A NOTE CONCERING THE RISK OF USING GLOBAL KINETICS INSTEAD OF DETAILED KINETIC MODELS IN EVALUATING THE RUNAWAY BOUNDARIES OF INDUSTRIAL (SEMI-)BATCH REACTORS

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Modelele cinetice reduse sunt folosite în mod frecvent la simularea reactoarelor chimice. Totuşi, această abordare poate avea un impact negativ asupra estimării condiţiilor de operare în siguranţă, în special când pot să aibă loc reacţii secundare foarte exoterme. Această lucrare evidenţiază riscul de utilizare a unei cinetici globale în locul unui model cinetic detaliat la evaluarea limitelor de siguranţă ale unui reactor industrial catalitic semi-continuu utilizat la aceto-acetilarea pirolului cu dicetena în fază lichidă omogenă. În acest scop, au fost utilizate atât criteriul de senzitivitate Morbidelli-Varma, cât şi metode de divergenţă, evidenţiind predicţiile distorsionate generate de utilizarea modelului cinetic redus pentru aceleaşi condiţii nominale de operare.

Reduced kinetic models are often used to simulate chemical reactors. However, this approach might have a negative impact when estimating the safe operating conditions, especially when highly exothermic side reactions may occur. This paper presents the risk of using a global kinetics instead of a detailed kinetic model in evaluating the runaway boundaries of an industrial semi-batch catalytic reactor used for the acetoacetylation of pyrrole with diketene in homogeneous liquid phase. Both the Morbidelli-Varma sensitivity criterion and divergence-methods were used, proving the biased predictions generated with using the reduced kinetic model under the same nominal set of reaction conditions.

Keywords: global kinetics; runaway conditions; semi-batch reactor; pyrrole; diketene

1. Introduction

Chemical reactor's technological constraints and runaway boundaries of the operating conditions are important for both risk assessment and over-design avoidance. Usage of global kinetics may have several drawbacks either leading to risky operation and runaway or to exceedingly conservative operation with poor yields. Safety assessment is using runaway criteria classified by Adrover et al. [1]

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into four categories: geometry-based criteria, parametric sensitivity-based criteria, divergence-based criteria, and stretching based criteria [2,3].

Geometry-based methods (GM) analyse the shape of the temperature or heat-release rate profile over the reaction (contact) time. Critical conditions correspond to an accelerated temperature increase, i.e. to an inflexion point before the curve maximum in a temperature - time plot $T(t)$.

Sensitivity-based methods (PSA) detect unsafe conditions as being those characterized by high parametric sensitivities of state variables x_i with respect to operating parameters ϕ_j, i.e. $s(x_i;\phi_j)=\partial x_i/\partial\phi_j$ (in absolute terms), that is where "the reactor performance becomes unreliable and changes sharply with small variations in parameters"[4].

Divergence (div-)based criteria identify any instability along the system/process evolution and detect any incipient divergence from a reference (nominal condition) state-variable trajectory over the reaction time $x_i(t)$. Any increased sensitivity of the system stability in the proximity of runaway boundaries in the parametric space is detected from analysing the eigenvalues of the process model Jacobian (***J***) and Green's (***G***) function matrices, evaluated over the reaction time [5,6]. More elaborated versions use more sophisticated *div*-indices to characterize the expansion of volume elements in phase-space (having state variables as coordinates), e.g. Lyapunov exponents based on the analysis of the time-dependent $\boldsymbol{J}^T\boldsymbol{J}$ matrix [7,8].

Stretching based analysis (SBA), recently introduced by Adrover et al. [1] combines sensitivity and *div*-methods by investigating the dynamics of the tangent components to the state-variable trajectory. Critical conditions are associated with the system's dynamics acceleration ('stretching rates' of the tangent vectors), corresponding to a sharp peak of the normalized stretching rate due to the accelerate divergence from the nominal trajectory.

The scope of this paper is to point-out the risk of using global kinetics instead of a detailed kinetic model in evaluating the runaway boundaries of an industrial semi-batch catalytic reactor. A concrete example is provided for the exothermic acetoacetylation of pyrrole with diketene in homogeneous liquid phase, when very dangerous exothermic side-reactions can also occur. Both the Morbidelli-Varma sensitivity criterion and divergence-methods have been used, proving the biased predictions generated with the reduced kinetic model under the same nominal set of reaction conditions.

