CHEMICAL REACTORS AND RUNAWAY PHENOMENA

S. Copelli, M. Derudi, V. Busini, M. Masi, M. Morbidelli, R. Rota

Politecnico di Milano, Dip.CMIC "G. Natta"
Via Mancinelli 7, 20131 Milano, Italy

Fast and strongly exothermic chemical processes are particularly difficult to optimize and scale-up from laboratory to full plant scale because of the possible triggering of 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 each type of reactor 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. Aim of this work has been to illustrate all the methods developed to detect runaway (that is, the set of operating conditions corresponding to a triggering of the runaway phenomenon) and QFS boundaries (that is, the set of operating conditions where the reactor exhibits an almost linear conversion with respect to the desired product and a pseudo-stationary temperature profile) for exothermic isoperibolic semibatch reactors, which are common chemical reactor in fine chemical and pharmaceutical Italian enterprises.

1. INTRODUCTION

Runaway phenomena are a very common problem in pharmaceutical and fine chemical industries. For instance, in a typical European country more than 100 runaways are expected to occur annually (Benuzzi and 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 last twenty-five years.

Particularly, many 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 performed (Hugo and Steinbach (1985), Steensma and Westerterp (1988, 1990, 1991), Morbidelli and Varma (1982, 1985, 1988), Alós et al. (1998), Wu et al. (1998a, 1998b), Varma et al. (1999), Steinbach (1999), Strozzi et al. (1999), van Woezik and Westerterp (2000, 2001), Zaldívar et al. (2003, 2005), Bosch et al. (2004), Maestri and Rota (2005a, 2005b)).

The first general criterion able to handle multiple reactions systems and different reactor typologies (e.g., batch reactor (BR), continuous stirred tank reactor (CSTR), plug-flow reactor (PFR), etc.) was the generalized parametric sensitivity criterion (Morbidelli and Varma (1982, 1985, 1988), Wu et al. (1998a, 1998b), Varma et al. (1999)). 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 and 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).

A different generalized criterion for the detection of the runaway boundary, able to operate with multiple reactions, different temperature control modes and reactor typologies, was the divergence criterion (Strozzi et al. (1999), Zaldívar et al. (2003, 2005), Bosch et al. (2004)). This criterion states that if the system of ordinary differential equations (ODEs) that describes the analyzed process exhibits positive divergence, the synthesis is operating under runaway conditions. The criterion shows the relevant advantage of being usable both on-line (the divergence is 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).

However, from a practical point of view, the optimization of all (or some) operating parameters (e.g., coolant temperature and dosing time) is the relevant aspect. Knowing the runaway boundaries allows for avoiding the selection of potentially hazardous operating conditions, but it does not allow one to optimize the analyzed process.

The first combined "safety-optimization" 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, that is of the type $r = k(T) \cdot [A][B]$ (where r represents the reaction rate, [kmol/(m3 s)], $k(T) = A \cdot \exp(-E/RT)$ is the Arrhenius kinetic constant, [(m3 s)/kmol], $[A]$ and $[B]$ are the molar concentrations of, respectively, the dosed reactant and the initially loaded reactant, [kmol/m3]). 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 and excessive accumulation operating conditions without solving the mathematical model of the reactor (see Fig. 1).
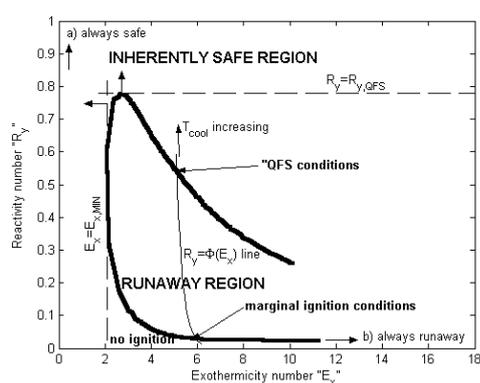

Fig. 1. Boundary diagram for an isoperibolic semibatch process involving one reaction (Maestri and Rota (2005a).

