Safe optimization of potentially runaway processes using topology based tools and software

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Abstract: In chemical industries, fast and strongly exothermic reactions are often to be carried out to synthesize a number of intermediates and final desired products. Such processes can exhibit a phenomenon known as "thermal runaway" that consists in a reactor temperature loss of control.

During the course of the years, lots of methods, aimed to detect the set of operating parameters (e.g., dosing times, initial reactor temperature, coolant temperature, etc..) at which such a dangerous phenomenon can occur, have been developed. Moreover, in the last few years, the attention has been posed on safe process optimization, that is how to compute the set of operating parameters able to ensure high reactor productivity and, contextually, safe conditions.

To achieve this goal, with particular reference to industrial semibatch synthesis carried out using both isothermal and isoperibolic temperature control mode, a dedicated optimization software has been implemented. Such a software identifies the optimum set of operating parameters using a topological criterion able to bind the so-called "*QFS* region" (where reactants accumulation is low and all the heat released is readily removed by the cooling equipment) and, then, iteratively searching for the constrained system optimum. To manage the software, only a few experimental parameters are needed; essentially: heat(s) of reaction, apparent system kinetics (Arrhenius law), threshold temperature(s) above which unwanted side reactions, decompositions or boiling phenomena are triggered, heat transfer coefficients and reactants heat capacities. Such parameters can be obtained using simple calorimetric techniques (*DSC*, *ARC*, *RC1*, etc..). Over the optimization section, the software posses a simulation section where both normal and upset operating conditions (such as pumps failure and external fire) can be tested.

Keywords: Thermal Runaway, Chemical reactors, Safe Optimization, Topological Criterion

1. INTRODUCTION

In pharmaceutical and fine chemical industries, fast and strongly exothermic reactions are often carried out in semibatch reactors (*SBRs*) in order to better control the heat evolution by the feeding rate. In fact, for such processes, a phenomenon known as "thermal runaway" may be triggered whenever the rate of heat removal by a dedicated cooling system becomes lower than the rate of heat production. Such a dangerous phenomenon consists in an uncontrolled reactor temperature increase that, occurring in practically adiabatic conditions, can trigger (at temperatures higher than a certain threshold value that, in the following, will be referred to as *MAT*, acronym of "Maximum Allowable Temperature") secondary undesired exothermic reactions or, worse, decompositions of the whole reacting mixture with consequent reactor pressurization due to incoercible gases formation. If the internal reactor pressure overcomes a critical value, the reactor can explode releasing high amounts of toxic and/or flammable gases into the atmosphere and leading to disastrous consequences for both the workers and the inhabitants of the damaged factory neighboring. Terrible examples of such scenarios are Seveso (1976) and Bhopal (1984) accidents. Minor and recent examples are the T2 laboratories accident in Jacksonville, Florida (2007), where 4 workers died and 32 people were injured, and the Bayer CropScience LP, West Virginia (2008), where 2 workers died and 8 people were injured [1].

As a consequence, during the last 25 years, a considerable number of studies on the detection of the so called "runaway boundaries", namely the set of operating parameters at which a runaway phenomenon may be triggered, has been performed [2-5]. However, from a practical viewpoint, the desired goal of whatever enterprise is to define a set of operating parameters (e.g. initial reactor temperature and dosing time) for which the maximum reactor productivity is attained, maintaining safe conditions.

Recently, a criterion able to search for the optimum operating conditions of a generic exothermic semibatch reactor, operated in the isoperibolic temperature control mode and accounting for thermal stability and productivity constraints, has been developed: the topological criterion [6-10].

Successively, such a criterion has been extended by introducing jacket temperature and dosing stream control equations, mixing rules, cooling system energy balance and global material balance into the system of ordinary differential equations describing the process dynamics [10]. Such an extension of the theory allows for the topological criterion use to optimize processes carried out at the full-plant scale, where complex feeding strategies and temperature control systems (e.g. isothermal, isoperibolic, etc..) make other runaway boundary detection and optimization criteria practically unreliable. A brief description of the criterion and its topological theory is provided in section 3.

