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SETTING RUNAWAY BOUNDARIES UNDER PARAMETRIC UNCERTAINTY FOR THE BENZENE OXIDATION INDUSTRIAL CATALYTIC REACTOR

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Safe operation of highly thermally sensitive industrial chemical catalytic reactors remains a major engineering issue when highly exothermic reactions are conducted under randomly fluctuating operating and control variables around their nominal values (the so-called "set-point" or "operating point"), and especially when the set-point is located in a close vicinity of the runaway boundaries for increasing the reactor productivity. This study is aiming to derive the runaway boundaries and their associated region of confidence in the operating variable plans for such a risky fixed-bed catalytic reactor of high thermal sensitivity by applying the effective Morbidelli & Varma generalized sensitivity criterion. Such an early safety assessment will be further used to derive the critical surface in the multi-variable space, and their associated region of confidence, very useful for the subsequent industrial reactor multi-objective robust optimization step. Exemplification is made for an industrial fixed-bed multi-tubular reactor for catalytic benzene oxidation to maleic anhydride in vapour-phase using a more detailed kinetic model in order to increase the results precision.

Keywords: runaway boundaries; confidence region; catalytic reactor; maleic anhydride production

Notations

$\overline{c_p}$	-	Average mixture specific heat
D_z	-	Axia dispersion
D_M	-	Molar flow rate
$D_{m,t}$	-	Mass flow rate of the feed mixture
D_m	-	Molecule diffusion coefficient of benzene in air
D_{ef}	-	Effective diffusion coefficient
d_p	-	Catalyst particle diameter
d_t	-	Catalytic bed diameter (equal with pipe interior diameter)

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$d_{t,ext}$ - Pipe exterior diameter
$d_{t,i}$ - Pipe interior diameter
E_a - Activation energy
f - Friction coefficient
G - Green's function matrices
ΔH - Heat of reaction
J - Jacobian
K_T - Overall heat transfer coefficient
k_i - Pseudo-order 1 kinetic constant of reaction „*i*"
L - Total reactor length
M - Molecular weight
Nu_{gaz} - Nusselt number for gases
Pr - Prandtl number
p_j - Partial pressure of species „*j*"
p - Total pressure
R - Ideal gas constant
Re_p - Reynolds number for flow through the catalytic bed
S - Cross-sectional area of the pipe
$s\left(x_i;\varphi_j\right)$ - Parametric sensitivities
T_a - Cooling agent temperature
T - Temperature
t - Time
u_j - Sensitivity functions of the control variables
u - Gas flow velocity
$v_{p,j}$ - Volumetric specific reaction rate of species „*j*"
$v_{R,i}$ - Volumetric specific reaction rate of reaction „*i*",
$v_{r,i}$ - Mass specific reaction rate of reaction „*i*"
V_{TP} - Total pore volume
V - Molecule volume
x_i - State variables
y_j - Molar fractions of chemical species
z - Reactor length

Greeks

α - Heat transfer partial coefficient
α_i^0 - Static contribution of the catalytic bed
β - Coefficient that depends on the particle geometry $\left(\beta = 0.9 \div 1.0\right)$
δ_G - A measure of gas film thickness, normalized relative to the particle diameter
$\delta_{G,1}$, $\delta_{G,2}$ - Represent values of the δ_G parameter which corespond to the most rarefied packing ($\varepsilon_1 = 0.476$) and most compact packing ($\varepsilon_2 = 0.260$)
δ_t - Wall thickness

$\delta(\phi_j - x_o)$ - Kronecker delta function
ε - Void fraction
η_j - The total effectiveness factor of the catalyst particle
λ_{OL} - Wall thermal conductivity
λ_G - Gas thermal conductivity
λ_R^0 - Static contribution of the catalytic bed to the thermal conductivity
λ_S - Catalytic bed thermal conductivity
μ_G - Gas viscosity
$\nu_{i,j}$ - Stoichiometric coefficient of species „*j*” in reaction „*i*”;
ρ_{SC} - Density of the catalytic bed
ρ_G - Gas density
ρ_c - Catalyst density (bulk)
τ - Tortuosity
φ_j - Operating parameters
Φ_i - Thiele modulus

Index

* - Nominal operating conditions
c - Critical conditions
i - Chemical reactions
j - Chemical species
o - Initial conditions

Abbreviations

AM - Maleic anhydride
B - Benzene
div- - *Divergence based criteria*
F - Phenol
GM - *Geometry-based methods*
HSO - “hot-spot” of the temperature axial profile in the tubular reactor
PAO - Pseudo-adiabatic operation
PSA - *Sensitivity-based methods*
Q - Quinone
QFS - Quick onset, Fair conversion and Smooth temperature profile

