta} - \frac{t_{dos}}{K_{iT}} \cdot (\tau_{cool,set} - \tau_{cool}) \right] = F_1(\bar{x}) \\
 \frac{dx_2}{dt} = \frac{d\tau_{cool}}{d\vartheta} = \theta_{cool} \cdot (\tau_{cool,IN} - \tau_{cool}) + NTU_{cool} \cdot v \cdot (\tau - \tau_{cool}) = F_2(\bar{x}) \\
 \frac{dx_3}{dt} = \frac{d\tau}{d\vartheta} = \frac{dv_{dos}}{d\vartheta} \cdot \frac{\varepsilon}{\rho \cdot v} \cdot R_H \cdot t_{dos} \cdot (\tau_{dos} - \tau) + \left(\frac{d\zeta_C}{d\vartheta} + \frac{d\zeta_D}{d\vartheta} \right) \cdot \frac{\Delta\tau_{ad,1}}{\rho \cdot v} + \frac{d\zeta_D}{d\vartheta} \cdot \frac{\Delta\tau_{ad,2}}{\rho \cdot v} + \frac{St}{\rho} \cdot (\tau - \tau_{cool}) - \frac{St_{ext}}{\rho \cdot v} \cdot (\tau - \tau_{ext}) + St_{stir} = F_3(\bar{x}) \\
 \frac{dx_4}{dt} = \frac{d\zeta_C}{d\vartheta} = Da_1 \cdot RE_1 \cdot \varphi_1 \cdot \kappa_1 - Da_2 \cdot RE_2 \cdot \varphi_2 \cdot \kappa_2 = F_4(\bar{x}) \\
 \frac{dx_5}{dt} = \frac{d\zeta_D}{d\vartheta} = Da_2 \cdot RE_2 \cdot \varphi_2 \cdot \kappa_2 = F_5(\bar{x}) \\
 \frac{dx_6}{dt} = \frac{dv}{d\vartheta} = \frac{\varepsilon}{\rho} \cdot \frac{dv_{dos}}{d\vartheta} - \frac{d\rho}{d\vartheta} \cdot \frac{v}{\rho} = F_6(\bar{x}) \\
 \frac{dx_7}{dt} = \frac{d\rho}{d\vartheta} = \frac{\varepsilon \cdot \frac{dv_{dos}}{d\vartheta} \cdot \left(1 - \frac{1}{\rho_{dos}} \right)}{\left(1 + \frac{\varepsilon}{\rho_{dos}} \cdot v_{dos} \right)^2} = F_7(\bar{x}) \\
 \frac{dx_8}{dt} = \frac{dv_{dos}}{d\vartheta} = 1 = F_8(\bar{x})
 \end{cases} \quad (19)$$

3.2. Consecutive reactions with autocatalytic behavior

Since even the nitric acid oxidation of 2-octanol to 2-octanone and further carboxylic acids has been extensively discussed elsewhere (Copelli, Derudi, & Rota, 2010a; van Woezik & Westerterp, 2000, 2001), it will be only briefly summarized in the following. Particularly, the following consecutive reactions with autocatalytic behavior represent the kinetic scheme considered into the 2-octanone synthesis:



where A is 2-octanol, B is nitrosonium ion (NO^+ , the species responsible for the oxidation of species A and C and also for the autocatalytic behavior of reaction 1), C is 2-octanone (product of reaction 1) and D is a mixture of carboxylic acids (products of reaction 2).

According to such a kinetic scheme, the reaction rates can be expressed as follows:

$$\begin{aligned}
 1) & r_1 = k_{\infty,1} \cdot \exp\left(-\frac{E_{att,1}}{RT}\right) \cdot \exp(-m_{H,1} \cdot H) \cdot [A]_c \cdot [B]_c \\
 2) & r_2 = k_{\infty,2} \cdot \exp\left(-\frac{E_{att,2}}{RT}\right) \cdot \exp(-m_{H,2} \cdot H) \cdot [C]_c \cdot [B]_c
 \end{aligned} \quad (18)$$

where $m_{H,1}$ and $m_{H,2}$ are the Hammett's reaction rate coefficients and H is the Hammett's acidity function.

The dynamics of the isoperibolic SBR can be modeled through the following ODEs system expressing, in dimensionless form: isoperibolic temperature PI control loop (first equation), energy balances on both jacket (second equation) and reactor (third equation), extent-of-reactions balances in terms of C and D yields (forth and fifth equations), global material balance (sixth equation), mixing rule (seventh equation) and dosing policy (equation eight).

