Thermal behavior of a semibatch reactor during upset conditions as a function of dosing and temperature controller type

S. Copelli & V. Torretta
Università degli Studi dell'Insubria, Varese, Italy

M. Derudi, R. Rota, C. Sala Cattaneo & G. Nano
Politecnico di Milano, Milano, Italy

ABSTRACT: In fine chemical industries, potentially runaway reactions are often carried out in semibatch reactors to better control the heat evolution. For such processes, an uncontrolled temperature increase can trigger secondary undesired reactions or, worse, decompositions of the reacting mixture with consequent reactor pressurization and, eventually, physical explosion. For this reason, during years, it has been tried to simulate how a runaway phenomenon evolves as a consequence of a number of upset operating conditions: e.g. dosing errors, cooling system failure or external fire. In this work, a dedicated software has been developed and used to simulate a dosing error occurring during an industrial synthesis. Particularly, it has been analyzed the effect of the different industrial temperature control modes (isoperibolic and isothermal) and their related controller parameters onto the time evolution of the main process variables. Theoretical simulations have shown that different scenarios can arise as a function of these control features.

1 INTRODUCTION

Runaway phenomena are a common problem in fine chemical and pharmaceutical industries. 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 (terrible examples are Seveso (1976) and Bhopal (1984) accidents). This aspect has motivated the great amount of work that has been done on runaway phenomena for batch (B) and SemiBatch (SB) reactors during the last twenty-five years (Steensma & Westerterp 1988, Balakotaiah et al. 1995, Varma et al. 1999, Zaldívar et al. 2003, Maestri et al. 2009a, Copelli et al. 2011, Maria & Stefan 2011, Copelli et al. 2013a, 2013b, 2013c). Particularly, a runaway reaction is the consequence of a reacting system thermal loss of control that can be triggered by a number of upset operating conditions: dosing errors, cooling system failure or external fire. Such an event, also called thermal explosion, is responsible for an increase of the desired reaction rate and can also lead to the triggering of unwanted decomposition reactions of the reacting mixture with consequent reactor pressurization and, eventually, its collapse.

Stoessel (1993), basing only on process information, classified exothermic reaction processes into five classes as a function of the relative ranking of: process temperature (T_p), maximum temperature that can be achieved by synthesis reaction as a consequence of cooling system failure ("Maximum Temperature due to Synthesis Reaction", $MTSR$), boiling point of the solvent (T_{eb}), Maximum Allowable Temperature (MAT) to avoid decomposition reactions taking place. Situations characterized by $MTSR$ values higher than the MAT values must be regarded as critical from a safety point of view and need particular attention. Such a thermal classification is very useful for a quick evaluation of the potential danger associated with a process but, since it summarizes all data related to unwanted side reactions into a single pieces of information, the MAT parameter, it does not permit to evaluate in details all the runaway consequences. Moreover, if a process is carried out under isothermal conditions, the temperature controller helps to face a runaway event preventing, in some cases, to reach the MAT. In such situations, a Loss of Control (LoC) involving a more general behavior than that identified for isoperibolic SBRs, where the loss of thermal control is always associated to a sharp temperature peak, can be identified. In fact, in

controlled isothermal SBRs a loss of thermal control can lead either to a sharp temperature peak or simply to a loss of the temperature setpoint. The latter situation is obviously less dangerous than the first one, but it cannot be considered suitable for operating the reactor from neither a product quality nor a safety point of view. Since no real control system can maintain the reactor temperature value exactly equal to the setpoint, it is necessary to define a range around the setpoint beyond which a loss of control is assumed. According to Copelli et al. (2013a), a maximum reactor temperature fluctuation of 2.5 °C has been assumed as the threshold value that, if overcome, evidences a LoC situation independently on the temperature versus time profiles.

For what concerns upset operating conditions, different literature studies have been dedicated to the problem of failure of the cooling system (Balchan et al. 1999, Kossoy & Akhmetshin 2012); but no studies regarding dosing errors have been carried out with the specific aim of analyzing the relation between the temperature control mode (isothermal or isoperibolic) used during the process and the probability of the occurrence of a loss of temperature control. This problem is particularly relevant because, industrially, the parameters of the temperature controller (that is, mainly, static gain and reset time) are tuned without considering a potential runaway triggerring caused by errors in the reactants dosing. Therefore, if this event occurs, there will be no information about the robustness of the temperature controller with respect to face such an anomaly during the synthesis.

The main aim of this work is to determine if, for some couples of static gain, K_p, and reset time, K_I, that can arise from a standard tuning procedure, an error on the dosing (e.g. doubling the reactant feeding rate) can cause a loss of the temperature control in a SBR where a potentially runaway reaction is carried out.

In order to achieve this goal, a complete characterization of the runaway phenomenon at full plant scale is fundamental and it must take into account all features related to reactants dosing, reactor temperature control (isothermal or isoperibolic) and thermo-chemical stability of the reacting mixture.