1. Introduction

The behaviour of physical and chemical systems depends on values of the parameters that characterise them. The analysis of how a system responds to changes in the parameters is called parametric sensitivity. For the purposes of reliable design and control, this analysis is important in virtually all areas of science and engineering. In many cases, when one or more parameters are slightly varied, while holding the remaining parameters fixed, the chemical system output variables also change slightly. However, under other sets of parametric combinations, the chemical system may respond with dramatic and dangerous changes, even if one or more parameters are varied only slightly. In this case, the system behaves in a parametrically highly sensitive manner. It becomes difficult to control the chemical system when it operates in a too sensitive parametric region, and sometimes this leads (for a high thermal sensitivity case) to so-called runaway behaviour that ends up with catastrophic results and chemical accidents [1]. Consequently, both chemical reactor's technological constraints and runaway boundaries of the operating conditions are important for the risk assessment, reactor optimal operation, and over-design avoidance. Derivation with high precision of the runaway boundaries (critical conditions) of the operating/ control variables can be made by using a large variety of methods, from simple to complex ones [1-3]. Simple explicit methods derive the safety limits from a thermal sensitivity analysis based on simple engineering numbers and relationships valid for singular zero- or first-order reactions [2]. Such methods are not sufficiently accurate for an advanced optimization of the process or for implementing an on-line instability detector, the practical approach (but not the most efficient one) providing sufficient overdesign of the system [4].

Alternatively, model based evaluations of critical operating conditions of a reactor, even computationally more intensive, can offer a quite accurate prediction of the safety limits, being generally applicable irrespectively of the reactor type or process. According to [5] such criteria can be classified into four categories: geometry-based criteria (interpreting the shape of the temperature or heat-release rate profile over the reaction / contact time of the reactants with the catalyst), parametric sensitivity-based criteria (detecting unsafe conditions characterized by high parametric sensitivities of state variables vs. operating parameters), divergence-based criteria (detecting any instability or incipient divergence from a reference state-variable trajectory over the contact time), and stretching based criteria (investigating the process divergence from the nominal condition from the dynamics of the tangent components to the state-variable trajectory). Each method presents advantages and limitations related to precision, real-time application, involved computational effort, and applicability. A detailed comparative analysis is given by [1], [5], [6-8].

Geometry-based methods (GM) analyse the shape of the temperature or heat-release rate profile over the reactor length (z). Critical conditions correspond to an accelerated temperature increase, i.e. to an inflexion point before the curve maximum in a temperature – contact time plot $T(z)$ (where z is the contact time or reactor length). *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 reactor length $x_i(z)$. 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 [9,10]. 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 [7,8,11,12].

The scope of this paper and its main novelty is coming from pointing-out the higher accuracy of the risk assessment when using extended kinetic models of the process by considering most of the side-reaction enthalpies in evaluating the runaway boundaries for an industrial fixed-bed multi-tubular catalytic reactor. A concrete example is provided for the exothermic benzene oxidation to maleic anhydride in vapour-phase. The Morbidelli-Varma sensitivity criterion has been used, proving the unbiased predictions generated with the extended kinetic model under nominal reaction conditions.

2. Generalized sensitivity criterion for deriving critical operating conditions

This study is aiming to derive the runaway boundaries and their associated region of confidence in the operating variable plans for a risky fixed-bed catalytic reactor by applying the effective Morbidelli & Varma generalized sensitivity criterion using an extended kinetic model. This runaway criterion is 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 reactor length, in respect to a certain operating parameter ϕ_j. In other words, critical value of a parameter $\phi_{j,c}$ corresponds to:

$$\begin{gathered}\varphi_{j,c} = \arg\left(\operatorname{Max}_{\varphi_j} \left| s\left(T_{\max};\varphi_j\right) \right|\right), \text{or}\ \varphi_{j,c} = \arg\left(\operatorname{Max}_{\varphi_j} \left| S\left(T_{\max};\varphi_j\right) \right|\right), \\ S(T_{\max};\varphi_j) = (\varphi_j^* / T_{\max}^*) s(T_{\max};\varphi_j) = (\varphi_j^* / T_{\max}^*)(\partial T_{\max} / \partial \varphi_j), \end{gathered} \tag{1}$$

[where: $S(T_{\max};\varphi_j)_z = s(T_{max};\phi_j)\phi_j^* / T^*$ = relative sensitivity function of $T_{\max}$ vs. parameter ϕ_j = operating parameter or control variable; '*' = nominal operating conditions (set point) in the parameter space; z = reactor length].

According to the MV criterion, critical conditions induce a sharp peak of the normalized sensitivity $S(T_{max};\phi)$ evaluated over the reactor length 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 [1,4]. A worthy alternative, also used in the present study, is the application of the numerical finite difference method, which implements certain differentiation scheme (of various precision and complexity) to estimate the derivatives of $s(x_i;\varphi_j)_z$ at various reactor lengths *z* [13]. The MV generalized senzitivity criterion is proved to be very effective and generally applicable irrespectively of the reactor type or process [5], [6-7], [14]. The only limitation (due to results poor precision) is reported for supercritical operating conditions, corresponding to the so-called "Quick onset, Fair conversion and Smooth temperature profile" (QFS), characterized by a high level but quite 'flat' temperature-over-reactor length-profile, and small sensitivities of state variable *vs.* operating conditions [8]. Such regions can be of economic interest rather for semi-batch operated reactors, but not for highly sensitive fixed-bed tubular reactors. It is also to underline that the MV criterion was applied in the so-called HSO operation region (corresponding to a "hot-spot" of the temperature axial profile in the tubular reactor), more interesting economically. The PAO (pseudo-adiabatic operation) with a continuously increasing temperature along the reactor catalytic tube was not approached as long as such a region is not usually applied in practice, corresponding to "the transition from the HSO to the runaway region" in the parametric space [1].