2. Sensitivity and divergence criteria of critical operating conditions

The current study is focused on the comparison between the critical conditions for a semi-batch reactor (SBR) obtained by using an extended vs. a

reduced kinetic model. The analysis is performed by using the Morbidelli-Varma (MV) sensitivity criterion, and a *div*-criterion. These runaway criteria are chosen to combine the evaluation precision/robustness with the sensitivity in detecting any system small instability of chemical process referring to a nominal evolution.

The generalized sensitivity criterion MV. This criterion associates the critical operating conditions with the maximum of sensitivity of the hot spot ($T_{max} - T_o$) in the reactor, evaluated over the reaction time, in respect to a certain operating parameter ϕ_j. In other words, critical value of a parameter $\phi_{j,c}$ corresponds to:

MV criterion:

$$\phi_{j,c} = \arg\left(\text{Max}_{\phi_j} \left| s(T_{max};\phi_j) \right| \right), \text{ or } \phi_{j,c} = \arg\left(\text{Max}_{\phi_j} \left| S(T_{max};\phi_j) \right| \right),$$

$$S(T_{max};\phi_j) = (\phi_j^* / T_{max}^*) s(T_{max};\phi_j) = (\phi_j^* / T_{max}^*)(\partial T_{max} / \partial \phi_j) \,, \quad (1)$$

[where: $S(T_{\max};\phi_j)$ = time-dependent relative sensitivity function of T_{max} vs. parameter ϕ_j; '*' = nominal operating conditions (set point) in the parameter space; *t*= reaction time]. According to the MV criterion, critical conditions induce a sharp peak of the normalized sensitivity $S(T_{max};\phi)$ evaluated over the reaction time and over a wide range of ϕ_j. The sensitivity functions $s(x_i;\phi_j)$ of the state variables x_i (including the reactor temperature) can be evaluated by using the so-called 'sensitivity equation' solved simultaneously with the reactor model [4]:

$$\frac{ds(\mathbf{x};\phi_j)}{dt} = \frac{\partial \mathbf{g}}{\partial \mathbf{x}} s(\mathbf{x};\phi_j) + \frac{\partial \mathbf{g}}{\partial \phi_j} \;;\; s(x;\phi_j)\big|_{t=0} = \delta(\phi_j - x_o) \,,$$

$$d\mathbf{x}/dt = \mathbf{g}(\mathbf{x},\boldsymbol{\phi},t) \,,\; \mathbf{x}\big|_{t=0} = \mathbf{x}_o \,, \quad (2)$$

(where the Kronecker delta function $\delta(\phi_j - x_o)$ takes the value 0 for $\phi_j \neq x_o$, or the value 1 for $\phi_j = x_o$; many times the considered parameter is the inlet value of a state variable). Evaluation of derivatives in (2) can be precisely performed by using the analytical derivation or, being less laborious, by means of numerical derivation. A worthy alternative, also used in the present study, is the application of the numerical finite difference method, which implements certain differentiation scheme (of variate precision and complexity) to estimate the derivatives of $s(x_i;\phi_j)_t$ at various reaction times [9].

Div-J criterion. The divergence criteria are derived from characterization of chaotic attractors in dynamical systems theory [1]. In the *div*-J variant of Hegdes & Rabitz [10], one considers a reference solution $\mathbf{x}^*(t)$, usually known as set point or nominal conditions, and one investigates the effect of any

perturbation in the initial conditions $\boldsymbol{x}_{i,o}$ or parameter ϕ_i by inspecting the eigenvalues of the system Jacobian $\lambda_i(\boldsymbol{J})$. These eigenvalues prescribe how perturbations behave for small time intervals near every considered moment. When the real part of only one eigenvalue becomes positive at a certain time, this perturbation induces system instability and divergence of the state-variable time-trajectory from the reference solution. In the risk assessment, such instability is associated with the occurrence of critical conditions determining process runaway. Zaldivar et al. [6] introduced an early detection of loss of stability as those corresponding to the occurrence of the Jacobian trace positiveness, i.e. for $Trace(\boldsymbol{J}) = \sum_i \lambda_i > 0$. Starting from the Vajda & Rabitz [5] observation that critical conditions correspond to the positive extreme point of $Re(\lambda(\boldsymbol{J}))$ evaluated at the temperature peak, the critical value of a checked parameter $\phi_{j,c}$ is estimated, in the present work, based on:

div-J criterion:

$$\phi_{j,c} = \mathrm{Min}(\phi_j), \text{ for which } \mathrm{Max_i}(\mathrm{Max_t}(Re(\lambda_i(\boldsymbol{J}(\phi_j))))) > 0,$$
$$\text{where: } \boldsymbol{J} = (\partial \boldsymbol{g}/\partial \boldsymbol{x})_t;\ d\boldsymbol{x}/dt = \boldsymbol{g}(\boldsymbol{x}, \boldsymbol{\phi}, t),\ \boldsymbol{x}\big|_{t=0} = \boldsymbol{x}_o, \qquad (3)$$

(when more severe conditions correspond to smaller ϕ_j, then $\mathrm{Max}(\phi_j)$ must be taken in the criterion, e.g. for $\phi_j = Da$, or $\phi_j = Da/St$). The evaluation rule starts by computing $Re(\lambda_i(\boldsymbol{J}))$ values at various reaction times for a certain small ϕ_j value, and keeping the other parameters at nominal values. If the condition (3) is not satisfied, the parameter ϕ_j is increased with a small increment (to ensure a reasonable evaluation precision) and the procedure is repeated until the critical value is identified. Evaluation of the *J*-matrix elements is made analytically with high precision, for instance by applying commercial software for symbolic calculation, such as Maple package in the present work [11].

3. Acetoacetylation of pyrrole – process characteristics

The acetoacetylation of pyrrole (P) with diketene (D) is conducted in homogeneous liquid phase (toluene), at around 50°C and normal pressure, using pyridine as catalyst, for producing pyrrole derivates such as PAA used in the drug industry. The process is of high thermal risk due to the tendency of the very reactive diketene to polymerise at temperatures higher than 60-70°C, or in the presence of impurities that can initiate highly exothermic side reactions difficult to be controlled [12]. The complex process kinetics have been investigated by Ruppen et al. [13] in a bench-scale isothermal SBR operated at 50°C using a high excess of toluene as solvent.

The proposed kinetic model from Table 1 accounts for only four exothermic reactions: (a) the synthesis of PAA (P+D→PAA) is accompanied by several side-reactions of diketene, leading to its dimmer; (b)(2D→DHA; DHA= dehydroacetic acid), and oligomers; (c)(nD→D_n), or to a by-product denoted by G; (d) PAA+D→G (the intermediate reaction of diketene with DHA has been neglected from the model). Because the co-reactant diketene presents an extreme reactivity and hazardous properties, the temperature regime must be strictly controlled and the diketene and DHA concentrations in the reactor kept lower than certain critical thresholds (empirically determined, see Table 1)[13,14]. The rate constants have been evaluated by Ruppen et al. [13] at 50^{o}C and [PAA] > 0.1 mol L^{-1}.

Maria et al. [15] completed the model by including the Arrhenius dependence of the main rate constants, and by adopting an activation energy of E/R = 10242 K for all reactions of diketene, by analogy with the diketene derivate polymerisation, and with the initiation energy of olefin polymerization. The resulted Arrhenius constants (A_i, E_i) are displayed in Table 1. All reactions are moderately exothermic, except for the diketene oligomerization of standard heat around -1423 kJ mol^{-1}.

For a quick process simulation, a simple SBR model was adopted, corresponding to a perfectly mixed vessel, with no mass and heat transfer resistances in the liquid [16]. The solution of diketene in toluene is continuously added with a variable fed flow-rate $F(t)$ over the continuously stirred pyrrole solution (including impurities) initially loaded to the jacketed reactor, and the reaction heat is continuously removed through the reactor wall. The mass and heat balance equations, presented in Table 1, explicitly account for the liquid volume and heat transfer area increase during the batch. The continuous catalyst dilution is accounted for when correcting the reaction rates, except for reaction (c) presumed to be promoted not by pyridine but by some impurities (of quasi-constant concentration).

To speed-up the computational steps, the physical properties of the reaction mixture have been approximated to those of the toluene solvent, and a constant overall heat transfer coefficient has been evaluated (Table 1).