In this work, a previously validated model (Copelli et al. 2013d) has been suitably modiefied and used to simulate a dosing error in an industrial isoperibolic SBR (9 m³) where the nitration of 4-Chlorobenzotrifluoride (4-Cl BTF) to 4-Chloro-3-nitrobenzotrifluoride (4-Cl-3-nitroBTF—a chemical intermediate) by the means of mixed acids is carried out. Its implementation has been realized using MATLAB®. The mathematical model on which the software code is based, is able to simulate the time evolution of all the system dependent variables: reactor temperature, inlet and outlet coolant temperatures, conversion, reactor volume, liquid density, pressure and dosing policy thanks to a complete description of both the desired reaction (nitration) and the unwanted reacting mixture decomposition kinetics.

2 MATHEMATICAL MODEL

In the following, all the equations necessary for the complete system description will be briefly summarized. Particularly, a single desired reaction is assumed to occur in the liquid phase as follows:

$$A_{(l)} + B_{(l)} \Rightarrow C_{(l)} + D_{(l)} \qquad (1)$$

where A and B are the dosed and loaded reactants, respectively, C is the desired product and D represents all the side products. In addition to (1), the decomposition reaction of the desired product (formally, species C) must be also considered; this reaction is assumed to take place producing a gaseous (g) species G (G is a pseudo-species representing, in real conditions, a mixture of different gases):

$$C_{(l)} \Rightarrow G_{(g)} \qquad (2)$$

Reactions (1) and (2) are characterized by their corresponding microkinetic expressions:

$$r_1 = A_1 \cdot \exp\left(-E_{att,1}/RT\right) \cdot [A] \cdot [B] \qquad (3)$$

$$r_2 = A_2 \cdot \exp\left(-E_{att,2}/RT\right) \cdot [C]^2 \qquad (4)$$

The reacting system is heterogeneous (consisting of two liquid phases) and the reaction occurs in the continuous (c) phase.

The following model assumptions can be reasonably stated: 1) the reaction mass is perfectly macromixed; 2) the influence of the chemical reactions on the volume of the liquid phases is negligible; 3) no phase inversions occur; 4) heat generation effects are due to the chemical reactions only; 5) heat removal effects are related to both cooling and ambient dispersions; 6) the reactor can operate under both isoperibolic (jacket temperature controlled by a suitable controller) and isothermal conditions (reactor temperature controlled by a suitable controller); 7) dosing of species A is carried out at a constant rate.

Considering such hypotheses, the overall system of ordinary differential equations can be written as follows:

$$\frac{dT_{cool,IN}}{dt} = -K_p\left[\frac{dT_{contr}}{dt} - \frac{1}{K_I}\left(T_{set,contr} - T_{contr}\right)\right]$$

$$\frac{dT_{cool}}{dt} = \frac{Q_{cool}}{V_{cool}}\left(T_{cool,IN} - T_{cool}\right)$$
$$+ \frac{UA}{\rho_{cool}c_{p,cool}V_{cool}}\left(T - T_{cool}\right)$$

$$\frac{dT}{dt} = \varphi_{dos}\frac{c_{p,dos}}{\rho V c_{p,mix}}\left(T_{dos} - T\right)$$
$$+ \sum_{j=1}^{2} r_j\left(-\Delta H_{rxn,j}\right)V_{rxn,j}$$
$$- \frac{UA}{\rho V c_{p,mix}}\left(T - T_{cool}\right) - \frac{UA_{ext}}{\rho V c_{p,mix}}\left(T - T_{ext}\right)$$

$$\frac{dP}{dt}\left(V_{nom} - V\right) - P\frac{dV}{dt} = \frac{dn_{top}}{dt}RT + n_{top}R\frac{dT}{dt}$$
$$\frac{dn_i}{dt} = \sum_{j=1}^{2} r_j V_{rxn,j} \qquad i = C, G$$
$$\frac{dV}{dt} = \frac{\varphi_{dos}}{\rho} - \frac{V}{\rho}\frac{d\rho}{dt}$$
$$\frac{d\rho}{dt} = \varphi_\rho$$
$$\frac{dm_{dos}}{dt} = \varphi_{dos} = \frac{m_{TOT,dos}}{t_{dos}} \qquad (5)$$

Initial conditions:

$$T_{cool,IN} = T_{cool,IN,0},\ T_{cool} = T_{cool,0},\ T = T_0,$$
$$P = P_0,\ n_C = n_G = 0,\ V = V_0,\ \rho = \rho_0,\ m_{dos} = 0 \quad (6)$$

where m_{dos} is the dosing mass (kg), φ_{dos} is the dosing stream function, $T_{cool,IN}$ is the inlet coolant temperature (K), T_{cool} is the actual coolant temperature (K), $T_{contr,set}$ is the setpoint temperature of the controlled variable (K), T is the reactor temperature (K), T_{dos} is the dosing stream temperature (K), T_{ext} is the ambient temperature (K), K_p is the proportional (or static) gain of the temperature controller (-), K_I is the reset time of the temperature controller (s), φ_ρ is a function accounting for mixing rules (that can assume a number of different time, temperature and compositions dependent expressions), V is the total liquid reacting volume (m³), Q is the volumetric flow rate (m³/s), UA is the global heat transfer coefficient for the cooling system (W/K), UA_{ext} is the global heat transfer coefficient for the ambient (W/K), r_j is the j-th reaction rate (kmol/m³/s), $\Delta H_{rxn,j}$ is the

j-th reaction enthalpy (J/kmol), c_p is the specific heat capacity (J/kg/K), R is the ideal gas constant (= 8314 J/kmol/K), ρ is the density (kg/m³), and P is the pressure (Pa). Pedices *dos*, *mix*, *cool*, *contr*, *nom* and *top* mean dosing stream, reacting mixture, coolant, controlled variable (T_{cool} or T), reactor nominal volume and liquid free reactor volume, respectively.