3. The gas phase catalytic oxidation of benzene reactor model and evaluation of the parametric sensitivity

To illustrate the parametric sensitivity analysis, the case of catalytic oxidation of benzene to maleic anhydride in vapour phase was considered [15]. The multi-tubular reactor (of heat exchanger type) with the catalytic fixed bed inside tubes of small diameters (under 3 -4 cm) is continously cooled by a molten salt mixture (nitrates, nitrits mixture; Nenitescu, 1954, citation under [16]) circulated outside and among rows of pipes. The raw materials are air (oxygen) and benzene. The compressed and filtered air is heated into a preaheter (using the heat coming from the reactor outlet), and then mixed with benzene vapours at a concentration below the lower explosion limit (LEL, 1.5%vol.). The benzene/air mixture is fed into the reactor at approx. 385°C where the oxidation to maleic anhydride takes place. The reaction temperature is kept under an permissible limit

(450^{o}C) by quickly dissipating the heat of reaction through reactor intertubular space molten salt heavy circulation. The catalyst used for the reaction is a mixture of vanadium/chromium oxides on a silica bed [15]. The oxidation reaction is complex, with succesive and parallel reactions, involving a relative large number of intermediate products. To solve this study objective, the complex reaction kinetics was used for a better understanding of the industrial reactor behaviour (R1-R9). The reactions and their enthalpy (taken from Aspen Hysys software) are displayed below:

$$C_6H_6 + {}^1\!/_2 O_2 \xrightarrow{k_1} C_6H_5OH \ ; \ \Delta H_{R_1,298} = -1{,}7939\cdot 10^5 \ kj/kmol \qquad (R1)$$

$$C_6H_6 + {}^3\!/_2 O_2 \xrightarrow{k_2} C_6H_4O_2 + H_2O \ ; \Delta H_{R_2,298} = -4{,}4769\cdot 10^5 \ kj/kmol \qquad (R2)$$

$$C_6H_6 + {}^9\!/_2 O_2 \xrightarrow{k_3} C_4H_2O_3 + 2CO_2 + 2H_2O \ ; \ \Delta H_{R_3,298} = -1{,}7525\cdot 10^6 \ kj/kmol \qquad (R3)$$

$$C_6H_6 + {}^{15}\!/_2 O_2 \xrightarrow{k_4} 6CO_2 + 3H_2O ; \ \Delta H_{R_4,298} = -3{,}1712\cdot 10^6 \ kj/kmol \qquad (R4)$$

$$C_6H_5OH + O_2 \xrightarrow{k_5} C_6H_4O_2 + H_2O \ ; \ \Delta H_{R_5,298} = -2{,}6830\cdot 10^5 \ kj/kmol \qquad (R5)$$

$$C_6H_4O_2 + 3O_2 \xrightarrow{k_6} C_4H_2O_3 + 2CO_2 + H_2O ; \ \Delta H_{R_6,298} = -1{,}3048\cdot 10^6 \ kj/kmol \qquad (R6)$$

$$C_4H_2O_3 + 3O_2 \xrightarrow{k_7} 4CO_2 + H_2O \ ; \ \Delta H_{R_7,298} = -1{,}4187\cdot 10^6 \ kj/kmol \qquad (R7)$$

$$C_6H_5OH + 4O_2 \xrightarrow{k_8} C_4H_2O_3 + 2CO_2 + 2H_2O ; \ \Delta H_{R_8,298} = -1{,}5731\cdot 10^6 \ kj/kmol \qquad (R8)$$

$$C_6H_5OH + 7O_2 \xrightarrow{k_9} 6CO_2 + 3H_2O ; \ \Delta H_{R_9,298} = -2{,}9918\cdot 10^6 \ kj/kmol \qquad (R9)$$

In order to achieve such an analysis, a simplified mathematical model of the reactor was used by considering a pseudo-homogeneous, one-dimensional, plug-flow reactor hypotheses. Model equations are presented in Table 1 in terms of the mass balance of the considered chemical species, heat and momentum balance:

Table 1

The fixed bed multi-tubular reactor model used for benzene oxidation to maleic anhydride

Mass balance differential equations:
Mass balance (index j denotes species): $\left.\begin{array}{l} \dfrac{dD_{M_j}}{dz} = -\eta_j v_{p,j} S \\ v_{p,j} = \sum_{i=1}^{9} v_{i,j} \cdot v_{R,i} \\ v_{R,i} = v_{r,i}\rho_{SC} \\ v_{r,i} = k_i p_j \end{array}\right\} \Rightarrow \dfrac{dD_{M_j}}{dz} = -\eta_j \rho_{SC} S \sum_{i=1}^{9} v_{i,j} k_i p_j, \quad j = \mathrm{B, F, Q, AM, CO_2, H_2O, O_2, N_2}$ $z = 0 \to y_j = y_{j,0}, T = T_0, P = P_0$ B = Benzene, F = Phenol, Q = Quinone, AM = Maleic anhydride; i = Chemical reactions; D_{M_j} - molar flow rate of „j” species, kmol/s; S - cross-sectional area of the pipe;