In the time range $0 \leq \vartheta < 1$:

with initial conditions:

$$\begin{aligned}
 \tau_{cool,IN} &= \tau_{cool,IN,0}, \quad \tau_{cool} = \tau_{cool,0}, \quad \tau = \tau_0, \quad \zeta_C = \zeta_D = 0, \\
 v = \rho &= 1, v_{dos} = 0
 \end{aligned} \quad (20)$$

Some of the equations above changes for $\vartheta \geq 1$ as follows:

$$\begin{cases}
 \frac{d\rho}{d\vartheta} = 0 \\
 \frac{dv_{dos}}{d\vartheta} = 0
 \end{cases} \quad (21)$$

Referring to the ODEs system (19) and (21), it is possible to calculate the divergence according to both the original divergence criterion for runaway detection (div_{orig}) and its corresponding modified version (div_{mod}).

$$div_{orig} = \sum_{i=1}^8 \frac{\partial F_i(\bar{x})}{\partial x_i} \quad (22)$$

$$div_{mod} = \frac{\partial F_3(\bar{x})}{\partial x_3} + \frac{\partial F_4(\bar{x})}{\partial x_4} + \frac{\partial F_5(\bar{x})}{\partial x_5} + \frac{\partial F_6(\bar{x})}{\partial x_6} + \frac{\partial F_8(\bar{x})}{\partial x_8} \quad (23)$$

As it can be easily observed, the following terms are always equal to zero and, therefore, they do not contribute to the divergence magnitude.

$$\frac{\partial F_1(\bar{x})}{\partial x_1} = \frac{\partial F_7(\bar{x})}{\partial x_7} = \frac{\partial F_8(\bar{x})}{\partial x_8} = 0 \quad (24)$$

As previously observed for a single reaction, the only difference between div_{orig} and div_{mod} calculation is the term $\partial F_2(\bar{x})/\partial x_2$.

Looking for runaway boundaries considering as non-constant parameter the set point coolant temperature, the results reported in Fig. 2 (which has been generated using the recipe reported in Table 2) have been obtained. Particularly, in Fig. 2a, the maximum divergence vs. time evolution is reported for both the original ($div_{orig,MAX}$) and the modified divergence criterion ($div_{mod,MAX}$), while in Fig. 2b the sign of the maximum divergence is represented. We can note that using the original divergence criterion a unique runaway boundary at $T_{cool,set} = 8^\circ\text{C}$, is detected. Such a value corresponds to that at which the modified divergence criterion identifies a second runaway boundary. In fact, the modified divergence criterion is able to identify also another thermal runaway effect, of small magnitude (as it can be seen from Fig. 2a), occurring at a lower set point coolant temperatures ($T_{cool,set} = -9^\circ\text{C}$). This first runaway boundary has been previously identified both experimentally and theoretically (Copelli et al., 2010a; van Woezik & Westerterp, 2001) and it is a key point in the safe process optimization for what concerns the maximization of the 2-octanone production.

Similarly to that found in the first case investigated, the failure of the original divergence criterion in predicting the runaway

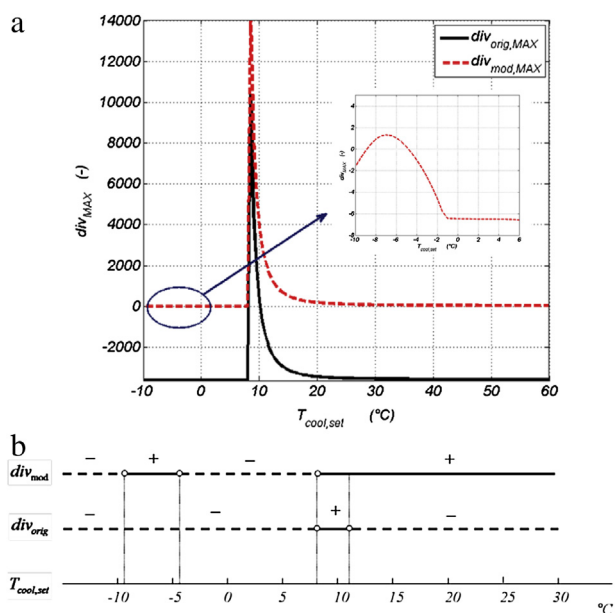


Fig. 2. Comparison between original and modified approach for runaway detection based on the divergence criterion. a) Maximum value of the divergence, and b) sign (positive, +, or negative, -) of the divergence as a function of set point coolant temperature for the nitric acid oxidation of 2-octanol to 2-octanone and further mixture of carboxylic acids.

Table 2

Process recipe, reactor and cooling system for the nitric acid oxidation of 2-octanol to 2-octanone and further carboxylic acids.

