Safe Optimization of 2-Octanol Oxidation and Vinyl Acetate Emulsion Polymerization

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In this work the possibility to develop reliable optimization procedures, particularly suitable for full plant exothermic semibatch processes operated in the isoperibolic temperature control mode, has been investigated. It has been found that a general optimization procedure could be developed by using a particular curve, called topological curve, resulting from the numerical solution of the ordinary differential equation system describing the process dynamics. Such a curve exhibits a series of inversion points that represent, physically, transitions between different system thermal behaviour regions.

The optimization procedure based on the analysis of the topological curve uses the QFS inversion as a boundary beyond which the optimum operating conditions can be searched accounting for reacting mixture thermal stability and desired productivity constraints.

Experimental temperature vs. time data spring from laboratory studies of two different potentially runaway systems (the nitric acid oxidation of 2-octanol to 2-octanone and the free radical emulsion homopolymerization of vinyl acetate) have been modelled to demonstrate that the topological criterion for the QFS detection is independent of all the thermodynamic and process variables control equations used to describe the system. Such a result suggests that this approach could be safely used to optimize even processes operated at the full plant scale.

1. Introduction

In pharmaceutical and fine chemical industries, fast and exothermic reactions are often carried out in semibatch reactors (SBRs) in order to better control the heat evolution during the synthesis. In fact, for such processes, a phenomenon known as "thermal runaway" may be triggered whenever the rate of heat removal becomes lower than the rate of heat production.

During the last 25 years, a considerable number of studies on the detection of the runaway boundaries has been performed by both theoretical and experimental tools (Jiang et al., 2011; Maschio et al., 2010; Rudniak et al., 2011). However, from a practical viewpoint, the desired goal 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 (Copelli et al., 2010, 2011a).

In this work the topological criterion theory is 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. 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 make other runaway boundary detection and optimization criteria practically unreliable). The extended topological criterion has been validated through literature experimental data and laboratory tests.

2. Extended topological criterion theory

The topological criterion theory 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 behaviour regions of an isoperibolic SBR obtainable by varying one system constitutive parameter (e.g dosing time) or initial condition (e.g. coolant temperature) in a suitable range. The topological curve can be drawn by solving the 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 coolant temperature, $\Psi_{MAX}=T_{MAX}/T_{cool}$, 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 behaviour 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).

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 reacting mixture thermal stability (that is, MAT) and desired productivity constraints.

In this work 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 because only two dependent variables contribute effectively to characterize the system thermal behaviour: 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 volumes determination, global material and jacket energy balance equations have been inserted into the system of ordinary differential equations (ODEs) describing the analysed process. An example of such a system of ODEs is reported on the following, (1). In this equation a single reacting phase is considered, where t is time (s), m is the total reacting mass (kg), φ_{dos} is the dosing stream function, $T_{in,cool}$ 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$_i$), 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, 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)), $\Delta \tilde{H}_{rxn,j}$ is the j-th reaction enthalpy (J/kmol), $v_{i,j}$ is the i-th stoichiometric coefficient in the j-th reaction

(-), $\dot{n}$ is the molar flow rate (kmol/s), $\dot{V}$ is the volumetric flow rate (m^3/s), $\hat{\rho}$ 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.

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

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

3. Optimization Procedure

From the extended topological criterion for QFS detection, a procedure aimed to optimize dosing time (t_{dos}) and mean coolant temperature (T_{cool}) arises straightforward along the same lines previously proposed by Copelli et al. (2011a). 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 isoperibolic SB process involving whatever complex kinetic scheme, t_{dos} should be minimum to obtain the maximum productivity of species X fulfilling the safety constraints.

The general optimization procedure can be summarized as follows:

1- Search for microkinetic and thermochemical system parameters, reactor and cooling equipment characteristics and definition of a suitable coolant temperatures [$T_{cool,MIN}$; $T_{cool,MAX}$] and dosing times [$t_{dos,MIN}$; $t_{dos,MAX}$] range;

2- Identification of the QFSX coolant temperature ($T_{cool,QFSX}$) in the X-space for $t_{dos}=t_{dos,n}$, and $T_{cool} \in$ [$T_{cool,MIN}$; $T_{cool,MAX}$] (analogously, we can identify QFSX dosing time ($t_{dos,QFSX}$) in the X-space for $T_{cool}=T_{cool,n}$ and $t_{dos}\in$ [$t_{dos,MIN}$; $t_{dos,MAX}$]);

3- At the QFSX 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 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 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 in the isoperibolic temperature control mode.

4. Experimental Validation

Experimental temperature vs. time data spring from laboratory studies of two different potentially runaway systems (the nitric acid oxidation of 2-octanol to 2-octanone (van Woezik and Westerterp, 2000, 2001) and the free radical emulsion homopolymerization of vinyl acetate (Copelli et al., 2011b)) have been modelled to validate this topological approach.

