Derivation of Operating Region Runaway Boundaries for the Vapour Phase Catalytic Reactor used for Aniline Production

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The safety in operation of a fixed-bed catalytic reactor remains a sensitive issue when a highly exothermic reaction is conducted and various process development elements such as controllability, stability, risk, and economic aspects have to be considered. Nominal operating conditions are set at a certain distance from safety limits in order to control the hot spot in the tubular reactor and to avoid excessive thermal sensitivity to random variations in process parameters. In the present study, a robust and precise sensitivity criterion, i.e. the model-based z-MV generalized criterion of Morbidelli & Varma, is used to establish the runaway boundaries in the operating variable space. The method sets the global runaway conditions as corresponding to the maximum sensitivity of the temperature peak in the reactor vs. operating parameters. A concrete example is provided for the case of the fixed-bed catalytic reactor for aniline production. Because the process operating variables, such as the inlet temperature or fed ratio, inlet pressure, cooling agent temperature, etc., are subjected to random fluctuations within a certain range, confidence intervals of the derived process runaway boundaries are also predicted, to be further considered in the optimal location of the reactor set-point.

Keywords: runaway boundaries, confidence region, catalytic reactor, aniline production

In an industrial chemical plant, the reactor is the core equipment on which the optimization efforts are focused due to the high value of raw materials and products related to the production cost, but also due to its high sensitivity to operating conditions, risk, and stability problems. Optimization procedures are usually employed to set the reactor's nominal operating conditions within a stable and economic region in the parametric space, while elaborated control schemes are usually implemented to keep the reaction synthesis within the safety limits [1]. For the tubular reactor cases, safe operation tries to limit the hot spot and avoid excessive sensitivity to variations in the process parameters. Various optimization criteria have been proposed taking state variable sensitivity as constraints [2,3], keeping a certain distance vs. the runaway boundaries [4], or explicitly accounting for the uncertainty in the operating parameters [5-7].

However, frequent perturbations in the operating parameters, raw-material recycle conditions, catalyst replacement or reactivity modifications, all require periodical updates of the safety margins for the operating variables. Unsafe conditions correspond to sensitive operating regions when "the reactor performance becomes unreliable and changes sharply with small variations in parameters" [8]. Risky operating conditions for highly exothermic primary or secondary reactions are determined by using simple shortcut techniques, or by using more elaborated model-based methods to appreciate the high thermal sensitivity of the reactor to operating conditions [11]. For a catalytic tubular reactor, the runaway sensitivity analysis can be developed for a single particle at a certain reactor location (usually at the reactor inlet, i.e. the so-called *local runaway conditions*), or extended over the whole reactor length looking for the hot-spot sensitivity to concomitant variations of parameters (the so-called *global runaway conditions*).

Approximate risk assessment of the reactor derives the safe conditions based on certain inequalities constructed for every reactor type by using engineering numbers (such as Damköhler-Da, Stanton-St, or Lewis-Le), or safety indices that replace the systematic model-based safety analysis of the process [9,11,12,28]. Such a risk assessment tries to evaluate interactions between primary and secondary reactions expressed by means of risk measures, such as: adiabatic induction time to explosion (τ_{ad}); reaction violence index B [$\Delta T_{ad} E/(R_g T_o^2)$, where E = activation energy of the reaction; T_o = initial temperature of the reaction; R_g = universal gas constant; $DT_{ad}=(-\Delta T_{ad})c_{j,o} / (\rho_g c_{pg})$ = adiabatic temperature rise; $(-\Delta H)$= heat of reaction; $c_{j,o}$ = initial concentration of key species; ρ_g = reacting mixture density; c_{pg} = average specific heat of gas]; rate of generating the reaction heat compared to the rate of heat removal by the cooling system; adiabatic temperature limits of reactions ΔT_{ad}, ADT_{24}, reaction T_{onset} levels from dual scanning calorimeter DSC measurements, etc. Values of reaction heat of $(-\Delta H) > 10$ kcal/mol, TMR_{ad} <8h, $\Delta T_{ad} >50$K, and B>5 indicate potential dangerous reactions, presenting a fast evolution and a significant exothermicity (where TMR_{ad} = time to maximum rate under adiabatic conditions; ADT_{24} = sample initial temperature for an adiabatic decomposition within 24 h).