Referring to Fig. 1, the area inside the continuous bold curve is the "runaway" or "excessive co-reactant accumulation" region; outside this region, there are the "no-ignition" region, for low-reactivity numbers, and the "inherently safe" region, for high reactivity numbers (or extremely low exothermicity numbers). The portion of the last area fulfilling $R_y \geq R_{y,QFS}$ constraint, which is also referred to as the "Quick onset, Fair conversion, Smooth temperature profile" (QFS) region (Steensma and Westerterp (1988)), is characterized by both an almost linear conversion to the desired product and a pseudo-stationary reactor temperature profile, that means high cooling efficiency.

Maestri and Rota (2005a, 2005b, 2006a), 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 can not 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.

According to the boundary diagrams method, the QFS region is considered the most safe and productive for an exothermic SBR. However, it can be noted that the definition of such a region (and, consequently, of the boundary that divides such a region from the runaway region) is somehow arbitrary (Alós et al. (1998)). Moreover, it is true that an isoperibolic SBR operating in the QFS region is safe from the co-reactant accumulation point of view (no runaway that is due to the desired reaction can occur) and it exhibits a high conversion degree at the end of the dosing time, but nothing is known about the thermal stability of the system in such a region because the model that generates the BD is based on the thermal effects associated only with the synthesis reaction.

To deal with the thermal stability problem, Stoessel (1993) classified exothermic reaction processes into five classes as a function of their relative ranking: process temperature (PT), maximum temperature that can be achieved by the synthesis reaction as a consequence of a cooling system failure (Maximum Temperature due to the Synthesis Reaction, MTSR), boiling point of the solvent (BP), maximum allowable temperature (MAT) to avoid decompositions (or highly exothermic side reactions) taking place. Situations characterized by MTSR values higher than the MAT value must be regarded as critical from a safety point of view: for instance, a less exothermic reaction system with a relatively low decomposition temperature can be much more dangerous than a more exothermic one with a very high decomposition temperature.

It is important to stress that similar conclusions arise also when a product decomposition or a side reaction, which is not critical for safety (because it is neither very exothermic nor produces large amounts of gases), can take place above a threshold temperature: such situations are very frequent in the fine chemical and pharmaceutical industries, where several processes involve products that can chemically degrade above an experimentally determined temperature also referred to as MAT. Also in this case the MAT value must not be reached; otherwise the plant productivity would be compromised.

This means that, regardless the typology of problem we are dealing with (safety or productivity), one of the constraints we have to fulfill in the production plant is often summarized through a threshold temperature value (that is the MAT) that can not be exceeded during neither normal reactor operations nor upset conditions, such as those ones arising from a cooling system failure.

On the basis of this concept, the so-called temperature diagrams (TDs) have been proposed (Maestri and Rota (2006b)). Such diagrams allow for upperbounding the maximum reactor temperature as a function of some parameters that define the BDs (that is, E_x and R_y). The value of such a maximum temperature can be compared with the experimentally determined value of the maximum allowable temperature for the considered system. If the maximum reactor temperature is above the MAT value, the operating parameters are not safe from the thermal stability point of view and they must be rejected.

The combined use of boundary and temperature diagrams seems to be the right way to develop a simple and reliable procedure able to safely optimize and, eventually, scale-up hazardous chemical processes.

Unfortunately, two relevant problems exist:

1) Boundary and temperature diagrams are easy to be generated for single reaction systems but nothing is known about their construction for systems involving different kinetics;

2) Whatever optimization procedure based on such diagrams (BD and TD) will utilize an arbitrary definition of optimum operating conditions (that is, the QFS one).