In this work the implementation of the extended topological criterion into a dedicated optimization software is presented. Particular accent has been posed onto model equations which are the software core and allow to simulate both normal and upset (such as pump failure and external fire) operating conditions as well as to optimize the target process using the extended topological criterion.

2. MODEL EQUATIONS

As previously mentioned, model equations represent the core of the runaway reaction optimization software developed in this work.

Particularly, they consist into a system of ordinary differential equations (*ODEs*) able to simulate the time evolution of all the main process variables; namely: reactor and inlet/outlet jacket temperatures, conversions with respect to all chemical species involved, mixture density and reacting volume/level.

An example of such a system of *ODEs*, for a single reacting phase, is reported on the following, (1).

$$\left\{ \begin{aligned}
&\frac{dm}{dt} = \varphi_{dos}(t) \\
&\frac{dT_{cool,IN}}{dt} = -K_{pT} \cdot \left[\frac{dT_{cool}}{dt} - \frac{1}{K_{iT}} \cdot \left(T_{cool,set} - T_{cool}\right) + K_{dT} \cdot \frac{d^2 T_{cool}}{dt^2} \right] \\
&\frac{dV}{dt} = \varphi_V\left(t, T, \vec{n}\right) \\
&\hat{\rho}_{cool} \cdot \hat{c}_{p,cool} \cdot V_{cool} \cdot \frac{dT_{cool}}{dt} = \hat{\rho}_{cool} \cdot \hat{c}_{p,cool} \cdot \dot{V}_{cool} \cdot \left(T_{cool,IN} - T_{cool}\right) + UA \cdot \left(T - T_{cool}\right) \\
&\frac{d(m \cdot h)}{dt} = \frac{dm}{dt} \cdot \hat{c}_{p,dos} \cdot \left(T_{dos} - T_{rif}\right) + V_0 \cdot \sum_{j=1}^{n^\circ rxn} r_j \cdot \left(-\Delta \tilde{H}_{rxn,j}\right) - UA \cdot \left(T - T_{cool}\right) - UA_{ext} \cdot \left(T - T_{amb}\right) \\
&\frac{dn_i}{dt} = \dot{n}_{i,IN} - \dot{n}_{i,OUT} + \sum_{j=1}^{n^\circ rxn} \nu_{i,j} \cdot r_j \qquad\qquad i = 1, compound \quad number
\end{aligned} \right. \tag{1}$$

$$I.C \qquad t = 0 \Rightarrow m = m_0,\; T_{in,cool} = T_{in,cool,0},\; V = V_0,\; T_{cool} = T_{cool,0},\; T = T_0,\; n_i = n_{i,0}$$

where t is time (s), m is the total reacting mass (kg), φ_{dos} is the dosing stream function (that can assume a number of different time dependent expressions which can not be *a priori* specified), $T_{cool,IN}$ 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), T_{dos} is the dosing stream temperature (K), T_{amb} is the ambient temperature (K), T_{rif} is the reference temperature (= 300 K), K_{pT} is the proportional gain (-), K_{iT} is the reset time (s), K_{dT} is the derivative time (s), n_i are the moles of the i-th compound (kmol), V is the total volume (m^3), V_0 is the initial mixture volume (m^3), φ_V is a function accounting for mixing rules (that can assume a number of different time, temperature and compositions dependent expressions which can not be *a priori* specified), h is the molar enthalpy of the reacting mixture (J/kmol), 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/(m^3 s)) according to, e.g., Arrhenius Law, $\Delta \tilde{H}_{rxn,j}$ is the j-th reaction enthalpy (J/kmol), $\nu_{i,j}$ is the i-th stoichiometric coefficient in the j-th reaction (-), $\dot{n}_i$ is the molar flow rate (kmol/s), $\dot{V}$ is the volumetric flow rate (m^3/s), ρ is the density (kg/m^3) and $\hat{c}_p$ is the specific heat capacity (J/(kg K)). Subscript *cool* is referred to the coolant fluid, *IN* and *OUT* are referred to inlet and outlet streams.

In this system, the first equation accounts for the characteristics of the dosing stream and allows for the simulation of different and even complex feed strategies (typical of the full-scale synthesis); the second equation implements the controller logic onto the inlet jacket coolant temperature; particularly, a velocity algorithm has been used in order to speed up calculation times during simulation and optimization steps.