$v_{p,j}$ - volumetric specific reaction rate of species „*j*”, $\frac{kmol}{m^3 \cdot s \cdot atm}$;

$v_{R,i}$ - volumetric specific reaction rate of reaction „*i*”, $\frac{kmol}{m^3 \cdot s \cdot atm}$;

$v_{r,i}$ - mass specific reaction rate of reaction „*i*”, $\frac{kmol}{kg_{cat} \cdot s \cdot atm}$ (pseudo-order “1” reaction);

ρ_{SC} - density of the catalytic bed, $\frac{kg_{cat}}{m^3_{reactor}}$; $\rho_{sc} = (1-\varepsilon) \cdot \rho_p$,

ρ_p - density of catalyst particle, $\frac{kg_{cat}}{m^3_{cat}}$; ε - void fraction;

$\nu_{i,j}$ - stoichiometric coefficient of species „*j*” in reaction „*i*”;

p_j - the partial pressure of species „*j*”, *atm;*

η_j - the total effectiveness factor of the catalyst particle;

k_i - pseudo-order 1 kinetic constant of reaction „*i*”, $\frac{kmol}{kg_{cat} \cdot s \cdot atm}$; $k_i = k_{i_0} \cdot e^{-\frac{E_a}{RT}}$ (values in Table 2); R – ideal gas constant $R = 8.314 \frac{kj}{kmol \cdot K}$, $R = 1.987 \frac{kcal}{kmol \cdot K}$, $R = 0.082 \frac{m^3 \cdot atm}{kmol \cdot K}$;

Heat balance:

$$\frac{dT}{dz} = \frac{\sum_{i=1}^{9} \left(-\Delta H_{R,i}\right) v_{r,i} \rho_{SC} S - K_T \pi d_t \left(T - T_a\right)}{D_{m,t} \cdot \overline{c_p}}$$

; *T* – gas temperature, *K*; *z* – reactor length, *m*;

$\left(-\Delta H_{R,i}\right)$ - heat reaction of reaction „*i*”, *kJ/kmol*; K_T - overall heat transfer coefficient, $\frac{W}{m^2 K}$;

d_t - pipe diameter, *m*; T_a - cooling agent temperature, *K*;

$D_{m,t}$ - mass flow rate of the feed mixture, *kg/s*; $\overline{c_p}$ - average mixture specific heat, $\frac{kJ}{kg_{am} K}$.

Momentum balance:

$$\frac{dp}{dz} = -f \left(\frac{D_{m,t}}{S}\right) \frac{1}{\rho_G d_p} = -f \frac{u^2 \rho_G}{d_p}$$

- friction coefficient calculated by Ergun and Hicks formula [17]:

$$f = \begin{cases} \frac{1-\varepsilon}{\varepsilon^3}\left[1.75 + 150\frac{1-\varepsilon}{\mathrm{Re_p}}\right], & \frac{\mathrm{Re_p}}{1-\varepsilon} < 500 \\ 6.8\frac{\left(1-\varepsilon\right)^{1.2}}{\varepsilon^3}\mathrm{Re}_p^{-0.2}, & \frac{\mathrm{Re_p}}{1-\varepsilon} > 500 \end{cases} ; \varepsilon = 0.38 + 0.073\left[1 + \frac{(d_t/d_p - 2)^2}{(d_t/d_p)^2}\right]$$

,bed void fraction

$\mathrm{Re_p} = \frac{u \rho_G d_p}{\mu_G}$ - Reynolds number for flow through the catalytic bed. d_p - catalyst particle diameter, m; u - gas flow velocity, m/s; ρ_G - gas density, $\frac{kg_G}{m_G^3}$; μ_G - gas viscosity, $Pa \cdot s$ [17].

The model hypotheses:

Molten salt bath temperature (cooling agent) is considered of uniform characteristics;

The heat transfer coefficient is considered to be uniformly along the length of the pipe and is rated using the following formula:

$$K_T = \frac{1}{\frac{1}{\alpha_i}\frac{d_{t,ext}}{d_{t,i}} + \frac{\delta_t}{\lambda_{OL}}\frac{d_{t,ext}}{d_{t,i}} + \frac{1}{\alpha_{sare}}}, \quad \frac{W}{m^2 K}\ ; \ \alpha_i = \frac{\lambda_G Nu_G}{d_p}, \quad \frac{W}{m^2 K}$$

α_i - heat transfer partial coefficient gas – reactor pipe wall incorporates the contribution of the heat transfer of both gas and catalyst (conduction and radiation heat transfer)

$$Nu_{gaz} = \frac{\alpha_i^0 \cdot d_p}{\lambda_G} + 0.33 \cdot \mathrm{Re_p} \cdot \mathrm{Pr}\ ; \quad \alpha_i^0 = 2.44 \cdot \frac{\lambda_R^0}{d_t^{1.33}}, \quad \frac{W}{m^2 K}$$