Table 1

Process and semi-batch reactor model, nominal operating conditions, and technological constraints [15]

Process main reactions and reduced kinetic model (Footnote a):

$P + D \xrightarrow{k_a, Py} PAA$; $r_a = k_a c_P c_D$; $k_a = 3.1324\times10^{12}\, exp(-10242.4/T)$, L mol^{-1} min^{-1};

ΔH_a = -132.69 kJ mol^{-1} ; ΔT_{ad} = 61.8 K

$D + D \xrightarrow{k_b, Py} DHA$; $r_b = k_b c_D^2$; $k_b = 7.5651\times10^{12}\, exp(-10242.4/T)$, L mol^{-1} min^{-1};

ΔH_b = -91.92 kJ mol^{-1} ; ΔT_{ad} = 5.3 K

$nD \xrightarrow{k_c} (D)_n$; $r_c = k_c c_D$; $k_c = 1.6549\times10^{12}\, exp(-10242.4/T)$, min^{-1};

ΔH_c = -1426.12 kJ mol^{-1} ; ΔT_{ad} = 83.0 K

$PAA + D \xrightarrow{k_d, Py} G$; $r_d = k_d c_{PAA} c_D$; $k_d = 1.7731\times10^{12}\, exp(-10242.4/T)$, L mol^{-1} min^{-1};

ΔH_d = -132.69 kJ mol^{-1} ; ΔT_{ad} = 7.7 K

Differential balance equations:

- species mass balance: $\frac{dc_D}{dt} = (-\tilde{r}_a - 2\tilde{r}_b - \tilde{r}_c - \tilde{r}_d) + (c_{D,in} - c_D)\frac{F(t)}{V(t)}$; $\frac{dc_P}{dt} = -\tilde{r}_a - c_P\frac{F(t)}{V(t)}$;

$\frac{dc_{PAA}}{dt} = (\tilde{r}_a - \tilde{r}_d) - c_{PAA}\frac{F(t)}{V(t)}$; $\frac{dc_{DHA}}{dt} = \tilde{r}_b - c_{DHA}\frac{F(t)}{V(t)}$; volume variation: $\frac{dV}{dt} = F(t)$;

- reaction rate correction with the catalyst dillution: $\tilde{r}_j = r_j \frac{V_o}{V(t)}$; $j = a,b,d$

- heat balance: $\frac{dT}{dt} = \frac{F(t)(T_{in} - T)}{V(t)} + \frac{\sum_j (-\Delta H_j)\tilde{r}_j V(t) - UA_r(T - T_a)}{\overline{\rho}\,\overline{c}_p V(t)}$, j=a,b,c,d

Observations: I) at $t = 0$, $c_j = c_{j,o}$, $T = T_o$; ii) r_c is not corrected with the catalyst dillution, the reaction displaying another mechanism (the stoichiometric coefficient was included in the rate constant)

Model hypotheses:

- semi-batch reactor model with perfect mixing and uniform concentration and temperature field
- cyllindrical reactor of variable liquid volume and heat transfer area: $A_r = \frac{\pi d_r^2}{4} + \frac{4}{d_r}V(t)$
- heat transfer coefficient evaluated with criterial formula [16] (approximate value for nominal conditions is U = 581 Wm^{-2}K^{-1})
- heat of solvent vaporisation in the reactor is neglected
- heat capacity and density of fed solution are the same with those of reactor content, $\overline{\rho}_{in}\,\overline{c}_{p,in} \approx \overline{\rho}\,\overline{c}_p$

Nominal operating conditions and range of variation

Initial liquid volume (V_o, L):	1	Initial [PAA] (mol L^{-1}):	0.08 ≤ 0.10 ≤ 0.20
Reactor inner diameter (d_r, m):	0.1	Initial [DHA] (mol L^{-1}):	0.01 ≤ 0.02 ≤ 0.04
Stirrer speed (rot min^{-1}):	640	Fed D solution flow rate (F ×100, L min^{-1}):	0.05 ≤ 0.15 ≤ 0.20

Liquid physical properties: toluene solvent		Batch time (t_f, min):	$120 \le 145 \le 378$
Inlet [D] (mol L^{-1}):	$4 \le 5.82 \le 6$	Initial temperature (T_o, °C):	$40 \le 50 \le 60$
Initial [P] (mol L^{-1}):	$0.4 \le 0.72 \le 0.8$	Cooling agent temperature (T_a, °C):	50
Initial [D] (mol L^{-1}):	$0.005 \le 0.09 \le 0.14$	Feeding solution (T_{in}, °C):	50