Particularly, the first equation expresses the reactor temperature control mode (isoperibolic or isothermal); the second equation respresents the energy balance onto the external cooling jacket (assuming uniform coolant temperature); the third equation is the energy balance onto the reactor; the forth equation describes how the pressure inside the reactor varies as a function of temperature and permanent gases formation; the fifth and the sixth equation represent material balances for desired product C and its decomposition products G, respectively; the seventh equation expresses the global material balance onto the reactor; the eighth equation synthesizes the mixing rules for density determination; and, finally, the ninth equation expresses the dosing policy.

For what concerns upset operating conditions, an error in the dosing has been arbitrary considered due, for instance, to an operator mistake; particularly, since the beginning of the dosing period, the feeding rate has been doubled with respect to the correct value. Temperature controller saturation (T_{MIN} = 15 °C and T_{MAX} = 100 °C, coolant: water) and automatic reset have been also modeled.

3 REACTING SYSTEM

The dynamic behavior of an aromatic nitration in mixed acids involves a number of problems related to simultaneous interphase and intraphase transfer phenomena that strongly influence heat and mass transfer efficiencies. In order to operate under kinetically controlled conditions (where no heat or mass transfer limitations lower the overall conversion of the process), it is necessary to work with a sufficiently high stirrer speed.

In chemical and pharmaceutical industries, aromatic nitrations are normally carried out into an indirectly cooled SBR under intensive stirring conditions. In the present case, the species to be nitrated (that is, 4-Cl BTF) is added to a mixture of sulfuric and nitric acids in which sulfuric acid acts both as a solvent and as a dehydrating agent versus nitric acid to form the nitronium ion, NO_2^+, which is the electrophilic species reacting with the aromatic ring. The desired overall reaction is:

$$(7)$$
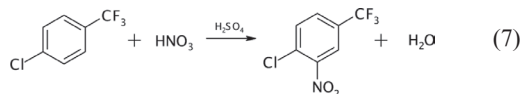
All information related to both the desired reaction and decomposition kinetics can be found in literature (Copelli et al. 2011, 2013d, Maestri et al. 2009b). In particular, the microkinetic parameters of reaction (1) are: $A_1 = 3.228 \times 10^{12}$ m^3 s/kmol and $E_{att,1} = 87260$ kJ/kmol, respectively. For what concerns reaction (2): A_2 is equal to 2.718×10^7 m^3 s/kmol if $T \leq 197$ °C, 3.814×10^6 m^3 s/kmol if $197 < T \leq 216$ °C, 2.783×10^6 m^3 s/kmol if $216 < T \leq 226$ °C and 1.276×10^4 m^3 s/kmol if $T > 226$ °C; $E_{att,2}$ is equal to 108279 kJ/kmol if $T < 197$ °C, 108940 kJ/kmol if $197 < T \leq 216$ °C, 107940 kJ/kmol if $216 < T \leq 226$ °C and 92121 kJ/kmol if $T > 226$ °C.

4 RESULTS AND DISCUSSION

In this section dynamic simulations of both normal and upset operating conditions, referring to a 9 m^3 indirectly cooled SBR operated in both isoperibolic and isothermal temperature control mode, are reported and compared as a function of the values of the temperature controller parameters K_p and K_I.

Since reactor characteristics and operating conditions for this process have been already reported elsewhere (Maestri et al. 2009b), they are only summarized in Table 1.

4.1 Normal conditions

The 4-Chlorobenzotrifluoride nitration reaction can be operated under safe and productive conditions using both isothermal and isoperibolic temperature control mode. Using an isothermal temperature control mode the process should be operated at about 35 °C (T_{set}) using a dosing time equal to 300 min; while, using an isoperibolic temperature control mode, the process must be operated using the same dosing time but at temperatures

Table 1. Characteristics and operating parameters for the industrial reactor.

Parameters	Value	Unit
$(UA)_0$	4910	W/K
T_0	308	K
t_{dos}	300	min
ΔT_{ad}	129	K
V_0	4.688	m^3
V_{dos}	1.633	m^3
$c_{p,0}$	1477	J/kg/K
$c_{p,dos}$	869	J/kg/K
ρ_0	1787	kg/m^3
ρ_{dos}	1353	kg/m^3

higher than 35 °C ($T_{cool,set}$) because of the presence of a runaway operating region for lower temperatue values (Maestri et al. 2009b). Since these operating conditions have been established using both runaway detection and optimization criteria, it is expected that, independently of the temperature control parameters K_p and K_I, the process is substantially zero sensitive (that is, it exhibits a low parametric sensitivity) with respect to whatever consistent perturbations.