More precise methods for predicting the operation safety limits are based on the process/reactor model, of complexity depending on the available information on kinetics, thermodynamics, and reaction pathway. For the tubular reactor case, including the catalytic fixed-bed operated with a hot spot (HSO) or pseudo-adiabatic (PAO), the thermal sensitivity conditions are identified mainly by using three types of methods[8]: explicit, geometrical, and sensitivity methods. Explicit criteria derive the approximate critical operation conditions based on simple and explicit

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relationships derived from the process/reactor model using a certain safety criterion. Geometry-based methods interpret the shape of the axial temperature profile $T(\tau)$ (where τ is the contact time or reactor length), by relating it to the sensitivity of the reactor to variations in the operating parameters. For the HSO of the tubular reactor, the critical runaway conditions correspond to a high sensitivity of the hot-spot, identified by apparition of an inflexion point before the curve maximum. Various derived conditions are reported in the literature, even if their precision in the PAO region is low [8]. Sensitivity-based methods are based on the parametric sensitivity functions of state variables y_i with respect to parameters ϕ_j, i.e. $s(y_i; \phi_j) = \partial y_i / \partial \phi_j$ (in absolute terms), or $S(y_j\phi_j) = (\phi_j^* / y_j^*)s(y_j; \phi_j)$ (in relative terms with respect to a nominal operating point ϕ_j^*). Unsafe conditions correspond to highly sensitive operating regions of the parametric space. The reactor length dependent sensitivity functions of the states $s(y; \phi)_z$ (i.e. temperature, conversion, selectivity, species concentrations, pressure) can be expressed vs. various process parameters, such as the inlet temperature T_o, partial pressures, $p_{j,o}$ concentrations $c_{j,o}$, flow-rate F_m, cooling agent temperature T_a, overall reaction order n, reaction violence index B, Thiele modulus Φ, engineering numbers (Da, St, Le) reflecting the mass and heat transfer intra- or inter-particle resistance, or a mixture of them. Combinations of sensitivity and loss of stability methods are based on the observation that near the critical operating conditions every small perturbation is amplified and the reactor evolves toward thermal runaway. Various safety criteria are proposed, by checking the loss of local stability from inspecting the negativeness of the real part of Jacobian matrix $\mathbf{J}$ eigenvalues $Re(\lambda_j(\mathbf{J}))$, and identifying critical conditions as being the point where $Re(\lambda_{max}(\mathbf{J}))$ reaches his positive maximum, or when at least one eigenvalue of Green's matrix $\mathbf{G} = [G_{ij}]$, $G_{ij} = \partial y_i(\tau) / \partial y_{j,o}$, diverges from zero, or when the Lyapunov numbers $\sigma_j(t) = \ln|\lambda_j(\mathbf{G})| / (t - t_o)$ diverges [13,14]. A general runaway criterion was established by linking the parametric high sensitivity and the system divergence at critical conditions [15].

One powerfull criterion of thermal runaway is the co-called generalized sensitivity MV [16], that identifies the critical operating conditions as corresponding to a sharp increase of the normalized sensitivity $|S(T_{max}; \phi)|$, independently of the physico-chemical or operating parameter considered ϕ (or a combination of them). The state $\mathbf{y}$ sensitivity functions $S(\mathbf{y}; \phi)_z$ are usually computed by means of a finite difference numerical method, involving repeated simulations of the reactor behaviour under various conditions, every time solving the mass, heat and momentum differential balance equation of the reactor model. The z-MV criterion (referring the state sensitivity functions to the reactor length z) has been reported as being robust to complex kinetic models, indicating less conservative predictions of runaway boundaries than most of geometrical or explicit methods [8, 17].

The scope of this paper is to check the effectiveness of the generalized MV-criterion to assess the safe operating region of a tubular reactor, in terms of precision and computational costs. When the uncertainty in nominal operating parameters is accounted for, it is to estimate the confidence region of derived runaway boundaries, to be further considered as restricting the searching space in a reactor optimization step. Exemplification is made in the case of the industrial fixed-bed reactor for catalytic nitrobenzene hydrogenation in vapour-phase to aniline.

Catalytic reactor model and preliminary process sensitivity

Gas-phase catalytic hydrogenation of nitrobenzene is the main industrial method to economically produce the aniline. The exothermic process (ΔH= -54 kJ/mol) is carried out in a fixed-bed or a fluidized-bed reactor with high yields (99%). The used catalyst is copper or palladium on activated carbon or an oxidic support, sometimes modified by adding other metals (Ni, Pb) or promoters to increase the selectivity (Mg, Ca, Zr, Th, V, Cr). The process is conducted at temperatures between 250-350°C, low pressures (below 10 atm) but with a large excess of hydrogen (up to 1:100÷1:200 molar NB/H_2) to make the nitrobenzene NB conversion practically complete, and to avoid large partial NB pressures leading to high generated heat of reaction (risk limits being around 1:10 fed ratios, see below discussion). A quite reduced numbers of systematic studies have been published on the process kinetics [18], most of the proposed models indicating an apparent power-law type kinetics of fractional orders in NB and H_2, $r = kp^n_{NB}p^m_H$. To perform the risk analysis, a relatively simple reactor model, of pseudo-homogeneous type, has been adopted. The considered differential balance equations are presented in table 1, together with the catalyst characteristics, nominal operating conditions, and the intra-particle mass transfer resistance through an isothermal effectiveness factor (table 1 footnote).