Process constraint expression:	*Significance*
$c_{DHA,f} - 0.15 \le 0$, (mol L^{-1})	Prevent precipitation of DHA at room temperature (solubility at 50°C is 0.20 mol L^{-1})[13]
$c_{D,f} - 0.025 \le 0$, (mol L^{-1})	Avoid high concentrations of toxic D in product;[13] empirical critical runaway condition [14].
$Max(T(t)) - 70 \le 0$, (T, °C)	Prevent toluene solvent excessive vaporization, pressure increase, and dangereous exothermic side-reactions (Footnote b)

(a) $\Delta T_{ad} = (-\Delta H) c_{j,o} / (\overline{\rho}\,\overline{c}_p)$.

(b) Empirically predicted by adding $2 \times \Delta T_c =$ 20 K to the nominal temperature, where $\Delta T_c = RT_o^2 / E$ correspond to the critical conditions of Semenov for zero-order reactions [19].

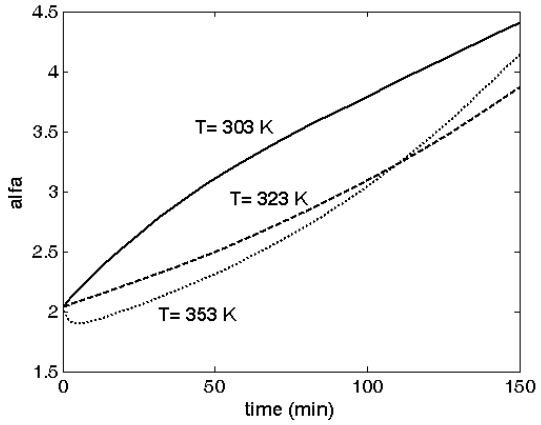

Fig. 1. Variation of α constant as a function of reaction time at three different temperatures (30°C, 50°C , 70°C).

Simulations of the reactor dynamics reveal a high thermal sensitivity due to side-reaction thermal effect [15]. The study of Maria et al. [15] revealed that the critical values of feeding rates $F_c(\boldsymbol{\phi})$ depend on the operating parameter vector $\boldsymbol{\phi} = [F, T_a, c_{D,in}, c_{P,o}, T_o]$ around which the evaluation is made.

4. Reduced chemical kinetic model and estimation of safety limits

The proposed overall reaction of the aceto-acetylation process has the following form: P+D $\rightarrow$ PAA. Because the side reactions from the mechanism are

parallel in relation to the key component D (diketene), the global reaction kinetic model can be considered as follows:

$$r = r_a + r_b + r_c + r_d = k_a \cdot c_D \cdot c_P + k_b \cdot c_D \cdot c_D + k_c \cdot c_D + k_d \cdot c_D \cdot c_{PAA} =$$

$$k_a \cdot c_D \cdot c_P \cdot \left(1 + \frac{k_b}{k_a} \cdot \left(\frac{c_D}{c_P} \right) + \frac{k_c}{k_a} \cdot \left(\frac{1}{c_P} \right) + \frac{k_d}{k_a} \cdot \frac{c_{PAA}}{c_P} \right) = \alpha \cdot k_a \cdot c_D \cdot c_P \ ,$$

in which:

$$\alpha = 1 + \frac{k_b}{k_a} \cdot \left(\frac{c_D}{c_P} \right) + \frac{k_c}{k_a} \cdot \left(\frac{1}{c_P} \right) + \frac{k_d}{k_a} \cdot \frac{c_{PAA}}{c_P} \ . \qquad (4)$$

This apparent reaction rate constant is assumed as presenting an Arrhenius type dependence with the temperature, as well as the "hybrid" rate constant $\alpha = \alpha_0 \cdot \exp(-E_\alpha / RT)$, included in the global kinetics.