Moreover, the presence of such an equation permits to simulate both isothermal and isoperibolic temperature control mode (or mixed schemes).

The third equation formally expresses mixing rules adopted to describe reacting mixture density variations during the synthesis. As it can be easily observed, the structure of φ_V strongly depends on both reactants, products and additives physical-chemical characteristics and reaction type.

Finally, the forth and five equations represent energy balances on, respectively, the jacket and the reactor; while the last group of equations represents the material balances on all the chemical species involved in the process kinetics.

It is important to stress that, for whatever simulation or optimization step, initial time always represents the start of the dosing stream supply.

3. OPTIMIZATION CRITERION

The original topological criterion theory [6] states that, for a semibatch process carried out under isoperibolic temperature control mode, the boundary between runaway and *QFS* conditions with respect to a desired product X is identified by an inversion of the topological curve showing a concavity towards right. Particularly, this curve shows all the possible thermal behavior regions of an isoperibolic *SBR* obtainable by varying one system constitutive parameter (e.g dosing time) or initial condition (e.g. coolant temperature), referred to as generating parameter, in a suitable range. The topological curve can be drawn by solving material and reactor energy balance equations describing the analyzed system for each investigated value of the generating parameter and, then, reporting onto a bidimensional diagram the obtained reactor temperature maxima divided by the initial temperature, $\Psi_{MAX}=T_{MAX}/T_0$, and the conversion with respect to the desired product in correspondence of such maxima, $\zeta(\Psi_{MAX})$.

Moreover, 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).

Whatever optimization algorithm 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 initial/coolant temperature) can be searched for accounting reacting mixture thermal stability (that is, *MAT*) and desired productivity constraints.

Recently, it has been demonstrated that the topological criterion theory for the *QFS* detection does not depend on the particular system of ordinary differential equations used to describe the process dynamics [10] because only two dependent variables contribute effectively to characterize the system thermal behavior: temperature and conversion with respect to the desired product X. Such variables appear in all possible systems of equations writable to describe a generic complex controlled process: they can be referred to as "core constants". Accounting for this feature, dosing stream and jacket temperature control equations, mixing rules for densities determination, global material and jacket energy balance equations can be inserted into the system of ordinary differential equations describing the analyzed process without invalidating the topological criterion.

Therefore, a new extended topological criterion theory can be developed and synthesized into the following theorem: "for a semibatch process, carried out under both isoperibolic and isothermal temperature control mode, the boundary between runaway and *QFS* conditions with respect to a desired product X is identified by an inversion of its topological curve showing a concavity towards right".

Some examples of topological curves are reported in Figure 1.