By simulating the reactor behaviour under nominal conditions, 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. Such a separate analysis, presented in figure 1, highlights the major influence on the hot spot $\Delta T_{peak} = (T_{max} - T_o)$ of the inlet NB pressure $p_{NB,o}$ (as function of inlet pressure p_o and molar H/NB ratio), of the cooling agent temperature T_a, and less of inlet temperature T_o.

Derivation of runaway boundaries and their confidence region in the parametric space

To precisely derive the critical operating conditions of the fixed-bed reactor, the MV sensitivity criterion has been applied. The reaction-time/reactor length dependent sensitivity functions $s(y; \phi)_z = \partial y(z) / \partial \phi$ are evaluated by taking temperature, partial pressure, NB conversion, ΔT_{peak}, T_{max} or as dependent state variables. Absolute sensitivities can be computed by using the differential sensitivity equations [8, 19], simultaneously integrated with the reactor model $dy/dz = g(y, \phi, z)$, $y(0) = y_o$. The derivatives of the model Jacobian and the local sensitivities $\partial y(z)/\partial \phi$ are usually evaluated numerically using finite difference methods, because direct differentiation is very laborious for complex kinetic/reactor model cases.

Based on the calculated normalized sensitivity functions $S(T; \phi)_z$, the generalized MV criterion identifies the critical operating conditions from requiring the absolute value of the maximum-temperature sensitivity with respect to a certain parameter ϕ to attain a maximum, that is $|S(Tmax, \phi)|$ to be maximal. Such a runaway condition for the tubular reactor also corresponds to the first occurrence of the maximum in the $|s(T_{max}; \phi|$-vs.-z plot that happens before the temperature maximum in the T-vs.- z plot. Because a

Table 1

TUBULAR FIXED-BED REACTOR MODEL, CATALYST CHARACTERISTICS AND NOMINAL OPERATING CONDITIONS

Differential balance equations (Froment & Bischoff [22]): mass balance: $F_{M,NB,o}\frac{dX_{NB}}{dz} = S_t \rho_c \eta\, r_{NB}$ heat balance: $(\sum_j F_{M,j} c_{p,j})\frac{dT}{dz} = (-\Delta H) S_t \rho_c \eta\, r_{NB} - U(\pi d_t)(T - T_a)$, j=*NB* (nitrobenzene), *H* (hydrogen), *A* (aniline), *W* (water). momentum balance: $\frac{dp}{dz} = -f\left(\frac{F_m}{S_t}\right)^2 \frac{1}{\rho_g d_p}$	*Observations:* At $z = 0$: $X_{NB,o} = 0$; $T = T_o$; $p = p_o$.
Kinetic model (Rihani et al. [23]): $r = k p_{NB}^n p_H^m$; $k = 4.104 \times 10^4\, exp(-8240/T)$, kmol/kgcat h atm; $n = 0.5$; $m = 0.5$; η = 0.9952 (at nominal conditions) (Footnote)	[23]

Catalyst characteristics:	*Value (Observations):*
Chemical composition: Cu-Ni/support	[23]
Catalyst density (bulk)	ρ_c = 1600 kg/m^3
Catalyst particle average diameter	d_p = 3 mm
Catalyst porosity [22]:	ε = 0.5
Catalyst tortuosity [24]	τ = 4
Reactor characteristics:	
Reactor inner diameter	d_t = 30 mm
Reactor tube thickness	δ_t = 5 mm
Reactor length	L = 3 m
Nominal operating conditions:	
Inlet overall pressure	p_o = 1.2 atm
Inlet gaz temperature	T_o = 573 K
Fed molar ratio (moles H_2 / moles NB)	M = 15
Fed NB flow-rate (per reactor tube)	$F_{NB,o}$ = 1 kg/h
Gas superficial velocity (related to void tube)	u_o = 1.14 m/s
Cooling agent average temperature	T_a = 558 K