The α rate constant has been computed by integrating the isothermal kinetic model at three different temperatures (30°C, 50°C, 70°C). Being a rough approximation derived from lumping the extended kinetic model, the "hybrid" constant α varies not only with the temperature, but also with the reactions time, as plotted in Fig. 1 at three different temperatures. However, the mean values are only retained for every temperature, calculated by using the common integral mean formula. Thus, the Arrhenius parameters α_0 and E_α are obtained by using a least squares statistical estimator [17] using the determined rate constant values at three temperatures. The resulted correlation is:

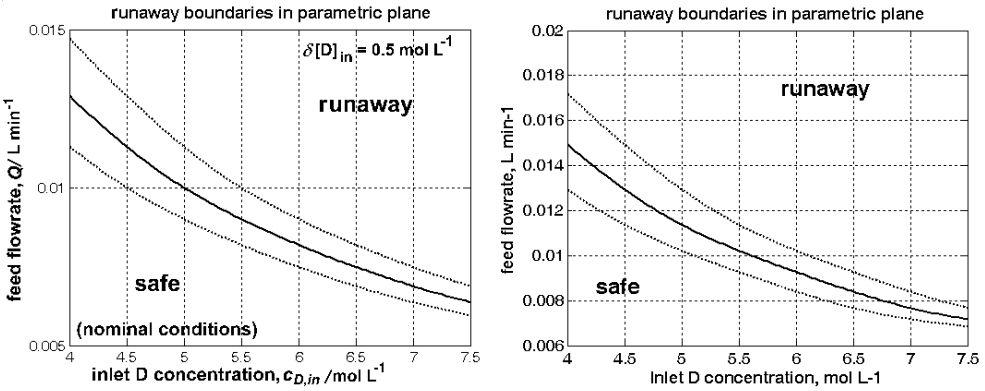

Fig. 2. Runaway boundaries in the [F vs. $c_{D,in}$] plane at nominal conditions predicted for the extended model (left) and reduced model (right) by MV sensitivity method. The confidence band (---) corresponds to the random deviations in the range of $\delta c_{D_{in}} = \pm 0.5$ mol L^{-1}.

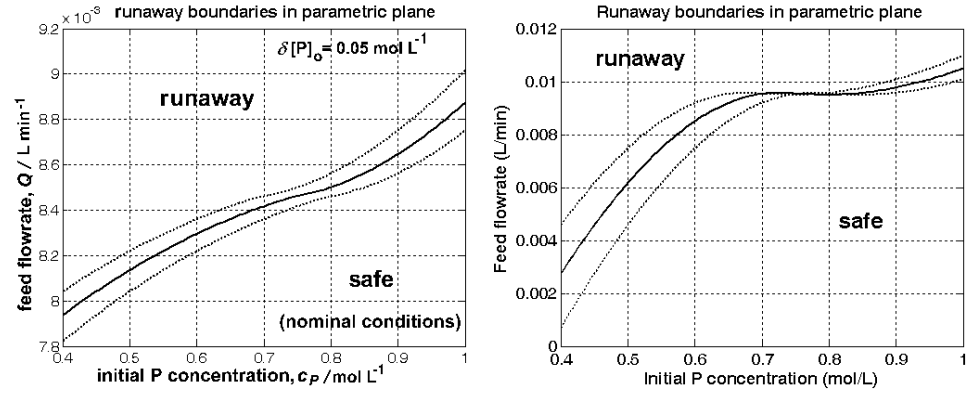

Fig. 3. Runaway boundaries in the [F vs. $c_{P,o}$] plane at nominal conditions predicted for the extended model (left) and reduced model (right) by MV sensitivity method. The confidence band (---) corresponds to the random deviations in the range of $\delta c_{P_0} = \pm 0.05$ mol L^{-1}.

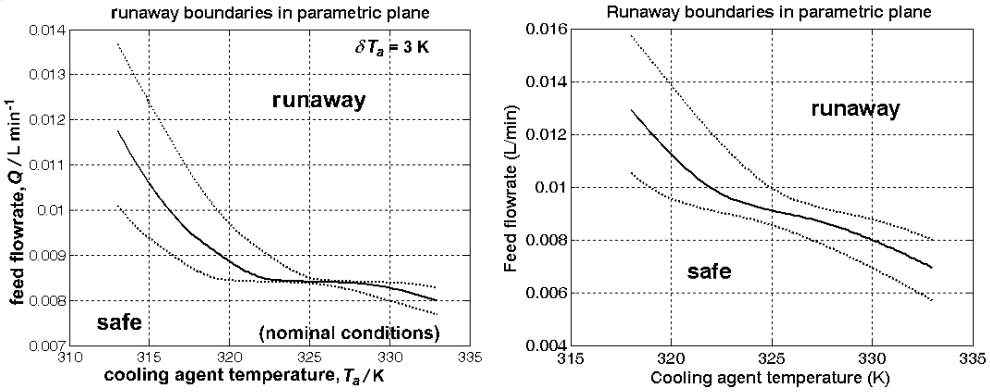

Fig. 4. Runaway boundaries in the [F vs. T_a] plane at nominal conditions predicted for the extended model (left) and reduced model (right) by MV sensitivity method. The confidence band (---) corresponds to the random deviations in the range of $\delta T_a = \pm 3$ K.