van Woezik and Westerterp (2000, 2001) tried to deal with the first problem extending 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. Practically, the QFS of the first and the second reaction are detected separately by using BDs generated, respectively, with the thermokinetic parameters of reaction 1 and 2. The problem of having an arbitrary definition of the QFS conditions has been discussed by Alós et al. (1998), who proposed, for reacting systems involving a single reaction, a definition of QFS using a suitable objective function. In particular, the QFS of an isoperibolic SBR is individuated, for a given value of the dosing time, by the coolant temperature $T_{cool,QFS}$ in correspondence of which the objective function "time at which the maximum reactor temperature, $t(T_{MAX})$, occurs" exhibits a local minimum. The intrinsic nature of this criterion can be proved by calculating the parametric sensitivity of $t(T_{MAX})$ with respect to any system parameter ϕ, $s_{t(T_{MAX}),\phi}$, as a function of T_{cool}. In correspondence of $T_{cool,QFS}$, it can be observed that $s_{t(T_{MAX}),\phi} = 0$, regardless of the ϕ parameter considered: this means that the selected objective function exhibits an intrinsic minimum. Such a criterion arises from an analysis of the target line used to generate BDs (Maestri and Rota (2005a, 2005b)), which is an ideal temperature profile that an isoperibolic SBR exhibits when the co-reactant conversion is linear during the dosing time and the heat developed by the desired reaction is readily removed by the cooling system. Such an ideal temperature profile is shown in Fig. 2, together with its corresponding real SBR profile.
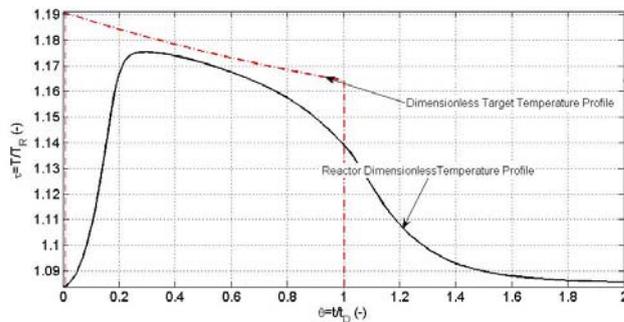

Fig. 2. A generic isoperibolic SBR dimensionless temperature profile (continuous bold line) and the corresponding target temperature ideal profile (dashed and dotted line) (Copelli et al. (2010a)).

As it can be easily observed from Fig. 2, the maximum of the ideal target temperature profile occurs at time zero. Such an observation explains the aforementioned choice of the objective function, $t(T_{MAX})$, for the definition of the QFS condition (Alós et al. (1998)).

After this brief excursion through the recent history of runaway studies concerning exothermic semibatch reactors, it is possible to state that, for both single and multireaction systems, it is not yet clear:

1) how to define the QFS conditions of an exothermic isoperibolic SBR without involving arbitrary definitions;

2) how to develop a suitable procedure to identify safe and productive operating conditions.

2. TOPOLOGY AND OPTIMIZATION PROCEDURES

In order to deal with the two problems previously cited, it has been found (Copelli et al. (2010a, 2010b, 2011)) that a definition of QFS conditions without involving any arbitrary function and a general optimization – scale-up procedure, able to handle both simple and extremely complex reacting systems, could be developed by the means of topology. Topology is a major area of mathematics concerning with spatial properties of objects, called manifolds or varieties, that are preserved under continuous deformations (for instance, stretching but neither tearing nor gluing).

In this work, only manifolds and spaces locally homeomorphic to the Euclidean space have been considered. Varieties of this typology are, as an example, all phase portraits (PP) generated by reporting the solution of a non-linear ordinary differential equations system onto its corresponding phase space while one of the system constitutive parameters or initial conditions is varying. As it can be easily observed, mass and energy balance equations needed to describe whatever complex reacting system fit in this category.

Usually, such manifolds can not be visualized by human eye because they can be represented only into spaces having dimension exceeding three. For this reason, in order to observe whatever notable topological property exhibited by the analyzed variety it is necessary to project it onto suitable viewable spaces.