For temperatures below 400 ^{o}C radiation heat transfer can be neglected:

$$\lambda_R^0 = \lambda_G \left[\varepsilon + (1-\varepsilon) \cdot \frac{\beta}{\delta_G + \frac{2}{3} \cdot \frac{\lambda_G}{\lambda_s}} \right], \quad \frac{W}{m \cdot K}$$

; β - coefficient that depends on the particle geometry $(\beta = 0.9 \div 1.0)$; δ_G - a measure of gas film thickness, normalized relative to the particle diameter, which is calculated from the linear interpolation equation:

$$\delta_G = \delta_{G,2} + \left(\delta_{G,1} - \delta_{G,2}\right)\frac{\varepsilon - 0.26}{0.476 - 0.26}$$

In this equation, $\delta_{G,1}$, $\delta_{G,2}$ represent values of the δ_G parameter which corespondes to the most rarefied packing (ε_1 = 0.476) and most compact packing (ε_2 = 0.260). The values $\delta_{G,1}$, $\delta_{G,2}$ are depending on the conductivities ratio λ_S / λ_G ($\lambda_S = 1.4 \frac{W}{m \cdot K}$ - for the selected catalyst) (Kulkarni and Doraiswamy, 1980, citation according to [18]). The approximate value at the feed conditions: $K_T = 119.4 \frac{W}{m^2 K}$

Transport resistance inside the particle is represented by overall effectiveness factor:

$$\eta_i = \frac{3}{\Phi_i}\left(\frac{1}{th(\Phi_i)} - \frac{1}{\Phi_i}\right)$$

Thiele modulus, Φ_i is evaluated for a pseudo- first order kinetics for large inlet ratios [20]:

$$\Phi_i = \frac{d_p}{6}\sqrt{\frac{k_i \rho_p \frac{1-\varepsilon}{\varepsilon} RT}{D_{ef}}}$$

Effective diffusion coefficient of the particle is evaluated based on the molecule diffusion coefficient of benzene in air, $D_{ef} \approx \varepsilon\ D_m / \tau$, calculated using the below equation [19]:

$D_m = (1-y_B)/\sum_{j\neq B} y_j / D_{m,j}$; $D_{m,j} = 4.3\times10^{-7}\dfrac{T^{1.5}}{p(V_B^{0.33}+V_j^{0.33})^2}\sqrt{\dfrac{1}{M_B}+\dfrac{1}{M_j}}$, ($m^2s^{-1}$) (surface and Knudsen diffusion can be neglected in this case) [18]
Ideal plug-flow reactor with concentration, temperature and pressure gradients variation only in the axial direction $\partial(c_j,T,p)/\partial R_t = 0$, for the case $L/d_t > 50; d_t/d_p > 10$
Axial dispersion coefficient is null : $D_z = 0$, since $L/d_t > 50$
Isothermal spherical catalyst particle, $\partial T_p/\partial R_p = 0$ - Catalyst particle average diameter, d_p
One neglects the resistance to inter-granular property transport (Satterfield criteria) because $L/d_p > 100$

Table 2

Kinetics constants for benzene oxidation [15]

Kinetic constants, $kmol/(kg_{cat}\cdot h\cdot atm)$	k_{i_0}	E_a, $kcal/mol$	Kinetic constants, $kmol/(kg_{cat}\cdot h\cdot atm)$	k_{i_0}	E_a, $kcal/mol$
k_1	$2.00\cdot10^{-3}$	2.448	k_6	0.176	2.401
k_2	$3.28\cdot10^{-3}$	2.530	k_7	0.388	5.882
k_3	0.106	2.410	k_8	73.7	12.059
k_4	0.129	2.454	k_9	13.8	12.085
k_5	65.31	12.059			

Thermal and risk analysis of the reactor begin with determination of the operating variables which have a strongly influence to the process performance (final conversion of the reactants) and the maximum temperature rise in the reactor (thermal spot value). By simulating the reactor behaviour under nominal operating conditions (Table 3), but every time perturbing one of the operating variables, it is possible to point out the reactor sensitivity to various operating parameters and rank their individual influence (Fig. 1-2).

Table 3

Industrial catalytic reactor and process characteristics

Catalyst density (bulk) [14]	$\rho_c = 1260$ kg/m^3		
Catalyst particle average diameter (similar to [14])	$d_p = 0.005\ m$		
Total pore volume [15]	$V_{TP} = 0.4$ m$^3_{void}$/m$^3_{bulk}$		
Fixed-bed void fraction	$\varepsilon = 0.48$		
Tortuosity	$\tau = 2.01$		
Pipe inner diameter	$d_t = 24\ mm$		
Reactor length	$L = 4\ m$		
Operating conditions:	Minimum	Nominal	Maximum
Inlet total pressure	$p_0 = 1.6\ atm$	$p_0 = 3\ atm$	$p_0 = 4\ atm$

Inlet gas temperature	$T_0 = 305\ ^oC$	$T_0 = 385\ ^oC$	$T_0 = 405\ ^oC$
Benzene inlet molar fraction	$y_{B,0} = 0.007$	$y_{B,0} = 0.014$	$y_{B,0} = 0.018$
Cooling agent average temperature	$T_a = 300\ ^oC$	$T_a = 380\ ^oC$	$T_a = 400\ ^oC$