4.1 Case study n°1: 2-octanol oxidation

As a first case study, it has been considered the oxidation of 2-octanol to 2-octanone by means of nitric acid (60 % w/w). The kinetic scheme of the process may be represented as follows:

$$1) \quad A + B \rightarrow 2B + C$$

$$2) \quad B + C \rightarrow D \tag{2}$$

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).

Since the most relevant system constitutive parameter and initial condition is the initial reactor temperature, it is possible to generate the desired topological curve (Ψ_{MAX} vs. $\zeta_C(\Psi_{MAX})$) for each dosing time to be investigated and perform the optimization procedure previously presented.

The first step in the optimization procedure is the search for system microkinetics and thermodynamic parameters. Since this reacting system has been extensively investigated elsewhere (van Woezik and Westerterp, 2000, 2001), microkinetic reaction rate equations and all the thermodynamic parameters necessary to generate the C-space by compiling (1) are already known. For this process the MAT parameter has been assumed to be 373 K (20 K below the boiling point of diluted nitric acid, b.p~393 K) 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: $T_{cool} \in$ [260, 325] K and $t_{dos} \in$ [300, 5400] s. A temperature step equal to 0.5 K and a dosing time step equal to 60 s have been used into the iterating part of the optimization procedure. After these preliminary steps, starting from $t_{dos,MIN}$=300 s, the optimum coolant temperature and dosing time can be searched for by performing the optimization procedure previously described. The optimum T_{cool} and t_{dos} couple has been found to be equal to 277 K and 3600 s, respectively. Such a result agrees with the experimental results of van Woezik and Westerterp (2001).

In order to demonstrate that the obtained C-space describes correctly the system thermal behaviour in the range of process parameters experimentally investigated by van Woezik and Westerterp (2000, 2001), the set of experimental isoperibolic RC1 runs reported in Table 1 has been used. Since no information about the dimensionless concentrations of products C and D has been reported in the literature, the experimental thermal classification provided by van Woezik and Westerterp (2001) has been directly compared with the theoretical one arising from the topological curves generated into the C and D-spaces. Such a comparison has also been reported in Table 1.

Table 1: Experimental classification of the experimental runs (van Woezik and Westerterp (2001)) and the theoretical predictions arising from the topological criterion.

RUN	$T_{cool,exp}$ [K]	Experimental Classification	Topological Criterion
1	272	QFS$_C$	QFS$_C$
2	281	RW	RW
3	290	RW	RW
4	304	QFS$_D$	QFS$_D$
5	333	QFS$_D$	QFS$_D$

A graphical comparison between experimental results and theoretical classification arising from the topological curves of the C and D-spaces, where no-ignition, runaway and QFS regions are marked, respectively, with a dashed-dotted, a continuous and a dashed line, is shown in Figure 1a and 1b. As it can be seen, a good agreement between theoretical predictions and experimental results has been achieved, because each experimental run is located into the correct thermal behavior region.
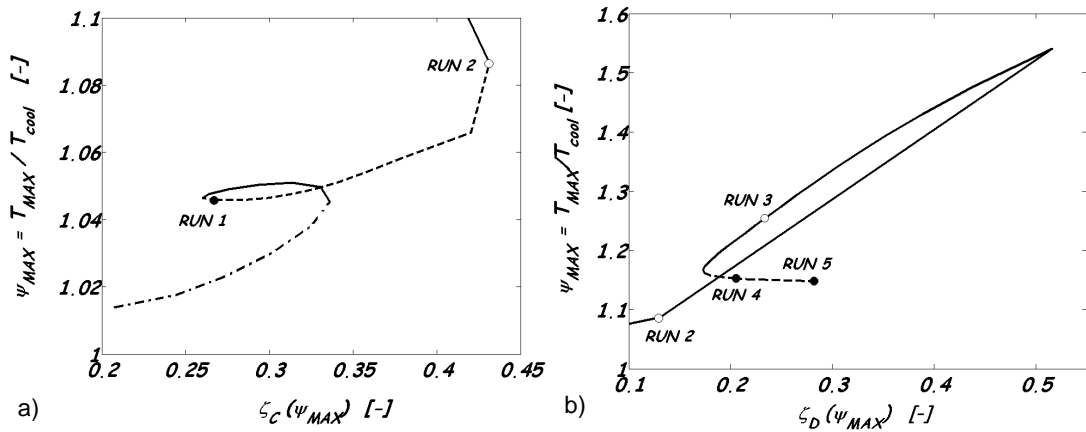
Figure 1: Graphical comparison between experimental runs and theoretical predictions for the nitric acid oxidation of 2-octanol to 2-octanone. (○) experimental runaway runs, (●) experimental QFS runs, (-.-) no ignition region, (-) runaway region, (--) QFS region. a) C-space, b) D-space.

4.2 Case study n°2: vinyl acetate emulsion polymerization

As a second case-study the emulsion polymerization of vinyl acetate has been investigated experimentally to assess the practical feasibility of the proposed topological procedure.