Initial load		Reactor and cooling system	
377 [g]	HNO ₃	Reactor nominal volume	2.0×10^{-3} [m ³]
251 [g]	H ₂ O	Jacket nominal volume	1.0×10^{-3} [m ³]
Dosed stream		Coolant flow rate	5.0×10^{-4} [m ³ /s]
164 [g]	2-octanol	UA ₀	4.3 [W/K]

boundary should be ascribed to the strongly negative magnitude of the term $\partial F_2(\bar{x})/\partial x_2$, which is associated to the jacket energy balance without being directly linked to the runaway behavior. Therefore, it must be disregarded into the divergence calculation to avoid a strong but not meaningful volume contraction in the phase space and to obtain consequently predictions in agreement with the experimental evidences.

4. Conclusion

In this work a modified version of the divergence criterion has been developed. Such a modified divergence criterion is able to deal with whatever type of complex controlled reacting system and its reliability has been demonstrated for isoperibolic semibatch reactors using literature experimental data concerning the nitration of 4-Chlorobenzotrifluoride in mixed acids and the nitric acid oxidation of 2-octanol to 2-octanone and further carboxylic acids.

It has been found that where the original approach fails to detect a runaway boundary, the modified divergence criterion is capable of predicting reliably such a boundary.

Acknowledgment

The authors wish to express their profound admiration to Professor J.M. Zaldívar inasmuch he should be taken as an example of a complete scientist and pioneer of mathematics applied to chemical reactors safety. During his career, professor Zaldívar explored many different fields, such as Neural Networks (Tomasin, Zaldivar, Gutierrez, Galvan, & Strozz, 2000; Zaldivar, Hernandez, & Panetsos, 1992), Chemistry (Zaldivar, Alós, Hernández, Molga, & Westerterp, 1995a, 1995b) and Chemical Engineering, without neglecting his collaboration in works on both neurotoxicity (Scelfo et al., 2012) and, as member of the JRC at Ispra, water and air pollution, with particular interest in PCB contaminations in northern Italy (Castro-Jiménez et al., 2009; Dueri, Castro-Jiménez, & Zaldívar, 2009).

Professor Zaldívar should be considered a pioneer of reactor safety because of his works on the divergence criterion which, as stated in this paper, is a simple but powerful tool to estimate runaway conditions in chemical reactors with enough precision to be used in chemical industries.

Finally, it is worth mentioning that starting from the pioneering Zaldívar's works, applied mathematics has been increasingly used in thermal safety and optimization criteria studies opening new research fields (e.g., Copelli, Derudi, Lunghi, Pasturenzi, & Rota, 2011; Copelli et al. 2010a; Copelli, Derudi, & Rota, 2011; Copelli et al., 2012; Copelli, Derudi, Sempere, et al., 2011).