Concerning the problem of the thermal behavior characterization of potentially runaway semibatch processes, the simplest solution is to employ projections of the corresponding variety onto bidimensional spaces, called 2-D charts, whose coordinated axes are couples of the N dependent variables generating the manifold that fulfill the following specific criteria: 1) only dependent variables that are involved into the energy balance equation can be employed to characterize the observed system thermal behavior; 2) temperature is the most relevant system dependent variable so that it must be compulsory involved in whatever possible couple generating 2-D charts.

According to these features, suitable 2-D charts can be built to search for the system thermal behavior boundaries and the optimum set of operating conditions fulfilling process safety and productivity constraints.

In order to achieve these goals, first, it must be defined the product X with respect to the optimum operating conditions (that is, QFS conditions) are searched for and, then, the maxima of the trajectories generating the analyzed PP must be projected onto a suitable 2-D chart, referred to as X-space. The X-space coordinated axes are constituted by the conversion with respect to the desired product X and the ratio between the reactor temperature and the coolant one. The result is a curve, referred to as topological curve, whose inversion points represent transitions between different system thermal behavior regions.

Particularly, it has been demonstrated that whenever the topological curve exhibits an inversion whose concavity is towards left one of the following three system thermal behavior boundaries is encountered: transition (the system thermal loss of control shifts its occurrence from times lower/larger than the dosing period to times larger/lower), runaway (the overall system thermal loss of control starts) or starving (the system state shifts from QFS conditions to low productivity operating conditions characterized by a squared pseudo-stationary reactor temperature profile and a forced linear conversion during the dosing period); on the contrary, whenever an inversion with a concavity towards right is observed a QFS boundary (the system shifts its state from runaway conditions to high productivity operating conditions characterized by a smooth pseudo-stationary temperature profile and an almost linear conversion during the dosing period) is detected.

It is possible to observe that the different left concavities appear only as singlets or doublets in an X-space. Therefore, by knowing only the generating parameter of the topological curve and the reaction scheme, it is relatively simple to define which ones among them may be encountered and, in the presence of doublets, the sequence of their appearance. Particularly, when dosing time t_{dos} is the generating parameter and one exothermic reaction occurs only the transition singlet or the transition/starving doublet may be observed (as a function of the system constitutive parameters values). It has been demonstrated that, in the presence of the transition/starving doublet, the transition inversion is always the first encountered when t_{dos} is increased. On the contrary, if the generating parameter is the coolant temperature T_{cool} only the transition singlet or the transition/runaway doublet may be observed according to the values of the system constitutive parameters and the kinetic scheme. Even in

this case, it has been demonstrated that when the transition/runaway doublet appears the transition inversion is always the first encountered when T_{cool} is increased.