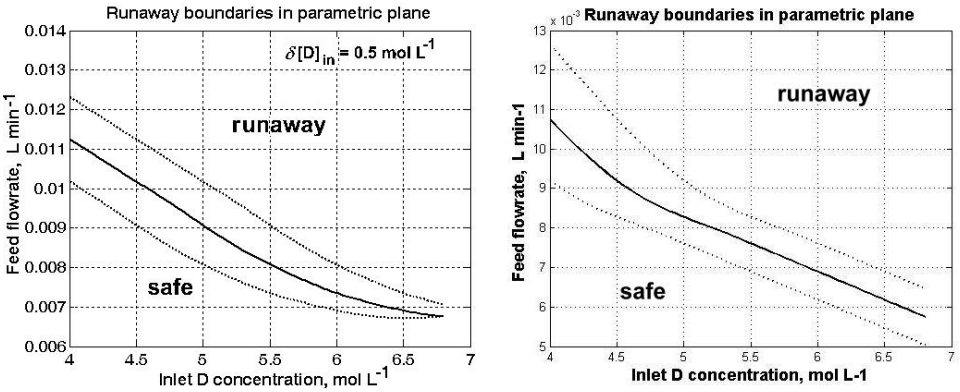

Fig. 5. Runaway boundaries in the [F vs. $c_{D,in}$] plane at nominal conditions predicted for the extended model (left) and reduced model (right) by *div*-J criterion. The confidence band (---) corresponds to the random deviations in the range of $\delta c_{D_{in}} = \pm 0.5$ mol L^{-1}.

$$\alpha = 0.55072 \cdot exp(+544.54 / T) . \tag{5}$$

The "abnormal negative" activation energy in the α-constant correlation (5) can be explained by the large number of mediated variables included in this model-matching parameters obtained by the applied lumping rule.

Another step in defining the reduced kinetic model is the overall reaction heat calculation. For the first-order parallel reactions, the overall heat can be calculated with the approximation formula [18]:

$$\Delta H = \left(k_a \cdot c_P \cdot \Delta H_a + k_b \cdot c_D \cdot \Delta H_b + k_c \cdot \Delta H_c + k_d \cdot c_{PAA} \cdot \Delta H_d\right) / \left(k_a \cdot c_P + k_b \cdot c_D + k_c + k_d \cdot c_{PAA}\right) \tag{6}$$

Runaway boundaries in the [F vs. $c_{D,in}, c_{P,o}, T_a$] planes have been predicted for both extended model and reduced model, by using the MV sensitivity method, or by using the *div*-J criterion. The results for using MV method are comparatively presented in Fig. 2 in the [F vs. $c_{D,in}$] plane, in Fig. 3 in the [F vs. $c_{P,o}$] plane, and in Fig. 4 in the [F vs. T_a] plane. Similarly, the results for using *div*-J criterion are comparatively presented in Fig. 5 in the [F vs. $c_{D,in}$] plane. The confidence band of these runaway boundaries are every time computed by using the Maria et al. [15] methodology, and correspond to the random variations of operating variables around nominalk condition in the range of: $\delta c_{D_{in}} = \pm 0.5$, $\delta c_{P_0} = \pm 0.05$ mol L^{-1} and $\delta T_a = \pm 3$ K (see the plots of Figs. 2-5). The runaway boundaries predicted by the reduced model are less conservative than the critical values predicted by the extended kinetic model, that

is higher values of feed flow rate of ca. 0.0020 L/min. Such a result clearly indicates the risk of utilisation of the reduced model instead of the extended one, the predicted critical conditions being with ca. 20% more "relaxed" than the true ones, with very negative consequences in the design and operation engineering calculations. Such a results has been confirmed by using both MV sensitivity method and *div*-J criterion over a wide range of operating condition variation.