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Nomenclature

- A: Area, [m²], Dosed reactant
 B: Loaded reactant
 C: Desired product
 \hat{c}_p : Specific heat capacity, [J/(kg K)]
 D: Byproduct or mixture of byproducts
 $div = \sum_{i=1}^N \partial F_i(\bar{x}(t)) / \partial x_i$, Divergence operator
 $Da = k_{\infty} \cdot \exp(-E_{att}/RT_{rif}) \cdot [B]_0 \cdot t_{dos}$, Damköler number for the aromatic nitration of 4-Chlorobenzotrifluoride, [–]
 $Da_1 = k_{\infty,1} \cdot \exp(-E_{att,1}/RT_{rif}) \cdot [A]_{dos} \cdot t_{dos}$, Damköler number for the first reaction of the nitric acid oxidation of 2-octanol, [–]
 $Da_2 = k_{\infty,2} \cdot \exp(-E_{att,2}/RT_{rif}) \cdot [A]_{dos} \cdot t_{dos}$, Damköler number for the second reaction of the nitric acid oxidation of 2-octanol, [–]
 E_{att} : Activation energy, [kJ/kmol]
 E_x : Exothermicity number, [–]
 F: Jacobian matrix
 f: Generic function, [–] or with dimension
 H: Hammett's acidity function, [–]
 ΔH_{rxn} : j-th reaction enthalpy, [J/kmol]
 $K_{rif} = 150$, Reset time, [s]
 $K_{pT} = 6$, Proportional gain, [–]
 k_{∞} : Pre-exponential factor, [m³ s/kmol]
 i: Index of equations in a generic ordinary differential equation system, [–]
 j: Index of reaction, [–]
 m: Mass, [kg]
 m_{Hj} : Hammett's reaction rate coefficient for the j-th reaction, [–]
 N: Dimension of the state space, [–]
 NC: Number of species, [–]
 NR: Number of reactions, [–]
 \bar{n} : Number of moles vector, [kmol]
 NTU: = $(UA)_0 \cdot t_{dos} / \hat{\rho}_{cool} \cdot \hat{c}_{p,cool} \cdot V_{cool}$, number of transfer units, [–]
 PI: Proportional-Integral control action
 R: gas constant = 8314, [J/(kmol K)]
 r: Reaction rate, [kmol/(m³ s)]
 RE: = m_A , Reactivity Enhancement Factor = Distribution coefficient for species A, [–]
 RE_j: = m_A , Reactivity Enhancement Factor = Distribution coefficient for species A, [–]
 RE₂: = m_C , Reactivity Enhancement Factor = Distribution coefficient for species C, [–]
 $R_H = \hat{c}_{p,dos} / \hat{c}_{p,mix}$, heat capacity ratio, [–]
 R_y : Reactivity number, [–]
 s: Normalized parametric sensitivity coefficient, [–]
 $St = (UA)_0 \cdot t_{dos} / \hat{\rho}_0 \cdot \hat{c}_{p,mix} \cdot V_0$, number, [–]
 $St_{ext} = (UA)_{ext} \cdot t_{dos} / \hat{\rho}_0 \cdot \hat{c}_{p,mix} \cdot V_0$, number referred to ambient dispersion and evaporation losses, [–]
 t: time, [s]
 T: Temperature, [K]
 U: overall heat transfer coefficient, [W/(m² K)]
 V: volume, [m³] state space volume
 \dot{V} : Volumetric flow rate, [m³/s]
 $v = V/V_0$, Dimensionless reactor volume, [–]
 $v_{dos} = V_{dos}/V_{TOT,dos}$, Dimensionless dosing volume, [–]
 \bar{x} : Dependent variables vector (for an ODEs system)
- Subscripts and superscripts**
 ad: Adiabatic
 c: Referred to as the continuous aqueous phase
 cool: Referred to as the coolant or the external jacket
 dos: Dosing stream or dosing time
 ext: Referred to as the external heat losses
 IN: Referred to as an inlet stream
 j: Referred to as the j-th reaction
 MAX: Maximum value of a quantity or at the maximum value of a quantity
 mix: Referred to as the reacting mixture

mod: Referred to as the modified divergence criterion
orig: Referred to as the original divergence criterion
QFS: "Quick onset", "Fair conversion", "Smooth temperature profile"
rif: Referred to as reference conditions
set: Referred to as the desired set point
0: Start of the dosing period
1: Referred to as the first reaction
2: Referred to as the second reaction

Greek symbols

$\Delta\tau_{adj}$: $= (-\Delta\hat{H}_{rxn,j}) \cdot n_{A,TOT,dos} / \hat{\rho}_0 \cdot V_0 \cdot \hat{c}_{p,mix} \cdot T_{rif}$, dimensionless adiabatic temperature rise of the *j*-th reaction, [-]
 γ : $= E_{att} / RT_{rif}$, dimensionless activation energy, [-]
 ε : $= m_{TOT,dos} / m_0$, relative mass increase at the end of the semibatch period, [-]
 ζ : dimensionless concentration or conversion of a generic species, [-]

κ_j : $= \exp(\gamma_j \cdot (1 - 1/\tau))$, dimensionless *j*-th reaction kinetic constant, [-]
 ρ : $= \hat{\rho} / \hat{\rho}_0$ Dimensionless reacting mixture density, [-]
 $\hat{\rho}$: Reacting mixture density, [kg/m³]
 τ : $= T / T_{rif}$, dimensionless temperature, [-]
 θ : $= \dot{V}_{cool} \cdot t_{dos} / V_{cool}$, dimensionless coolant contact frequency into the jacket, [-]
 ϑ : $= t / t_{dos}$, dimensionless time, [-]
 ϕ : Generic constitutive model parameter
 φ : Generic dimensionless function, [-] $= \left[\left(v_{dos} - \zeta \right) / \frac{\varepsilon}{\rho_{dos}} \cdot v_{dos} \right] \cdot (1 - \zeta)$,

Concentration function for the aromatic nitration of 4-Chlorobenzotrifluoride, [-]

φ_1 : $= (v_{dos} - \zeta_C - \zeta_D) \cdot (\zeta_{B,0} + \zeta_C) / v_{dos} \cdot \exp(-m_{H,1} \cdot H)$, Concentration function for the second reaction of the nitric acid oxidation of 2-octanol, [-]
 φ_2 : $= \zeta_C \cdot (\zeta_{B,0} + \zeta_C) / v_{dos} \cdot \exp(-m_{H,2} \cdot H)$, Concentration function for the second reaction of the nitric acid oxidation of 2-octanol, [-]