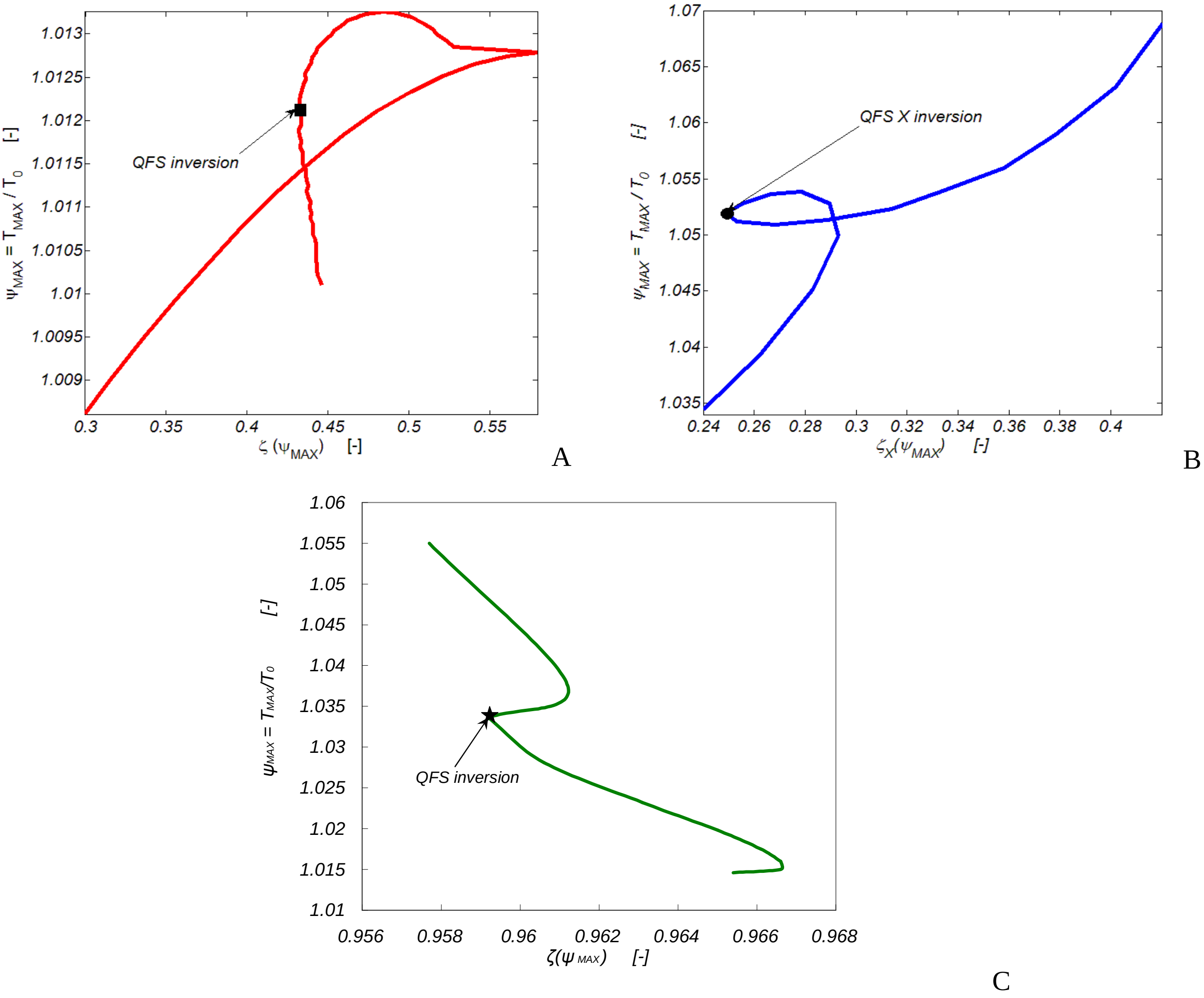

Figure 1. Bunch of topological curves. A) Single reaction system operated in the isothermal temperature control mode (generating parameter: T_0); B) Consecutive reactions system carried out in the isoperibolic temperature control mode (generating parameter: T_{cool}) [7]; C) Emulsion homopolymerization system operated in the isoperibolic temperature control mode (generating parameter: t_{dos}) [8].

As it can be noticed, independently on the temperature control mode (isoperibolic or isothermal) and the generating parameter (T_{cool}/T_0 or t_{dos}), the *QFS* inversion is always individuated by a concavity of the topological curve towards right.

Such a general optimization criterion can be easily implemented into an iterative optimization algorithm capable of optimizing both initial/coolant temperature and dosing time for a highly exothermic semibatch reactor.

4. OPTIMIZATION ALGORITHM

From the extended topological criterion for QFS detection, a procedure aimed to optimize dosing time (t_{dos}) and initial/mean coolant temperature (T_0/T_{cool}) arises straightforward along the same lines previously proposed by Copelli et al. [6-9]. In the following, the desired product will be considered the generic species X: such a species may be an intermediate or a final product. In particular, for any *SB* process involving whatever complex kinetic scheme, t_{dos} should be minimum to obtain the maximum productivity of species X fulfilling safety constraints.

After the manual insertion of reaction type (e.g. single reaction, consecutive reactions, homopolymerization reaction, etc..), all microkinetic and thermochemical system parameters, reactor and cooling equipment characteristics, controller parameters, temperature control mode (isothermal or isoperibolic), initial/coolant temperatures [$T_{0/cool,MIN}$; $T_{0/cool,MAX}$] and dosing times [$t_{dos,MIN}$; $t_{dos,MAX}$] ranges into a dedicated data acquisition system (see Section 5), the general optimization algorithm can be summarized as follows:

1- According to the selected reaction type and temperature control mode, straightforward identification of the topological curve generating parameter choosing among: T_0, T_{cool} or t_{dos}.