As an example, some topological curves generated using different kinetic schemes are reported in Fig. 3.
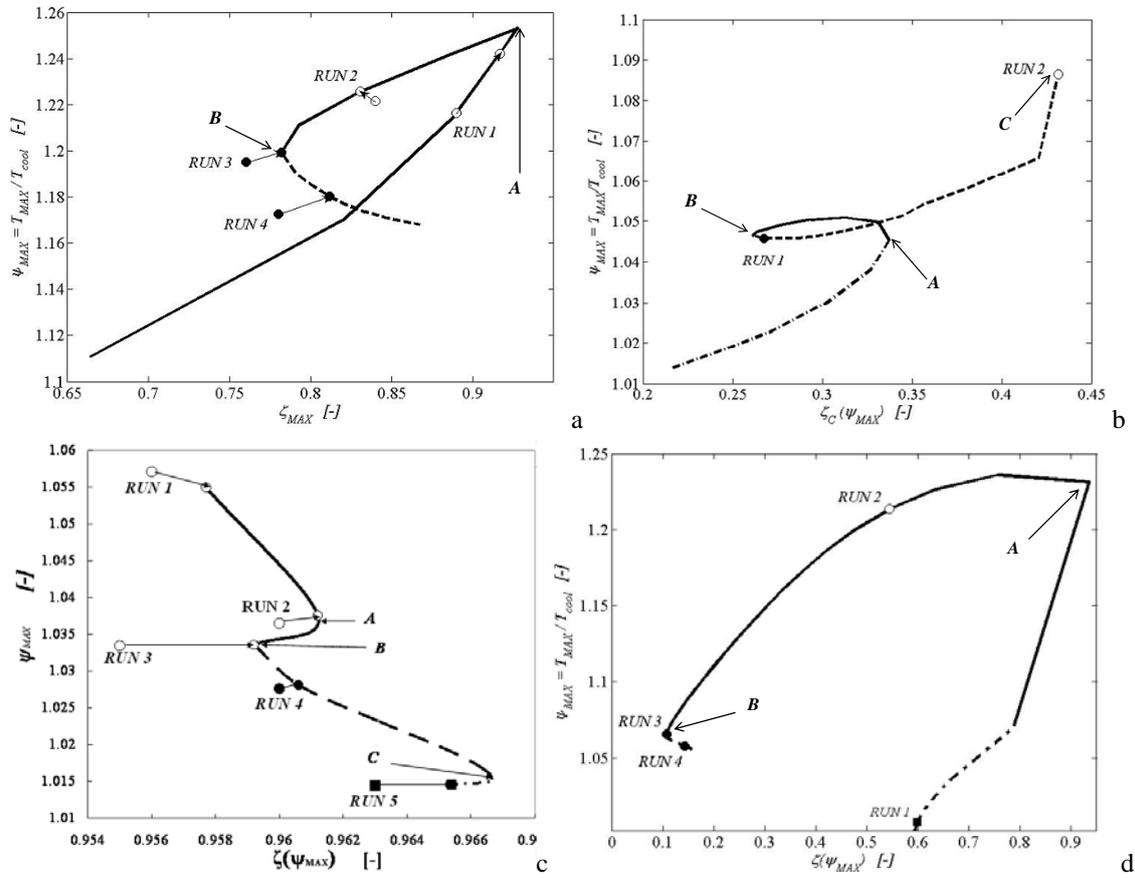

Fig. 3. Some different X-space plots and topological curves: (continuous line) system operates in runaway conditions; (dashed line) system exhibits QFS conditions; (dashed dotted line) system shows starving or no-ignition behavior. Points A - transition inversions, points B - QFS inversions, points C - runaway (if the topological curve generating parameter is T_{cool}) or starving inversions (if the topological curve generating parameter is t_{dos}). a) Loop topological curve for a single non-autocatalityc reaction system; b) Loop topological curve for two consecutive reactions with autocatalityc behavior and intermediate species as the desired product; c) Hooks topological curve for an emulsion homopolymerization system; d) Hook topological curve for a single autocatalityc catalyzed reaction system (Copelli (2011)).

In order to validate the use of the topological curve to detect QFS conditions, the relevant case studies of the 4-chlorobenzotrifluoride nitration by the means of mixed acids and the free radical emulsion homopolymerization of vinyl acetate have been analyzed experimentally at the RC1 scale. Moreover, the nitric acid oxidation of 2-octanol to 2-octanone (and further carboxylic acids) and the acid esterification between propionic anhydride and 2-butanol have been studied using literature experimental data for the sake of completeness.

Maximum temperatures ($T_{MAX,EXP}$) and calorimetric conversions at the maximum temperature ($\zeta_{MAX,EXP}$) for all experimental tests performed (RUN) have been reported in Fig. 3 and linked with their corresponding theoretical points lying onto the topological curve by the means of arrows. Contextually, each test has been experimentally classified into one of the different thermal classes available for an isoperibolic semibatch reactor

where T_{cool} or t_{dos} are considered as variable parameters and compared with the corresponding theoretical one provided by the topological curve. From the combined view of Table 1 and Fig. 3, it is possible to observe that each experimental point is located into the theoretically predicted thermal region.

Table 1. Theoretical and experimental classification of the experimental runs reported in Fig. 3.