Footnote: The effectiveness factor is evaluated at nominal conditions for a spherical catalyst particle of d_p diameter, i.e.: $\eta = \frac{3}{\Phi}\left(\frac{1}{th(\Phi)} - \frac{1}{\Phi}\right)$. For large inlet ratios M, the Thiele modulus Φ is evaluated with the pseudo n-th kinetic order formula [25]: $\Phi = \left(\frac{d_p}{6}\right)\sqrt{\left[\frac{n+1}{2}\left(k\rho_p \frac{1-\varepsilon}{\varepsilon} R_g T\right) p_{NB}^{n-1} p_H^m\right] / D_{ef}}$. The effective diffusivity in the particle is approximated with the effective molecular diffusivity in the gas mixture: $D_{ef} \approx \frac{\varepsilon}{\tau} D_m$. The molecular diffusivity is computed with the Gilliland-Maxwell formula [26]: $D_m = 4.3 \times 10^{-7} \frac{T^{1.5}}{p(v_{NB}^{0.33} + v_H^{0.33})^2}\sqrt{\frac{1}{M_{NB}} + \frac{1}{M_H}}$, (m^2/s), where: T= temperature (K); p= overall pressure (atm); v_A= molar diffusion volume of species A at the normal boiling point (cm^3/mol; [27]; M_j= molecular mass of species j (g/mol); ε = catalyst porosity; τ = particle tortuosity.

finite difference method has been applied in order to otain the sensitivity function z-profile for certain specified operating conditions, the MV-sensitivity method is time consuming. Good results are obtained by dividing the parameter range [$\phi_{j,min}$, $\phi_{j,max}$] in ca. 200-1000 equally spaced intervals $\Delta\phi_j$, and by replacing the derivatives with finite differences of the type $s(y; \phi_j)z = \Delta y(z) / \Delta\phi_j$. Because under certain operating conditions the rapid kinetics induces system stiffness, it is important to use an appropriate ODE differential model integrator, and to control the evaluation precision of sensitivity functions by means of an adequate discretization of the reactor length. To get the accurate position of the sensitivity function maximum at critical conditions, it was found that a minimum 45,000-50,000 equally spaced evaluation points over the reactor length are necessary, while the stiff integrator of Matlab package has been found to give satisfactory results. Due to such precision requirements, the computational time needed to obtain a risk curve in the parametric plane, based on a certain number of points, is relatively large on an ordinary PC.

The resulted $S(T_{max}; T_o)$ vs. T_o plots are displayed in figure 2 for various operating parameter values. By separately plotting the extreme position for all [$S(T_{max}; T_o)$ vs. T_o] curves obtained for various ϕ_j, the runaway boundaries can be established in every parametric plane [To vs. ϕ_j], as represented in figure 2, by successively using $\phi_j = p_o$, ϕ_j =M, and $\phi_j = T_a$. The same analysis was repeated for deriving the sensitivity functions $S(T_{max}$;