Such an identification bases on a simple consideration: in order to correctly draw the topological curve, its generating parameter have to be varied into a sufficiently wide range. As an example, if an emulsion polymerization system is considered, T_0 or T_{cool} (according to the selected temperature control mode) cannot be varied into a sufficiently wide range because of final product quality restrictions (such as mean particles size, average molecular weight distribution, etc.. which strongly depend on temperature). Therefore, T_0 or T_{cool} cannot be selected as generating parameter of the topological curve: t_{dos} must be compulsory selected by the algorithm.
Always taking into account the desired temperature control mode, the parameter which has not been chosen as generating parameter is automatically selected as iterative parameter.

2- According to the selected reaction type and temperature control mode, search for the *QFS*X initial/coolant temperature ($T_{0/cool,QFSX}$) in the X-space for $t_{dos}=t_{dos,n}$ (at the algorithm start-up, n=0, $t_{dos,n}=t_{dos,MIN}$), and $T_{0/cool} \in [T_{0/cool,MIN}; T_{0/cool,MAX}]$ (analogously, we can identify *QFS*X dosing time ($t_{dos,QFSX}$) in the X-space for $T_{0/cool}=T_{0/cool,n}$ (at the algorithm start-up, n=0, $T_{0/cool,n}=T_{0/cool,MAX}$) and $t_{dos} \in [t_{dos,MIN}; t_{dos,MAX}]$);

3- At the *QFS*X conditions, maximum reactor temperature T_{MAX} has to be checked with respect to the experimentally determined *MAT*. If $T_{MAX}>MAT$, the dosing time should be increased (or the initial/coolant temperature should be decreased) and step 2 repeated with this new value;

4- As a final check, the conversion of species X at the end of the dosing time $\zeta_{X,dos}$ is required to be larger than a given threshold value $\zeta_{X,MIN}$. If this is not true, the dosing time should be increased (or the initial/coolant temperature should be decreased) and step 2 repeated with this new value until convergence is reached. If convergence is not reached the process can not be carried out safely in the selected temperature control mode.

5. SOFTWARE DESCRIPTION

Scandium Optimization Simulation (ScOptSim) software has been designed to both simulate and safely optimize potentially runaway semibatch systems. Its implementation has been realized using GUIDE, the MATLAB Graphical User Interface Development Environment, which provides a set of tools for creating graphical user interfaces (GUIs) and allows for benefitting all the MATLAB calculation power. These tools greatly simplify the process of laying out and programming GUIs.
Because of some limitation concerning MATLAB GUIs, ScOptSim graphics is unsophisticated but all fundamental data acquisition and processing tools are provided.

5.1. Initial window

Figure 2 shows ScOptSim initial window. As it can be noticed, four different window menus are present:
- File: it allows for saving data, printing and exiting from ScOptSim environment.
- Simulation: it allows for selecting either normal or upset operating conditions. Choosing “Normal Operations”, a new window submenu appears and allows for selecting the desired reaction scheme; choosing “Upset Operations”, accidents window submenu appears allowing for the selection of either a “Pump Failure” or an “External Fire”. Clicking on one of the accident typology, a final window submenu containing reaction schemes is visualized.
- Optimization: it allows for selecting the desired reaction scheme to be optimized using the extended topological criterion for the QFS detection.
- Help: it allows for consulting the help section where a brief description of the software is provided.