RUN	T_{cool} [°C]	t_{dos} [min]	$T_{MAX,EXP}$ [°C]	Experimental Classification	Topological Classification
1 (4a)	32	10	98.00	RW	RW
2 (4a)	35	10	103.30	RW	RW
3 (4a)	37	10	97.50	RW/QFS	RW/QFS
4 (4a)	40	10	94.00	QFS	QFS
1 (4b)	-1	60	15.50	QFS_C	QFS_C
2 (4b)	8	60	24.90	RW	QFS_C/RW
1 (4c)	75	7.5	92.28	RW	RW
2 (4c)	75	10	85.32	RW	RW
3 (4c)	75	12.5	84.13	QFS	QFS
4 (4c)	75	15	82.02	QFS	QFS
5 (4c)	75	30	77.54	STV	STV
1 (4d)	11	60	14.06	NO IGN	NO IGN
2 (4d)	25	60	94.88	RW	RW
3 (4d)	60	60	78.58	QFS	QFS
4 (4d)	72	60	85.65	QFS	QFS

The optimization procedure based on the analysis of the topological curve uses the QFS inversion as a boundary beyond which the optimum operating conditions (that is, dosing time and coolant temperature) can be searched for accounting for reacting mixture thermal stability (that is, MAT) and desired productivity constraints.

It has been demonstrated that such a topological procedure can be applied both theoretically (through the knowledge of the system micro and macrokinetics) and experimentally (without any explicit knowledge of the system kinetics) in order to detect the optimum operating conditions for a fast and strongly exothermic semibatch process.

Finally, it is worth mentioning that, when reacting systems are operated in the runaway operating region, minor changes in process times (e.g. delays on reactant loading, thermocouples equilibration, etc.) and reactants amounts (or relative ratios) may have a great influence on the resulting reactor temperature profile because they affect directly initial conditions, I.C. Since potentially runaway systems exhibit deterministic chaos (that is, high sensitivity with respect to I.C.), little perturbations on I.C. lead to large changes in reactor temperature evolution that may be predicted only if the magnitude of such perturbations is known with a great precision, which is not possible in practice because of the sensitivity limits of measuring instruments. The optimization procedure based on the topological criterion is able to deal with these complex chaotic systems providing safe and productive operating conditions by knowing only the maximum reactor temperature and the conversion with respect to the desired product in correspondence of such a maximum. These pieces of information can be easily obtained using either a laboratory reaction calorimeter or, in principle, literature experimental data.

3. REFERENCES

Alós M.A., Nomen R., Sempere J., Strozzi F. and Zaldívar J.M., 1998, Generalized criteria for boundary safe conditions in semi-batch processes: simulated analysis and experimental results, Chem. Eng. Proc., 37, 405.

Benuzzi A., Zaldivar J.M., 1991, Safety of Chemical Reactors and Storage Tanks, Kluwer Academic Publishers, Dordrecht (The Netherlands).

Bosch J., Strozzi F., Zbilut J.P. and Zaldívar J.M., 2004, On-line runaway detection in isoperibolic batch and semibatch reactors using the divergence criterion, Computers Chem. Eng., 28, 527.

Copelli S., Derudi M. and Rota R., 2010a, Topological criteria to safely optimize hazardous chemical processes involving consecutive reactions, Ind. Eng. Chem. Res., 49, 4583.

Copelli S., Derudi M. and Rota R., 2010b, Safe operating conditions for semibatch processes involving consecutive reactions with autocatalytic behavior, Chem. Eng. Sci., 65, 5464.

Copelli S., Derudi M. and Rota R., 2011, Topological criterion to safely optimize hazardous chemical processes involving arbitrary kinetic schemes, Ind. Eng. Chem. Res., 50, 1588.

Copelli S., PhD Thesis, 2011, Mathematical and Topological criteria to safely optimize potentially runaway systems, Politecnico di Milano (ITA).

Hugo P. and Steinbach J., 1985, Praxisorientierte darstellung der thermischen sicherheitsgrenzen für den indirekt gekühlten semibatch-reaktor, Chemie Ingenieur Technik, 57, 780.