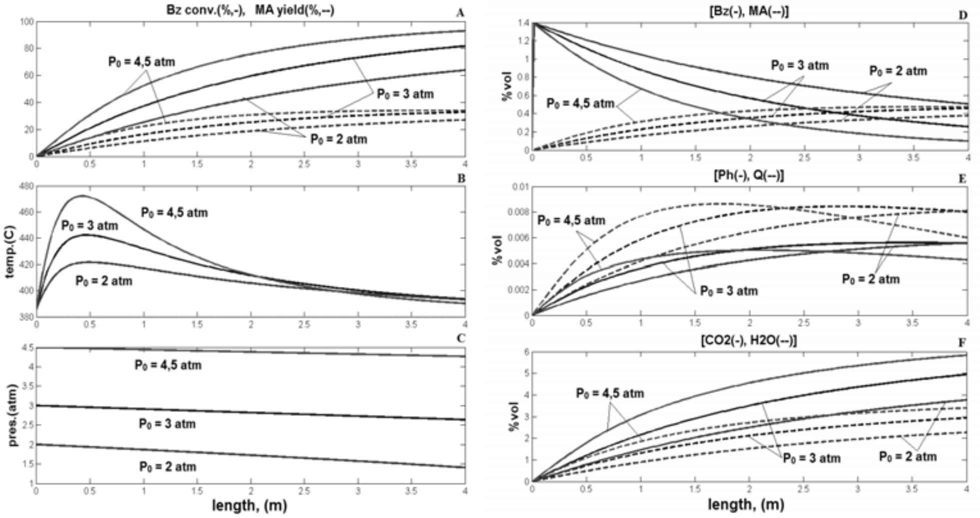

Fig. 1. Axial profiles of benzene conversion *(%)* and yield in maleic anhydride (%) (A), temperature (B), total pressure (C) and molar fractions of several species (D – F) for different values of the inlet total pressure (p_0).

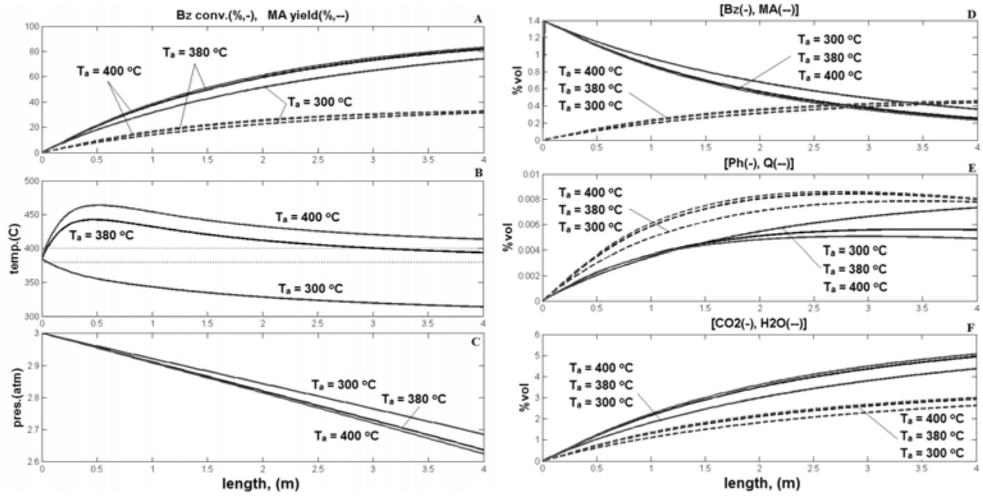

Fig. 2. Axial profiles of benzene conversion *(%)* and yield in maleic anhydride (%) (A), temperature (B), total pressure (C) and molar fractions of several species (D – F) for different values of cooling agent average temperature (T_a)