Considering an isothermal temperature control mode, Figures 1–4 show the effect of the variation
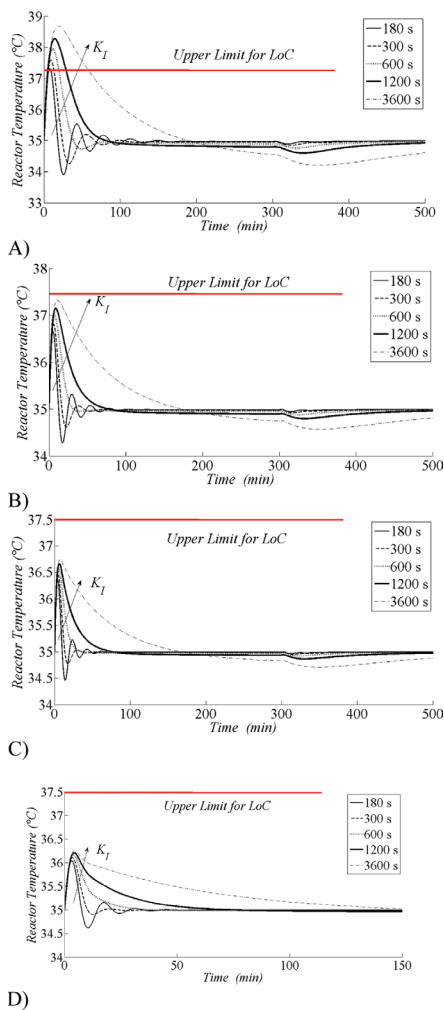

A)

B)

C)

D)

Figure 1. Reactor temperature vs. time profiles as function of static gain and reset time. A) $K_p = 2$ and 180 s $< K_I < 3600$ s; B) $K_p = 4$ and 180 s $< K_I < 3600$ s; C) $K_p = 6$ and 180 s $< K_I < 3600$ s; D) $K_p = 10$ and 180 s $< K_I < 3600$ 3 s. Normal operating conditions ($t_{dos} = 300$ min) and isothermal temperature control mode ($T_{set} = 35$ °C).
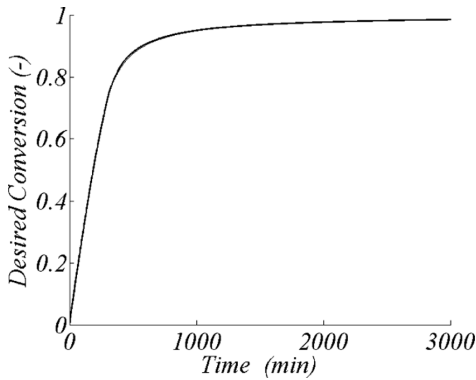
Figure 2. Conversion vs. time profile for all static gains and reset times analyzed for the 4-Chlorobenzotrifluoride nitration under normal operating conditions (t_{dos} = 300 min) and isothermal temperature control mode (T_{set} = 35 °C).
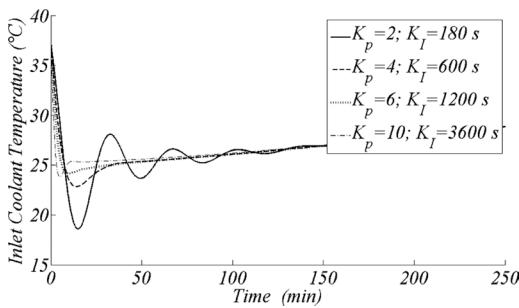

Figure 3. Inlet coolant temperature vs. time profiles as function of an extract of static gain and reset time couples (K_p = 2 and K_I = 180 s; K_p = 4 and K_I = 600 s; K_p = 6 and K_I = 1200 s; K_p = 10 and K_I = 3600 s). 4-Chlorobenzotrifluoride nitration under normal operating conditions and isothermal temperature control mode.
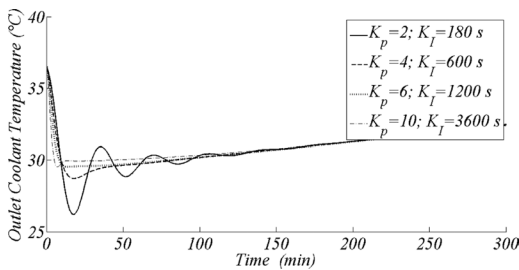

Figure 4. Outlet coolant temperature vs. time profiles as function of an extract of static gain and reset time couples (K_p = 2 and K_I = 180 s; K_p = 4 and K_I = 600 s; K_p = 6 and K_I = 1200 s; K_p = 10 and K_I = 3600 s). 4-Chlorobenzotrifluoride nitration under normal operating conditions and isothermal temperature control mode.

of the temperature control parameters K_p and K_I on: reactor temperature (Fig. 1), conversion with respect to the desired product C (Fig. 2), inlet (Fig. 3) and outlet (Fig. 4) coolant temperatures.