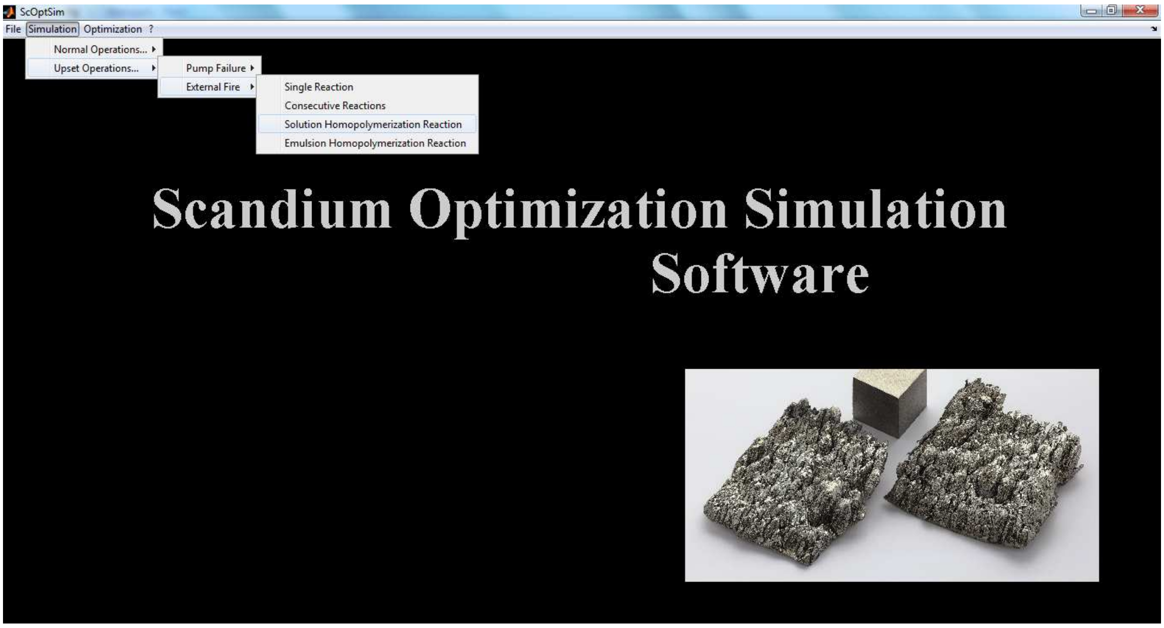

Figure 2. A sketch of the ScOptSim initial window.

5.2. Simulation section

As described in subsection 5.1, clicking on “Simulation” shows a submenu where it is possible to choose between normal and upset operating conditions. In the latter case, before selecting the desired reaction scheme, it is necessary to choose among different accident typologies (actually, ScOptSim allows for selecting only between “Pump Failure” and “External Fire”).
Once selected the desired simulation path, a simulation window is opened. Figure 3 shows how such an interactive window appears for single reacting systems operated in normal conditions.