4. Derivation of critical operating conditions under parametric uncertainty

In order to analyse the influence of the operating parameters uncertainty, the running parameters considered as randomly fluctuating around the nominal values ("set-point" with a fluctuation considered to be normally distributed), on the critical operating conditions for a fixed bed multi-tubular catalytic reactor, the Morbidelli-Varma sensitivity criterion has been used. Sensitivity functions time/reactor length (z) dependent $s(\mathrm{y};\phi)_{\mathrm{z}} = \partial y(\mathrm{z}) / \partial \phi$ are evaluated by considering the following operating parameters (abscissas in Figure 3): inlet temperature, feed pressure, benzene inlet molar fraction and cooling agent temperature. The following control variables are considered (i. e. ordinates in Figure 3): inlet pressure, cooling agent average temperature. Absolute sensitivity can be calculated by integrating the sensitivity equations concomitantly with the reactor model [1, 16]. Model Jacobian and local sensitivities $\partial y(\mathrm{z}) / \partial \phi$ were numerically evaluated by using the finite differences method, with an important computational effort. Based on the evaluation of the sensitivity functions $S(T_{max};\phi)_z$, (index *z* denoting their dependence on reactor length) application of the generalized MV criterion identifies the critical operating conditions by determining the maximum absolute value of maximum temperature sensitivity with respect to a reference parameter, before the temperature maximum with respect of reactor length appears, that is: $\varphi_{j,c} = \arg\left(\mathrm{Max}_{\varphi_j} \left| s\left(T_{\max};\varphi_j\right) \right|\right)$. In terms of sensitivity functions of the control variables (denoted by "*u*") can be written as $u_{j,c}(\phi_j) = max\left|S(T_{max};\phi_j)\right|$. For the case of $\phi_j = p_o$ and $\phi_j = T_{a,o}$ (i.e. inlet total pressure and cooling agent average temperature) and various control variables T_o**,** P_o **,** $y_{B,o}$ and T_a [5], the resulted dependences are plotted in Figure 3 - 4 (left) for different values of the control variable u_j. The graphical representation of the positions of the $S\left(T_{\max};\mathrm{y}_{Bo}\right)$ -vs p_o / $S\left(T_{\max};\mathrm{y}_{Bo}\right)$ -vs $T_{a,o}$ maximum with respect to the reference variable u_j, leads to set the runaway boundaries in every parametric plane $p_{o,c}$-vs.- u_j / $T_{ao,c}$-vs.- u_j , as represented in Figure 3 and Figure 4 (standard deviations of the control variable are indicated for every control variable / operating parameter in the figure caption, leading to a corresponding 68% confidence interval of the obtained risk curves in the parametric planes according to the assumed normal distribution of the control variable fluctuations).

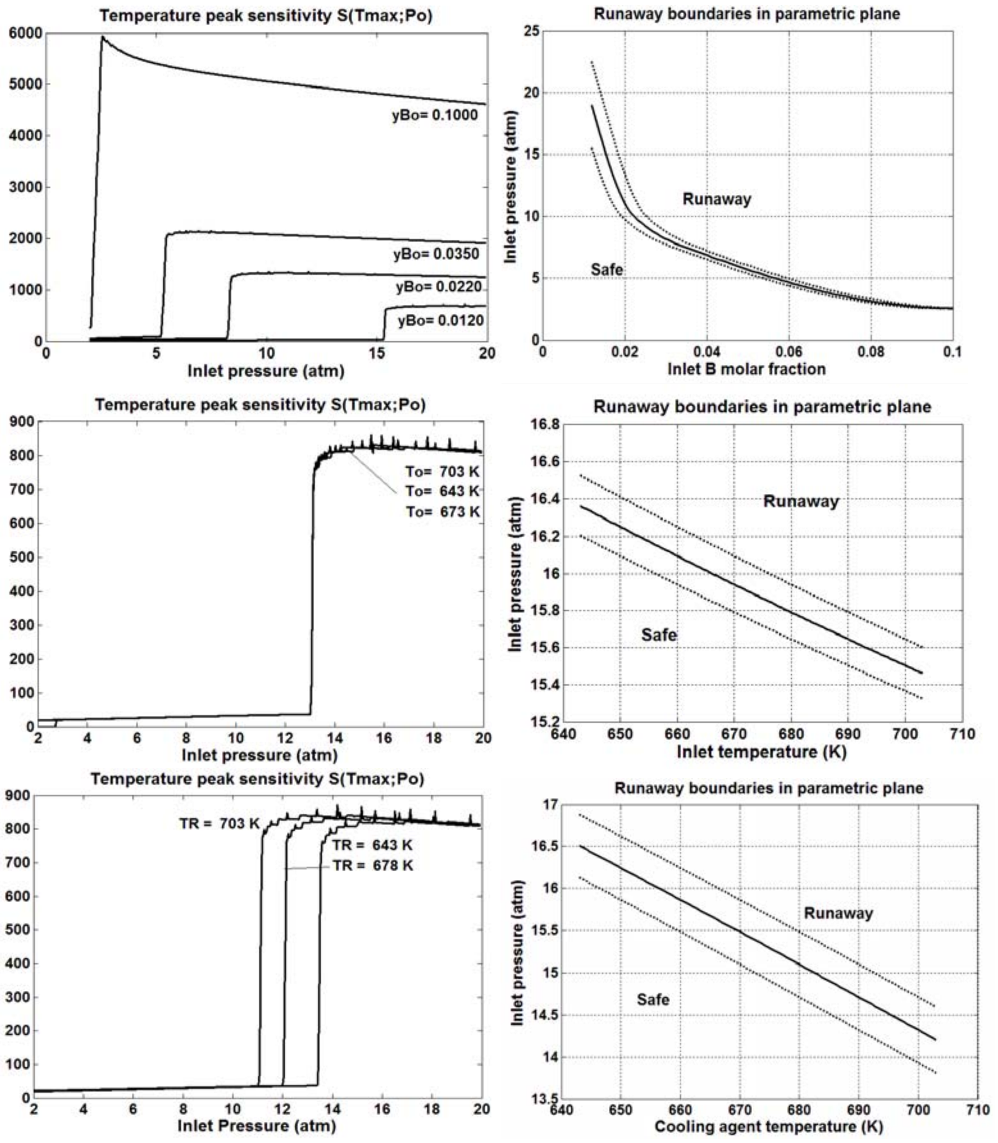

Fig. 3. (Left) Sensitivity of the temperature maximum in the fixed-bed reactor vs. the inlet total pressure $S\left(T_{\max};\mathrm{p}_o\right)$ for different operating parameters ($\phi_j = y_{B,o}, \phi_j = T_o$, and $\phi_j = T_a$). (Right) Runaway boundaries (−) in the parametric plane [P_o vs. y_{B0}] (up), [P_o vs T_0] (centre), [P_o vs. T_a] (down) and its confidence band for parametric deviations $\phi_j \pm \delta\phi_j$ with $\delta y_{B,o}$ = 0.003 mol/mol (---), δT_o = 10 K (---), δT_a = 10 K (---). Notation “B” on axes denotes benzene.