As it can be noted by observing both Figure 1 and Table 2, which reports (for all analyzed K_p and K_I couples) maximum and minimum reactor temperature registered during a simulation run under normal operating conditions (that is, T_{set} = 35 °C and t_{dos} = 300 min), the system operates without Loss of Control (LoC) for whatever reset time when the static gain is larger than 4. When K_p is equal to 2, only for K_I lower than 180 s, the LoC is avoided.

These evidences confirm that the process is effectively almost zero sensitive with respect to whatever type of consistent perturbation on the controller parameters.

It is worth to evidence that observed reactor temperature fluctuations are so small that no effect can be noticed in terms of desired product conversion: particularly, all conversion vs. time curves, independly on K_p and K_I values, overlap as shown in Figure 2.

Figure 3 shows the inlet coolant temperature (direct manipulated variable) vs. time profiles for the most significative couples of K_p and K_I analyzed in this work. It can be easily observed that no temperature controller saturation conditions (that is, T_{MIN} = 15 °C—minor saturation limit—or T_{MAX} = 100 °C—major saturation limit) are reached for whatever value of K_p and K_I, thus confirming stable operating conditions.

Finally, Figure 4 reports the outlet coolant temperature vs. time profiles for some K_p and K_I values. Also from these curves it is evident that stable conditions are achieved.

Table 2. Maximum (positive) and minimum (negative) deviation of the reactor temperature from the set point as a function of static gain and reset time. Normal operating conditions (t_{dos} = 300 min) and isothermal temperature control mode (T_{set} = 35 °C).

K_p	K_I					
	60	180	300	600	1200	3600
2	1.9	2.3	2.6	3.0	3.3	3.7
	−2.0	−1.1	−0.8	−0.3	−0.4	−0.8
4	1.6	1.7	1.8	2.0	2.2	2.3
	−1.6	−0.7	−0.4	−0.1	−0.2	−0.4
6	1.7	1.4	1.5	1.6	1.7	1.8
	−1.8	−0.6	−0.2	−0.1	−0.1	−0.3
8	1.3	1.2	1.2	1.3	1.4	1.4
	−1.4	−0.5	−0.1	−0.1	−0.1	−0.2
10	1.2	1.0	1.1	1.2	1.2	1.3
	−1.2	−0.4	−0.1	−0.1	−0.1	−0.2

It is important to state that values of K_I lower than 180 s lead to a strong oscillating behavior of both reactor and inlet/outlet coolant temperatures. This situation, even if it does not lead to a LoC as it can be observed from Table 2, is undesirable because the temperature controller is continuously urged to modify the inlet coolant temperature in order to maintain reactor temperature close to the setpoint (35 °C). Figure 5 reports, for the sake of example, one of these strongly oscillating profiles with reference to the reactor temperature ($K_p = 2$; $K_I = 60$ s).

Considering an isoperibolic temperature control mode, Figure 6 reports the reactor temperature evolution during time as a function of an extract of relevant K_p and K_I couples.
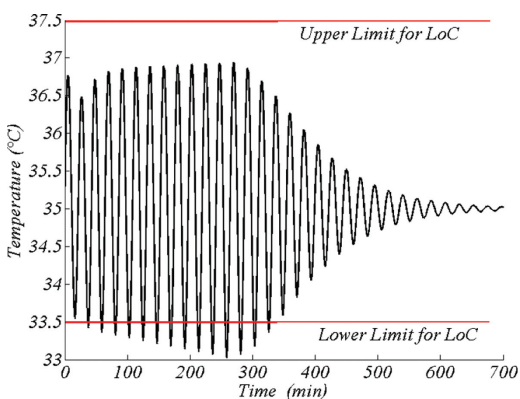

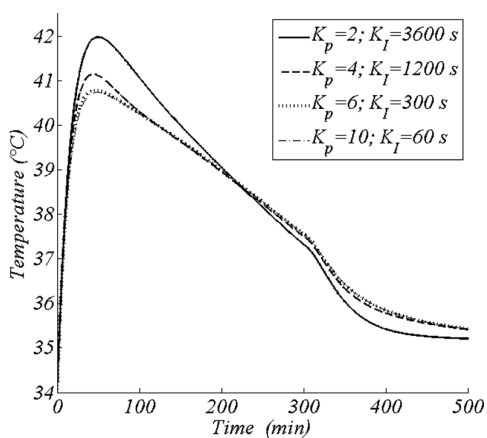Figure 5.   Reactor temperature vs. time profile for $K_p = 2$ and $K_I = 60$ s.

Figure 6.   Reactor temperature vs. time profiles as function of an extract of static gain and reset time couples ($K_p = 10$ and $K_I = 60$ s; $K_p = 6$ and $K_I = 300$ s; $K_p = 4$ and $K_I = 1200$ s; $K_p = 2$ and $K_I = 3600$ s). Normal operating conditions and isoperibolic temperature control mode.