Maestri F. and Rota R., 2005a, Thermally safe operation of liquid-liquid semibatch reactors. Part I: single kinetically controlled reactions with arbitrary reaction order, Chem. Eng. Sci., 60, 3309.

Maestri F. and Rota R., 2005b, Thermally safe operation of liquid-liquid semibatch reactors. Part II: single diffusion controlled reactions with arbitrary reaction order, Chem. Eng. Sci., 60, 5590.

Maestri F. and Rota R., 2006a, Safe and productive operation of homogeneous semibatch reactors. I: development of a general procedure, Ind. Eng. Chem. Res., 45, 8002.

Maestri F. and Rota R., 2006b, Temperature diagrams for preventing decomposition or side reactions in liquid-liquid semibatch reactors, Chem. Eng. Sci., 61, 3068.

Morbidelli M. and Varma A., 1982, Parametric sensitivity and runaway in tubular reactors, AIChE J., 28, 705.

Morbidelli M. and Varma A., 1985, On parametric sensitivity and runaway criteria of pseudo-homogeneous tubular reactors, Chem. Eng. Sci., 40, 2165.

Morbidelli M. and Varma A., 1988, A generalized criterion for parametric sensitivity: application to thermal explosion theory, Chem. Eng. Sci., 43, 91.

Steinbach J., 1999, Safety Assessment for Chemical Processes, WILEY-VCH Verlag GmbH.

Steensma M. and Westerterp K.R., 1988, Thermally safe operation of a cooled semi-batch reactor. Slow liquid-liquid reactions, Chem. Eng. Sci., 43, 2125.

Steensma M. and Westerterp K.R., 1990, Thermally safe operation of a semibatch reactor for liquid-liquid reactions. Slow reactions, Ind. Eng. Chem. Res., 29, 1259.

Steensma M. and Westerterp K.R., 1991, Thermally safe operation of a semibatch reactor for liquid-liquid reactions. Fast reactions, Chem. Eng. Technol., 14, 367.

Stoessel F., 1993, What is your thermal risk?, Chem. Eng. Progress, 10, 68.

Strozzi F., Zaldívar J.M., Kronberg A.E. and Westerterp K.R., 1999, On-line runaway detection in batch reactors using chaos theory techniques, AIChE J., 45, 2429.

van Woezik B.A.A. and Westerterp K.R., 2000, The nitric acid oxidation of 2-octanol. A model reaction for multiple heterogeneous liquid-liquid reactions, Chem. Eng. Proc., 39, 521.

van Woezik B.A.A. and Westerterp K.R., 2001, Runaway behaviour and thermally safe operation of multiple liquid-liquid reactions in the semibatch reactor. The nitric acid oxidation of 2-octanol, Chem. Eng. Proc., 41, 59.

Varma A. and Morbidelli M., 1997, Mathematical Methods in Chemical Engineering, Oxford University Press, New York (USA).

Varma A., Morbidelli M. and Wu H., 1999, Parametric Sensitivity in Chemical Systems, Cambridge University Press, Cambridge (UK).

Wu H., Morbidelli M. and Varma A., 1998a, An approximate criterion for reactor thermal runaway, Chem. Eng. Sci., 53, 3341.

Wu H., Morbidelli M. and Varma A., 1998b, Pseudo-adiabatic operation and runaway in tubular reactors. An approximate criterion for reactor thermal runaway, AIChE J., 44, 1157.

Zaldívar J.M., Cano J., Alós M.A., Sempere J., Nomen R., Lister D., Maschio G., Obertopp T., Gilles E.D., Bosch J. and Strozzi F., 2003, A general criterion to define runaway limits in chemical reactors, J. Loss Prev. Proc. Ind., 16, 187.

Zaldívar J.M., Bosch J., Strozzi F. and Zbilut J.P., 2005, Early warning detection of runaway initiation using non-linear approaches, Int. J. Nonlinear Sci. Numeric. Simul., 10, 299.