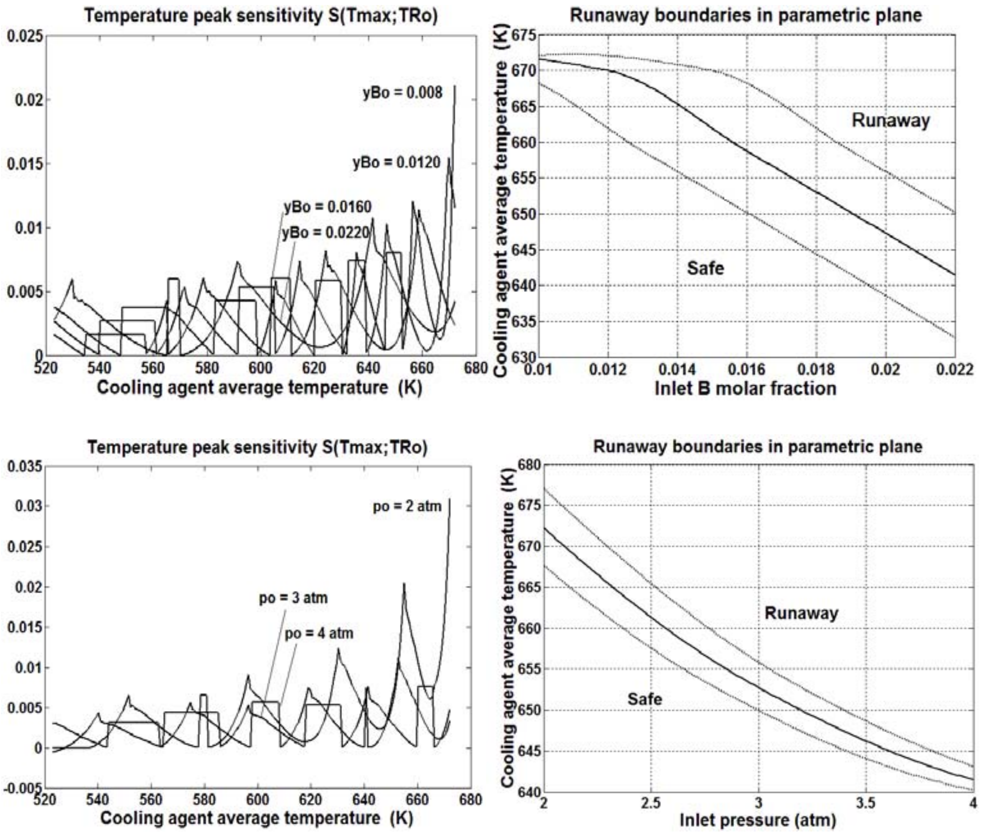

Fig. 4. (Left) Sensitivity of the temperature maximum in the fixed-bed reactor vs. cooling agent average temperature $S\left(T_{\max};T_{a,o}\right)$ for different operating parameters ($\phi_j = y_{B,o}$ and $\phi_j = p_o$).

(Right) Runaway boundaries (−) in the parametric plane [T_a vs. y_{B0}] (up), [T_a vs. P_o] (down) and its confidence band for parametric deviations $\phi_j \pm \delta\phi_j$ with $\delta y_{B,o}$ = 0.003 mol/mol (---) , δp_o = 0.2 atm (---). Notation "B" on axes denotes benzene.

5. 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. 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 requires a precise assessment of the runaway/critical conditions. From the above results we can conclude that by increasing the severity of the operating conditions, which leads to increased reactor productivity, more restrictive runway boundaries in the parametric plane are obtained. This conclusion has a high practical importance for the determination of the nominal operating point taking into account not only the optimization of the economic objective (productivity), but also the safety objective which can lead to an acceptable trade-off.

Another aspect investigated is related to uncertainty in assessing the safety limits of the operating region associated with random operating variable, ϕ_j, fluctuations around the nominal operating point on a given interval, $\phi_j \pm \partial\phi_j$. Such parameters uncertainty is generally linked to the performance of the reactor control systems. By repeated application of the MV criterion, taking as values $\phi_{j,min}$; $\phi_{j,max}$ lower and upper limits of the parameters, lower and upper limits of critical operating conditions can be calculated. Even if being more computational and requiring extensive information on the process, the present study proves the advantages of using of an extended process model and of a more sophisticated sensitivity criterion (such as the robust z-MV) to determine the runaway boundaries and their confidence in the parametric space, with accounting for parameter random fluctuations around the set point.

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