As it can be noticed observing both Figure 6 and Table 3 (which reports, for all analyzed K_p and K_I, the maximum reactor temperature registered during a simulation run under normal operating conditions; that is, $T_{cool,set} = 35$ °C and $t_{dos} = 300$ min), there is no significative influence of the temperature controller parameters onto the reactor behavior. In fact, reactor temperature increase spans from a minimum value of 6.7 °C (obtained for $K_p = 10$ and $K_I = 60$ s) to a maximum of 8.0 °C (obtained for $K_p = 2$ and $K_I = 3600$ s).

Since reactor temperature profiles are very close each other, no appreciable variations of the conversion profile can be detected. Anyway, the overall conversion to the desired product is always higher than the correspondent profile obtained using an isothermal temperature control mode.

For what concerns the outlet coolant temperature, all profiles are inside the range: $T_{cool,set} + 2.5$ °C – $T_{cool,set} - 2.5$ °C for whatever K_p and K_I value.

4.2   Upset conditions

In this work it has been hypothesised a setting error of the dosing stream that implies a doubling in the feeding rate: that is, dosing time is set equal to 150 min instead of 300 min (stable operating conditions).

Let us consider at first an isothermal temperature control mode. Figures 7 and 8 show the effect of the variation of the temperature control parameters K_p and K_I on: reactor temperature (Fig. 7) and inlet (Fig. 8) coolant temperatures.

As it can be noted by observing both Figure 7 and Table 4, which reports (for all analyzed K_p and K_I couples) maximum and minimum reactor temperature registered during a simulation run under upset operating conditions (that is, $T_{set} = 35$ °C and $t_{dos} = 150$ min), the system operates without Loss of Control (LoC) for whatever reset time only when the static gain is major of 10.

When K_p is equal to 2 or 4, LoC cannot be avoided. These evidences confirm that the process

Table 3.   Maximum deviation of the reactor temperature from the set point as a function of static gain and reset time. Normal operating conditions ($t_{dos} = 300$ min) and isoperibolic temperature control mode ($T_{cool,set} = 35$ °C).

K_p	K_I					
	60	180	300	600	1200	3600
2	6.8	6.88	6.9	7.2	7.5	8.0
4	6.7	6.8	6.8	6.9	7.1	7.4
6	6.7	6.8	6.8	6.9	7.0	7.2
8	6.7	6.8	6.8	6.8	6.9	7.1
10	6.7	6.7	6.8	6.8	6.9	7.0

A)

B)

C)

D)
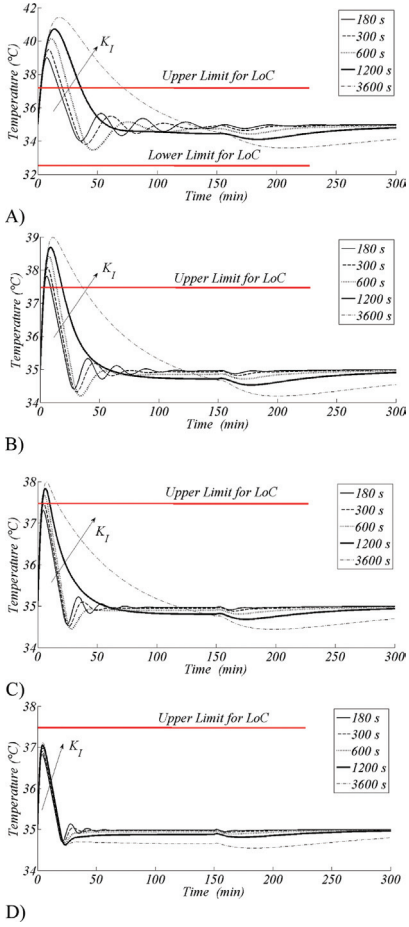
Figure 7. Reactor temperature vs. time profiles as function of static gain and reset time. A) $K_p = 2$ and 180 s < K_I < 3600 s; B) $K_p = 4$ and 180 s < K_I < 3600 s; C) $K_p = 6$ and 180 s < K_I < 3600 s; D) $K_p = 10$ and 180 s < K_I < 3600 s. Upset operating conditions and isothermal temperature control mode.
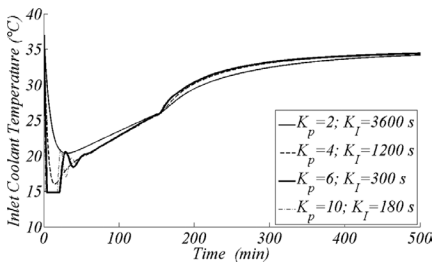

Figure 8. Inlet coolant temperature vs. time profiles as function of an extract of static gain and reset time couples ($K_p = 2$ and $K_I = 3600$ s; $K_p = 4$ and $K_I = 1200$ s; $K_p = 6$ and $K_I = 300$ s; $K_p = 10$ and $K_I = 180$ s). Upset operating conditions and isothermal temperature control mode.

Table 4. Maximum (positive) and minimum (negative) deviation of the reactor temperature from the set point as a function of static gain and reset time. Upset operating conditions ($t_{dos} = 150$ min) and isothermal temperature control mode ($T_{set} = 35$ °C).