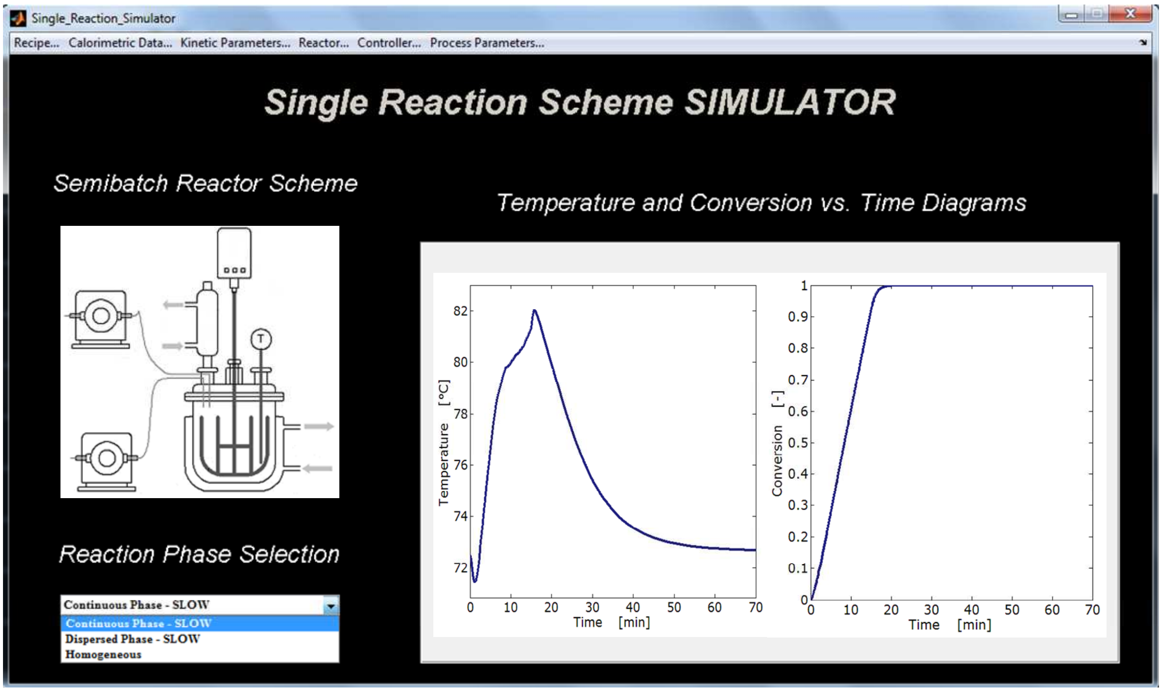

Figure 3. Simulation window for a single reacting system operated in normal conditions.

Observing Figure 3, a number of window menus can be observed. Such menus allow for inserting all input data necessary to solve equation (1) for the selected reaction scheme.
Proceeding from left to right, we encounter:

- Recipe: it opens another active window where all reactants/products amounts (masses) and properties (densities and molecular weights) can be manually inserted by the user.
- Calorimetric Data: it opens an active window where reaction(s) calorimetric data such as specific heats and reaction enthalpies can be inserted.
- Kinetic Parameters: it opens a dedicated active window where it is possible to digit Arrhenius Law parameters (such as pre-exponential factors, activation energies and reaction orders) for each reaction comprised in the selected reaction scheme, Arrhenius Law correcting parameters, reactions stoichiometry and material transfer coefficients.
- Reactor: it opens an active window divided into two sections: jacket and reactor. In the first section, jacket volume, coolant flow rate, density and specific heat can be inserted; in the second one, reactor nominal volume, global heat transfer coefficient at initial conditions, active surface and global heat transfer coefficient for external dispersion must be provided.
- Controller: it opens an active window where all controller parameters such as static gain (or equivalently, proportion band), reset (or integral) time and derivative time can be inserted for both temperature and level controllers. Moreover, saturation temperatures and maximum/minimum allowed reactor level must be provided.
- Process Parameters: it opens an active window where it is possible to choose the reactor temperature control mode (e.g. isothermal or isoperibolic) and insert dosing time, reaction time and all required temperatures (such as dosing stream temperature, initial reactor temperature, ambient temperature, initial coolant temperature and set point temperature – for reactor, if the isothermal mode has been selected; for jacket, if the isoperibolic mode is desired).

5.3. Optimization section

This is the software core section. In fact, as previously mentioned, in such a section the optimization algorithm (see section 4) based on the extended topological criterion for the *QFS* detection is implemented.

Clicking onto the Optimization option, the reaction scheme window menu is directly visualized allowing for the desired selection. Once the reacting path has been chosen, an active window is opened.

Such a window is substantially similar to the simulation section one; in fact, all window menus encountered from left to right are the same but the last one which is substituted by the Optimization Parameters window menu.

Optimization Parameters active window allows for inserting temperature control mode, minimum and maximum dosing time, minimum and maximum initial reactor/coolant temperature (according to the selected temperature control mode), dosing stream temperature, ambient temperature and optimization constraints: that is, *MAT* and minimum conversion with respect to the desired product at the end of the dosing period. Such parameters are those ones that are compulsory requested by the optimization algorithm previously presented in section 4.

Finally, clicking onto the evaluate button located into the Optimization window, optimum dosing time, initial/coolant temperature, stop time and conversion at both the end of the dosing period and the stop time are automatically calculated (by running iteratively the optimization algorithm) and listed in a suitable window report. Such a report can be saved in .txt format.

5.4. Help section

In such a section a brief description on how to use the different sections composing the software is provided.