6. Conclusions

Despite being computationally intensive, the model-based evaluation of runaway boundaries of the operating region of an industrial reactor remains a crucial issue in all design, operation and optimal control steps. Moreover, as no compromise should be made when it comes to safety, these method improvements should be applied at every step in the lifetime of the chemical plant. Particularly, the operation associated with inherent random parameter fluctuations around the set point, and/or operation in a higher productivity region in the vicinity of the safety limits require a precise assessment of the runaway/critical conditions. From this point of view, both *div*-methods, based on detection of loss of stability conditions, and parametric sensitivity methods can offer fair predictions [5].

The prediction precision of these methods is however dependent, among others, by the degree of detail used in deriving a kinetic model for a complex chemical process. The paper proves that the model adequacy is not enough to derive a comprehensive safety analysis of the industrial reactor, as long as the dangerous side-reactions (very exothermic and/or chain reactions) are not precisely included in the reduced kinetic model. Further derivation of the process safety limits clearly indicates the bias introduced by such a rough modellisation of the process kinetics with very negative consequences in all engineering analysis steps. The suitable case study chosen in this paper, as well two well-known methods to calculate the safety limits of an industrial reactor support such conclusions.

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Notations

A_r		heat exchange surface of the reactor measured inside the reactor, m^2
A	-	Arrhenius frequency factor, L $mole^{-1}$ s^{-1} , s^{-1}

$B = \Delta T_{ad} E / (RT_o^2)$	-	reaction violence index [18]
c_j	-	component *j* concentration, mole L^{-1}
c_p	-	molar specific heat, J kg^{-1} K^{-1}
d_r	-	reactor inner diameter, m
$Da = (-\nu_A)(r_A \tau_D) / c_{A,o}$	-	Damköhler number for SBR
E	-	activation energy, J $mole^{-1}$
E_α	-	activation energy for global kinetic model, J $mole^{-1}$
F	-	fed flow rate (liquid), L s^{-1}
$\boldsymbol{g}$	-	model function vector
$(-\Delta H)$	-	reaction enthalpy, J $mole^{-1}$
$\boldsymbol{J} = \partial \boldsymbol{g} / \partial \boldsymbol{x}$	-	system Jacobian
k	-	rate constants, L $mole^{-1}$ s^{-1} , s^{-1}
$\boldsymbol{q}$	-	orthogonalized vector of $\boldsymbol{x}$
R	-	universal gas constant, J $mole^{-1}$ K^{-1}
r	-	chemical reaction rate, mole L^{-1} s^{-1}
$s(x;\phi)$	-	absolute sensitivity, $\partial x(t) / \partial \phi$
$S(x;\phi)$	-	normalized sensitivity, $(\phi^* / x^*) s(x;\phi)$, or $\partial \ln(x(t)) / \partial \ln(\phi)$
t	-	time, s
T	-	temperature, K
$\Delta T_{ad} = (-\Delta H) c_{j,o} / (\overline{\rho}\, \overline{c}_p)$	-	temperature rise under adiabatic conditions, K
U	-	overall heat transfer coefficient, W m^{-2} K^{-1}
V	-	liquid (reactor) volume, m^3
$\boldsymbol{x}$	-	state variable vector
Greeks		
α	-	kinetic constant
α_0	-	kinetic constant for global kinetic model
Δ	-	finite difference
δ	-	Kronecker delta function, or small perturbation
$\delta \boldsymbol{x}$	-	perturbation of the fiducial trajectory
ϕ	-	operating parameter
λ_j	-	eigenvalues of a matrix
ν_j	-	stoichiometric coefficient of species *j*
ρ	-	liquid phase density, kg m^{-3}
σ	-	standard deviation, or relative sensitivity tolerance
τ	-	time constant, s
τ_D	-	time of addition of co-reactant D, s
Index		
a	-	cooling agent
ad	-	adiabatic
c	-	critical
f	-	final

in	-	inlet
max	-	maximum
min	-	minimum
o	-	initial
$\overline{\bullet}$	-	average value

Abbreviations

D	-	diketene
DHA	-	dehydroacetic acid
GM	-	geometry-based methods
MV	-	Morbidelli-Varma criterion
P	-	pyrrole
PAA	-	2-acetoacetyl pyrrole
PSA	-	sensitivity-based methods
Py	-	pyridine
Re(·)	-	real part
SBA	-	stretching-based method
SBR	-	semi-batch reactor
SZ	-	Strozzi & Zaldivar
Trace(·)	-	trace of a matrix

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