K_p	K_I					
	60	180	300	600	1200	3600
2	3.0	4.0	4.5	5.1	5.7	6.4
	−1.7	−1.0	−1.2	−1.5	−0.9	−1.4
4	2.3	2.8	3.1	3.4	3.7	4.0
	−1.6	−0.6	−0.7	−0.8	−0.5	−0.8
6	2.0	2.3	2.5	2.7	2.8	3.0
	−1.6	−0.4	−0.5	−0.6	−0.3	−0.6
8	1.8	2.0	2.1	2.3	2.4	2.5
	−1.4	−0.4	−0.4	−0.4	−0.5	−0.4
10	1.6	1.8	1.9	2.0	2.1	2.1
	−1.2	−0.3	−0.3	−0.4	−0.4	−0.5

is operating under upset operating conditions and no almost zero sensitivity is exhibited with respect to whatever type of consistent perturbation on temperature controller parameters (since upper LoC limit is passed). It is worth observing that, in this case, K_p and K_I play an important role in stabilizing the process from the thermal point of view. In fact, using values of K_p equal or major than 10, LoC is avoided regardless the reset time value.

Even in this case, reactor temperature fluctuations are small enough that no appreciable effect can be noticed in term of desired product conversion: particularly, all conversion vs. time curves, independently of K_p and K_I values, overlap.

Figure 8 shows the inlet coolant temperature (direct manipulated variable) vs. time profiles for some couples of K_p and K_I. It can be easily observed that temperature controller saturation conditions (that is, $T_{MIN} = 15$ °C—minor saturation limit—or $T_{MAX} = 100$ °C—major saturation limit) can be reached for some values of K_p and K_I (e.g. $K_p = 6$ and $K_I = 300$ s; $K_p = 10$ and $K_I = 180$ s), thus confirming that the system is operating under unstable operating conditions. Similar observations can be done looking at the outlet coolant temperature vs. time profiles.

Also in this case, values of K_I lower than 180 s lead to a strong oscillating behavior of reactor and inlet/outlet coolant temperatures.

Considering an isoperibolic temperature control mode, Figure 9 reports the reactor temperature evolution during time as a function for some K_p and K_I couple. As it can be noticed observing both Figure 9 and Table 5 (which reports, for all analyzed K_p and K_I couples, the maximum reactor temperature registered during a simulation run under upset
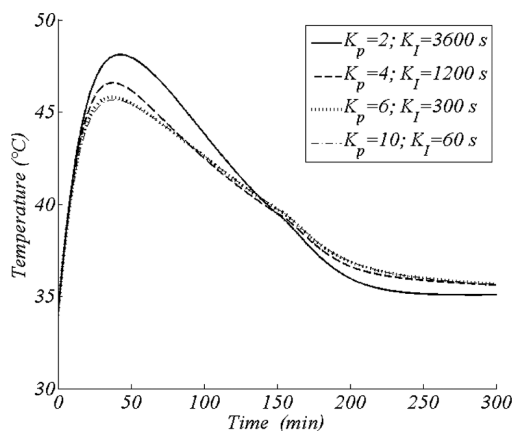
Figure 9. Reactor temperature vs. time profiles as function of an extract of static gain and reset time couples ($K_p = 2$ and $K_I = 3600$ s; $K_p = 4$ and $K_I = 1200$ s; $K_p = 6$ and $K_I = 300$ s; $K_p = 10$ and $K_I = 60$ s). Upset operating conditions and isoperibolic temperature control mode.

Table 5. Maximum deviation of the reactor temperature from the set point as a function of static gain and reset time. Upset operating conditions ($t_{dos} = 150$ min) and isoperibolic temperature control mode ($T_{cool,set} = 35$ °C).

K_p	K_I					
	60	180	300	600	1200	3600
2	11.7	11.9	12.2	12.8	13.4	14.1
4	11.7	11.8	11.9	12.2	12.6	13.1
6	11.7	11.7	11.8	12.0	12.3	12.7
8	11.7	11.7	11.8	11.9	12.1	12.4
10	11.7	11.7	11.7	11.9	12.1	12.3

operating conditions, that is, $T_{cool,set} = 35$ °C and $t_{dos} = 150$ min), there is no significative influence of the temperature controller parameters onto the reactor thermal behavior.

In fact, reactor temperature increase spans from a minimum value of 11.7 °C (obtained for $K_p = 10$ and $K_I = 60$) to a maximum of 14.1 °C (obtained for $K_p = 2$ and $K_I = 3600$).

Independently of the controller parameters values, a good setpoint management of the coolant temperature will be always achieved while reactor temperature evolution is mainly due to the balance between reaction rate and cooling system efficiency.

Also in this case, since reactor temperature profiles are close enough to each other, no appreciable variations of the conversion profile can be detected. Anyway, it has been observed that overall conversion to the desired product higher than

those correspondent to all the other analyzed cases are obtained. For what concern the outlet coolant temperature, temperature profiles comprised between $T_{cool,set} + 2.5$ and $T_{cool,set} -2.5$ °C have been obtained for all K_p and K_I values. Similarly, no temperature controller saturation is reached for all the investigated values of K_p and K_I.