For what concern the MAT determination, a set of three isoperibolic 50 mL scale tests at different monomer feeding rate has been carried out: particularly, the minimum temperature at which the reacting mixture starts to boil vigorously is 356 K. Such a temperature can be considered, as a first approximation, as the MAT parameter. In order to fit constitutive model parameters to be inserted into (1), an isoperibolic RC1 experiment with a dosing time equal to 600 s has been carried out. In Figure 2, experimental and simulated temperature vs. time profiles are compared, showing a good agreement among RC1 experimental data and numerical predictions. Using model parameters calculated from the fitting procedure, it is possible to draw the theoretical topological curve for the desired product (the polymer) by solving equations (1) for different dosing times (starting from $t_{dos,MIN}=450$ s to $t_{dos,MAX}= 1800$ s, t_{dos} step being equal to 30 s). Figure 3 shows the obtained topological curve. Then, the optimum dosing time is iteratively searched for by checking optimization procedure constraints from the dosing time at which the QFS inversion occurs to that one at which the starving inversion occurs.

For the analyzed system, the theoretical QFS boundary is detected for a dosing time equal to 750 s. The minimum dosing time able to satisfy thermal stability and productivity constraints is equal to 900 s (RUN 4). This dosing time can be considered optimized from both safety ($T_{MAX}=355.2$ K is lower than the MAT=356 K) and productivity point of view ($\zeta_{dos}= 0.9195$ – is larger than the minimum desired conversion at the end of the dosing period, $\zeta_{MIN}=0.90$). Both the theoretical topological curve and the optimum dosing time must be validated through a set of isoperibolic RC1 runs, whose dosing times have to cover the whole range used to generate the theoretical topological curve. In this work, five isoperibolic experiments, summarized in Table 2, have been carried out.

Table 2: Experimental classification of the experimental runs and the theoretical predictions arising from the topological criterion for the emulsion polymerization of vinyl acetate.

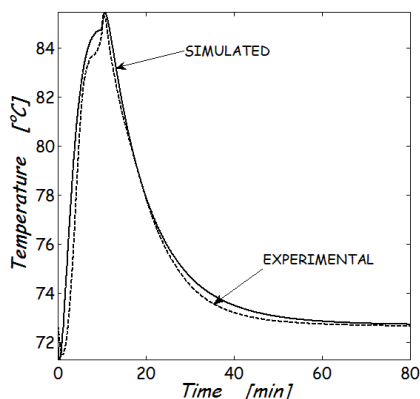| RUN [-]	t_{dos} [s]	$T_{MAX,exp}$ [K]	$\zeta_{MAX,cal}$ [-]	$\zeta_{dos,exp}$ [-]	Experimental classification	Topological Criterion
1	450	365.28	0.956	0.905	RW	RW
2	600	358.32	0.960	0.907	RW	RW
3	750	357.13	0.955	0.915	QFS	RW/QFS
4	900	355.20	0.960	0.920	QFS	QFS
5	1800	350.54	0.963	0.934	STV	STV

Figure 2. Experimental and simulated temperature profiles for the isoperibolic RC1 test used to fit the model parameters.
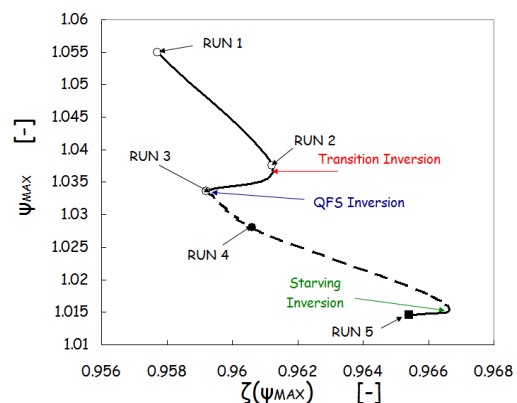

Figure 3. Topological curve for vinyl acetate homopolymerization. T_{cool}=345.5 K, $t_{dos}\in$ [300 - 1800] s. (▬) runaway, (--) QFS, (-.-) starving.

Moreover, the same table also compares theoretical and experimental classifications of each run in terms of thermal behaviour (RW, QFS or STV). Each ($T_{MAX,exp}$, $\zeta_{MAX,cal}$) couple has been located onto the diagram reported in Figure 3. From both Figure 3 and Table 2, it is possible to highlight that the boundary between RW and QFS thermal behaviour is the same from both model and experimental analysis. This cross-validation strongly supports the reliability of the obtained results.

5. Conclusion

In this work the topological criterion theory 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 ODEs describing the process dynamics. This criterion has been used for the QFS detection in exothermic semibatch reactors (operated under the isoperibolic temperature control mode) using literature experimental data. Its good predictive capability suggests the potential applicability of such a criterion to the safe optimization of full plant processes, where complex loading procedures and temperature control modes make simple optimization criteria practically unuseful.

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