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

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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 triggering 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, $K_r$, 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 modified and used to simulate a dosing error in an industrial isoperibolic SBR ($9 \text{ m}^3$) 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:

$$A_{(l)} + B_{(l)} \Rightarrow C_{(l)} + D_{(l)}$$  \hspace{1cm} (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):

$$C_{(g)} \Rightarrow G_{(g)}$$  \hspace{1cm} (2)

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

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

$$r_2 = A_2 \cdot \exp\left(-E_{\text{att.2}}/RT\right) \cdot [C]^2$$  \hspace{1cm} (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:

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

\[
\frac{dT_{\text{cool}}}{dt} = \frac{Q_{\text{cool}}}{V_{\text{cool}}} (T_{\text{cool,IN}} - T_{\text{cool}}) + \frac{UA}{\rho_c p_c \text{cool} V_{\text{cool}}} (T - T_{\text{cool}})
\]

\[
\frac{dT}{dt} = \frac{\varphi_{\text{dos}}}{\rho_{\text{p, dos}}} \left( T_{\text{dos}} - T \right)
\]

\[
+ \sum_{j=1}^2 r_j (\Delta H_{\text{rxn},j}) V_{\text{rxn},j}
\]

\[
- \frac{UA}{\rho_c \text{p,mix}} (T - T_{\text{cool}}) - \frac{UA_{\text{ext}}}{\rho_c \text{p,mix}} (T - T_{\text{ext}})
\]

\[
\frac{dP}{dt} (V_{\text{nom}} - V) - P \frac{dV}{dt} = \frac{d_{\text{top}}}{RT} + n_{\text{top}} R \frac{dT}{dt}
\]

\[
\frac{dn_i}{dt} = \sum_{j=1}^2 r_j V_{\text{rxn},j} i = C, G
\]

\[
\frac{dV}{dt} = \frac{\varphi_{\text{dos}}}{\rho} - \frac{V}{\rho} \frac{d\rho}{dt}
\]

\[
\frac{d\rho}{dt} = \phi_p
\]

\[
\frac{dm_{\text{dos}}}{dt} = \varphi_{\text{dos}} = \frac{m_{\text{TOT,dos}}}{t_{\text{dos}}}
\]

Initial conditions:

\[
T_{\text{cool,IN}} = T_{\text{cool,IN},0}, T_{\text{cool}} = T_{\text{cool},0}, T = T_0
\]

\[
P = P_0, n_C = n_G = 0, V = V_0, \rho = \rho_0, m_{\text{dos}} = 0
\]

where \( m_{\text{dos}} \) is the dosing mass (kg), \( \varphi_{\text{dos}} \) is the dosing stream function, \( T_{\text{cool,IN}} \) is the inlet coolant temperature (K), \( T_{\text{cool}} \) is the actual coolant temperature (K), \( T_{\text{set,contr}} \) is the setpoint temperature of the controlled variable (K), \( T \) is the reactor temperature (K), \( T_{\text{dos}} \) is the dosing stream temperature (K), \( T_{\text{amb}} \) is the ambient temperature (K), \( K_p \) is the proportional (or static) gain of the temperature controller (\(^{-1}\)), \( K_f \) is the reset time of the temperature controller (s), \( \varphi_p \) 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 (m\(^3\)), \( Q \) is the volumetric flow rate (m\(^3\)/s), \( UA \) is the global heat transfer coefficient for the cooling system (W/K), \( UA_{\text{ext}} \) is the global heat transfer coefficient for the ambient (W/K), \( r_j \) is the j-th reaction rate (kmol/m\(^3\)/s), \( \Delta H_{\text{rxn},j} \) is the j-th reaction enthalpy (J/kmol), \( c_p \) is the specific heat capacity (J/kg/K), \( R \) is the ideal gas constant (\( = 8.314 \text{ J/kmol/K} \)), \( \rho \) is the density (kg/m\(^3\)), and \( P \) is the pressure (Pa). Pedicess \( \text{dos, mix, cool, contr, nom} \) and \( \text{top} \) mean dosing stream, reacting mixture, coolant, controlled variable (\( T_{\text{cool}} \) 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 represents 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 (\( T_{\text{MIN}} = 15 \text{ °C} \) and \( T_{\text{MAX}} = 100 \text{ °C} \), 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 nitration 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, \( \text{NO}_2^+ \), which is the electrophilic species reacting with the aromatic ring. The desired overall reaction is:

\[
\text{CF}_4 + \text{HNO}_3 \rightarrow \text{CF}_3 \text{CF}_2 \text{Cl} + \text{HNO}_2 + \text{H}_2\text{O}
\]
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: $A_1 = 3.228 \times 10^{12} \text{ m}^3\text{s/kmol}$ and $E_{att,1} = 87260 \text{ kJ/kmol}$, respectively. For what concerns reaction (2): $A_2$ is equal to $2.718 \times 10^7 \text{ m}^3\text{s/kmol}$ if $T \leq 197 \text{ °C}$, $3.814 \times 10^6 \text{ m}^3\text{s/kmol}$ if $197 < T \leq 216 \text{ °C}$, $2.783 \times 10^6 \text{ m}^3\text{s/kmol}$ if $216 < T \leq 226 \text{ °C}$ and $1.276 \times 10^4 \text{ m}^3\text{s/kmol}$ if $T > 226 \text{ °C}$; $E_{att,2}$ is equal to $108279 \text{ kJ/kmol}$ if $T < 197 \text{ °C}$, $108940 \text{ kJ/kmol}$ if $197 < T \leq 216 \text{ °C}$, $107940 \text{ kJ/kmol}$ if $216 < T \leq 226 \text{ °C}$ and $92121 \text{ kJ/kmol}$ if $T > 226 \text{ °C}$.

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 $35 \text{ °C}$ ($T_{set}$) 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 higher than $35 \text{ °C}$ ($T_{cool,set}$) because of the presence of a runaway operating region for lower temperature 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

![Figure 1](image-url)

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 $180 s < K_I < 3600 s$. Normal operating conditions ($t_{dos} = 300$ min) and isothermal temperature control mode ($T_{set} = 35 \text{ °C}$).

| Table 1. Characteristics and operating parameters for the industrial reactor. |
|----------------------|---------|----------|
| Parameters          | Value   | Unit     |
| $(UA)_b$            | 4910    | W/K      |
| $T_0$               | 308     | K        |
| $t_{dos}$           | 300     | min      |
| $\Delta T_{ad}$     | 129     | K        |
| $V_0$               | 4.688   | m$^3$    |
| $V_{dos}$           | 1.633   | m$^3$    |
| $c_{pit}$           | 1477    | J/kg/K   |
| $c_{p,dos}$         | 869     | J/kg/K   |
| $\rho_0$            | 1787    | kg/m$^3$ |
| $\rho_{dos}$        | 1353    | kg/m$^3$ |
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 ($t_{dos} = 300 \text{ min}$) and isothermal temperature control mode ($T_{set} = 35 \degree \text{C}$).

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<tr>
<th>$K_p$</th>
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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.

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.

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, $T_{cool, set} = 35$ °C and $t_{dos} = 150$ min), the system operates without Loss of Control (LoC) for whatever $K_p$ and $K_I$ value.

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).

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

Figure 8. Inlet coolant temperature vs. time profiles as function of static gain and reset time. \(T_{MIN} = 15 \text{ ºC}—\text{minor saturation limit}—\text{or } T_{MAX} = 100 \text{ ºC}—\text{major saturation limit}\) can be reached for some values of \(K_p\) and \(K_I\) (e.g. \(K_p = 6\) and \(K_I = 300 \text{ s}\); \(K_p = 10\) and \(K_I = 180 \text{ s}\)), 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.

Figure 9 shows 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 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.

### 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 (\(t_{dos} = 150 \text{ min}\)) and isothermal temperature control mode (\(T_{set} = 35 \text{ ºC}\)).

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</tr>
<tr>
<td>1.6</td>
<td>1.8</td>
<td>1.9</td>
<td>2.0</td>
<td>2.1</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>-1.2</td>
<td>-0.3</td>
<td>-0.3</td>
<td>-0.4</td>
<td>-0.4</td>
<td>-0.5</td>
<td></td>
</tr>
</tbody>
</table>

is operating under upset operating conditions and

Considering an isoperibolic temperature control mode, Figure 9 reports the reactor temperature evolution during time as a function for some \(K_p\) and \(K_I\) couples. 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
those correspondent to all the other analyzed cases are obtained. For what concern the outlet coolant temperature, temperature profiles comprised between $T_{\text{cool,set}} + 2.5$ and $T_{\text{cool,set}} - 2.5$ °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