5 CONCLUSIONS

In this work, a detailed modelling of a dosing error occurring during the industrial synthesis of 4-Chloro-3-nitrobenzotrifluoride has been developed with the aim of determining if, for some couples of the temperature controller parameters (static gain, K_p, and reset time, K_I), a loss of the temperature control can be avoided. Results have shown that, in the isothermal temperature control mode, the LoC generated from a doubling of the feeding rate can be avoided if K_p values equal or higher than 10 are used (regardless the reset time). For what concerns the isoperibolic temperature control mode, it has been observed that temperature controller parameters do not play an important role in stabilizing the process since its thermal dynamics is mainly dominated by reaction rate and cooling efficiency.

REFERENCES

Balakotaiah, V., Kodra, D. & Nguyen, D. 1995. Runaway limits for homogeneous and catalytic reactors. *Chemical Engineering Science* 50: 1149–1171.
Balchan, A.S., Paquet D.A. Jr., & Klein, J.A. 1999. Emergency relief adequacy for acrylic polymerization processes. *Process Safety Progress* 18: 71–77.
Bosch, J., Strozzi, F., Lister, D.G., Maschio, G. & Zaldívar, J.M. 2004. Sensitivity Analysis in Polymerization Reactions Using the Divergence Criterion. *Process Safety and Environmental Protection* 81: 18–25.
Casson, V., Lister, D.G., Milazzo, M.F. & Maschio, G. 2012. Comparison of criteria for prediction of runaway reactions in the sulphuric acid catalyzed esterification of acetic anhydride and methanol. *Journal of Loss Prevention in the Process Industries* 25: 209–217.
Copelli, S., Derudi, M. & Rota, R. 2011. Topological criterion to safely optimize hazardous chemical processes involving arbitrary kinetic schemes. *Industrial & Engineering Chemistry Research* 50: 1588–1598.
Copelli, S., Torretta, V., Lunghi, A., Derudi, M., Sala Cattaneo, C. & Rota, R. 2013a. Emulsion Polymerization of Butyl Acrylate: Safe Optimization Using Topological Criteria. *Industrial & Engineering Chemistry Research,* doi: 10.1021/ie302356 s.
Copelli, S., Derudi, M., Sala Cattaneo, C., Nano, G., Torretta, V. & Rota, R. 2013b. Classification and Optimization of Potentially Runaway Processes using Topology Tools. *Computers and Chemical Engineering* 56: 114–127.

Copelli, S., Torretta, V., Pasturenzi, C., Derudi, M., Sala Cattaneo, C. & Rota, R. 2013c. On the divergence criterion for runaway detection: application to complex controlled systems. *Journal of Loss Prevention in the Process Industries,* doi: 10.1016/j.jlp.2013.05.004.

Copelli, S., Torretta, V., Raboni, M., Derudi, M., Sala Cattaneo, C., Nano, G. & Rota, R. 2013d. Synthesis of 4-Chloro-3-nitrobenzotrifluoride: Industrial Thermal Runaway Simulation due to Cooling System Failure. *Process Safety and Environmental Protection* submitted.

Kossoy, A.A. & Akhmetshin, Y.G. 2012. Simulation-based approach to design of inherently safer processes. *Process Safety and Environmental Protection* 90: 349–356.

Maestri, F., Copelli, S., Rota, R., Gigante, L., Lunghi, A. & Cardillo, P. 2009a. Simple procedure for optimally scaling-up fine chemical processes. I. Practical tools. *Industrial & Engineering Chemistry Research* 48: 1307–1315.

Maestri, F., Copelli, S., Rota, R., Gigante, L., Lunghi, A. & Cardillo, P. 2009b. Simple procedure for optimal scale-up of fine chemical processes. II. Nitration of 4-chlorobenzotrifluoride. *Industrial & Engineering Chemistry Research* 48: 1316–1324.

Maria, G. & Stefan, D.N. 2011. Evaluation of critical operating conditions for a semi-batch reactor by complementary use of sensitivity and divergence criteria. *Chemical and Biochemical Engineering Quarterly* 25: 9–25.

Steensma, M. & Westerterp, K.R. 1988. Thermally safe operation of a cooled semi-batch reactor. Slow liquid-liquid reactions. *Chemical Engineering Science* 43: 2125–2132.

Stoessel, F. 1993. What is your thermal risk? *Chemical Engineering Progress* 10: 68–75.

Varma, A., Morbidelli, M. & Wu, H. 1999. *Parametric Sensitivity in Chemical Systems*. Cambridge University Press: Cambridge.

Zaldívar, J.M., Cano, J., Alós, M.A., Sempere, J.M., Nomen, R., Lister, D., Maschio, G., Obertopp, T., Gilles, E.D., Bosch, J. & Strozzi, F. 2003. A general criterion to define runaway limits in chemical reactors. *Journal of Loss Prevention in the Process Industries* 16: 187–200.