6. EXAMPLE: SAFE OPTIMIZATION OF THE 2-OCTANOL NITRIC ACID OXIDATION WITH ScOptSim

In order to test ScOptSim calculation power and reliability, a case study concerning the oxidation of 2-octanol to 2-octanone by means of nitric acid (60 % w/w) has been considered. The process kinetic scheme may be represented as follows:

$$\begin{aligned} &1)\quad A+B \rightarrow 2B+C \\ &2)\quad B+C \rightarrow D \end{aligned} \tag{2}$$

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 desired product 2-octanone and D is a mixture of unwanted carboxylic acids. This is a heterogeneous liquid–liquid system and all reactions occur into the continuous aqueous phase (which is formed by the nitric acid). As several oxidations of organic compounds carried out in nitric acid, these reactions are fast, exothermic and they exhibit a strong selectivity problem with respect to the intermediate species (2-octanone), which is the desired one.

Nevertheless, product quality is almost insensitive with respect to temperature; therefore such a synthesis can be carried out under isoperibolic conditions without particular problems.

Taking into account these features, it is possible to infer that the most relevant system constitutive parameter and initial condition is the coolant temperature. Therefore, in order to generate the topological curve (Ψ_{MAX} *vs.* $\zeta_C(\Psi_{MAX})$), coolant temperature will be automatically selected as generating parameter by the ScOptSim optimization algorithm and, consequently, dosing time will be selected as iterating parameter (see section 4).

Since this reacting system has been extensively investigated elsewhere [11,12], microkinetic and all thermodynamic parameters necessary to generate the C-space by compiling (1) are already known and, therefore, can be easily inserted into their suitable acquisition windows.

For this process, *MAT* parameter has been assumed to be 100 °C (20 °C below the boiling point of diluted nitric acid, b.p~120 °C) for safety reasons, while the desired minimum dimensionless C concentration at the end of the dosing period, $\zeta_{C,MIN}$, has been set equal to 0.60 to avoid an excessive degree of co-reactant accumulation.

Finally, according to physical constraints (no solidification of the reacting mixture must occur) and *MAT* value (no boiling or decomposition of the reacting mixture must occur), the following ranges of variation can be defined: T_{cool} [-13, 37] °C and t_{dos} [300, 5400] s. Moreover, a temperature step equal to 0.5 °C and a dosing time step equal to 30 s have been used into the iterating part of the optimization algorithm (such parameters cannot be modified by users in this version of ScOptSim).

Running the software by clicking onto the evaluation button, the optimum $T_{cool} - t_{dos}$ couple has been found to be equal to: 4 °C – 3600 s. Such a result agrees with what has been experimentally found by van Woezik and Westerterp [12] and, therefore, confirms the reliability of ScOptSim with respect to its ability in simulating and optimizing potentially runaway systems.

ScOptSim has been tested on a number of different kinetic scheme using both isothermal and isoperibolic temperature control mode (some other examples are reported in [10]). In all cases, ScOptSim predictions well agreed with available experimental data (both from laboratory experiments and literature data).

7. CONCLUSIONS

In this work, a useful tool able to manage potentially runaway reactions carried out in semibatch reactors under both isothermal and isoperibolic temperature control mode has been developed and presented.

Such a tool, named ScOptSim, exhibits a simple but effective graphic interface and allows for both simulating normal (or upset) operating conditions and optimizing a suitable set of operating parameters. Particularly, ScOptSim optimization section uses the extended topological criterion theory to bind the *QFS* region and, then, iteratively search for the constrained system optimum.

To manage the software, only a few experimental parameters are needed; essentially: heat(s) of reaction, Arrhenius law parameters, *MAT*, heat transfer coefficients and reactants heat capacities. Such parameters can be obtained using simple calorimetric techniques (*DSC*, *ARC*, *RC1*, etc..).

ScOptSim calculation power and reliability have been demonstrated by testing it with a number of available experimental data. In all cases, a good agreement between theoretical predictions and experimental data has been achieved.

List of Abbreviations

ARC	Accelerated Rate Calorimeter
DSC	Differential Scanning Calorimeter
MAT	Maximum Allowable Temperature
ODE	Ordinary Differential Equation
QFS	Quick onset, Fair conversion, Smooth temperature profile
RC1	Reaction Calorimeter
SBR	SemiBatch Reactor

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