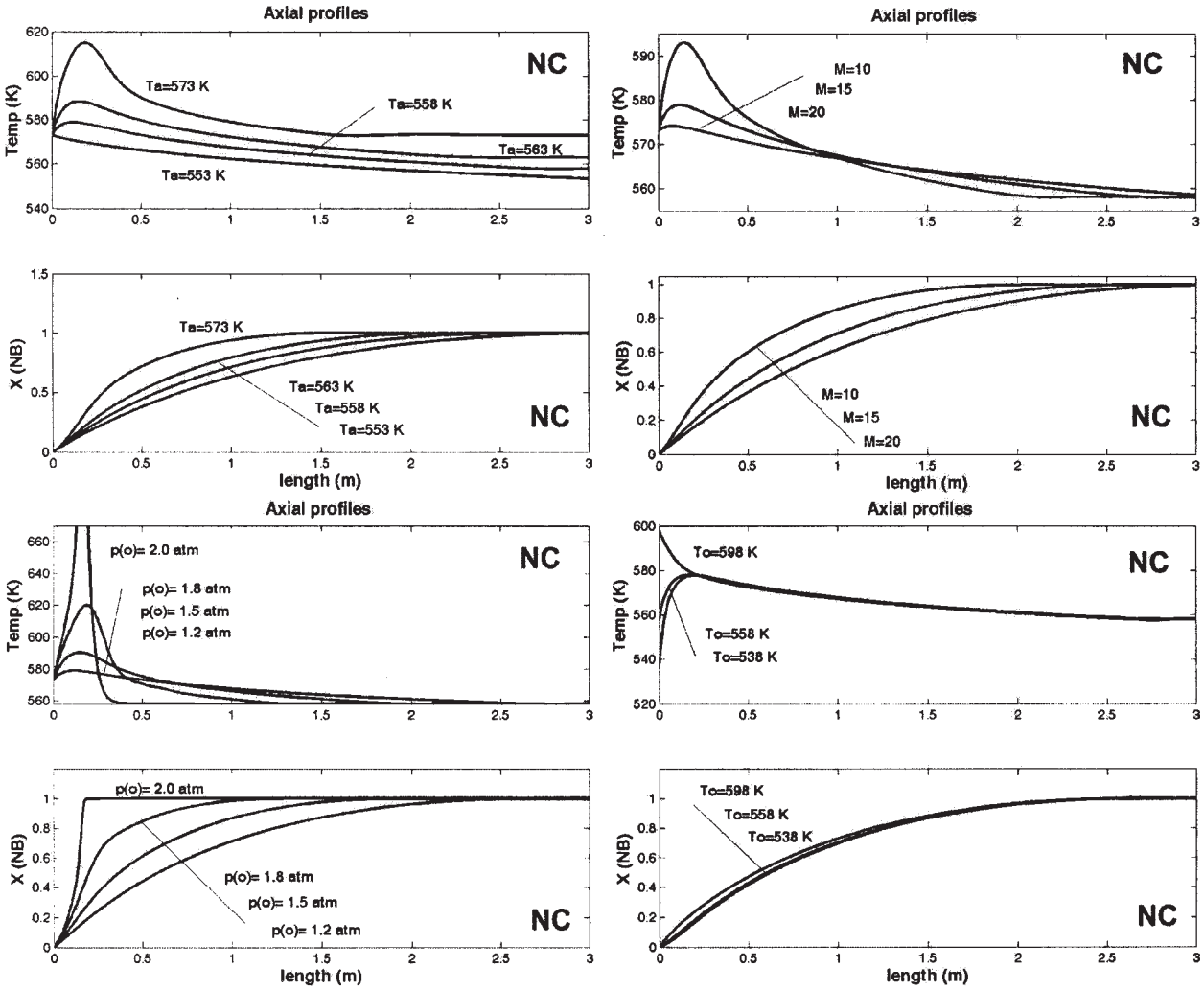

Fig. 1. Axial profiles of the temperature and conversion in the reactor obtained by successive variation of the following operating parameters at nominal conditions (catalyst of Rihani et al. [23]): the cooling fluid temperature T_a(K); the inlet fed ratio M (moles H_2 / moles NB); the inlet overall pressure p_a (atm); the gas inlet temperature T_a (K). (NC= nominal operating conditions)

Table 2

CRITICAL INLET TEMPERATURE (T_{OC}) PREDICTED BY MEANS OF MV-CRITERION AND BY AN EMPIRICAL CORRELATION:

T_{oc}=-2277.6489 - 93.1459 x p_o + 14.4202 x M + 11.6506 x T_a - 0.2554 x M2 - 0.0116 x T^2_a

(model standard deviation = 0.94 K; average relative residual = 0.41%)

Operating conditions			T_{oc}(MV-criterion), (K)	T_{oc}(empirical correlation), (K)	Relative deviation, (%)
p_o, (atm)	M, (mol/mol)	T_a, (K)			
1.20	6	558	574.25	570.19	0.71
1.20	8	558	583.09	591.88	-1.51
1.20	10	558	616.07	611.52	0.74
1.20	15	558	652.45	651.69	0.12
1.20	20	558	678.63	679.09	-0.07
1.20	15	500	691.55	689.15	0.35
1.20	15	520	681.35	685.06	-0.55
1.20	15	540	668.43	671.68	-0.49
1.20	15	560	650.24	649.01	0.19
1.20	15	570	636.64	634.18	0.39
1.20	15	580	612.84	617.03	-0.68
1.00	15	558	672.85	670.32	0.38
1.20	15	558	652.45	651.69	0.12
1.40	15	558	633.75	633.06	0.11
1.60	15	558	615.56	614.44	0.18
1.80	15	558	595.67	595.81	-0.02

p_o) vs. p_o, the resulted [$S(T_{max}; p_o)$ vs. p_o] curves being plotted in figure 3. Similarly, the runaway boundaries in the parametric plane [p_o vs.ϕ_j] can be obtained, as represented in figure 3 by successively using $\phi_j = T_a$ and ϕ_j = M. From the analysis of these results, it clearly appears that more severe operating conditions are (leading to an increase in aniline production), more restrictive runaway boundaries exist.

Another aspect to be investigated is related to the uncertainty in evaluating such safety limits of the

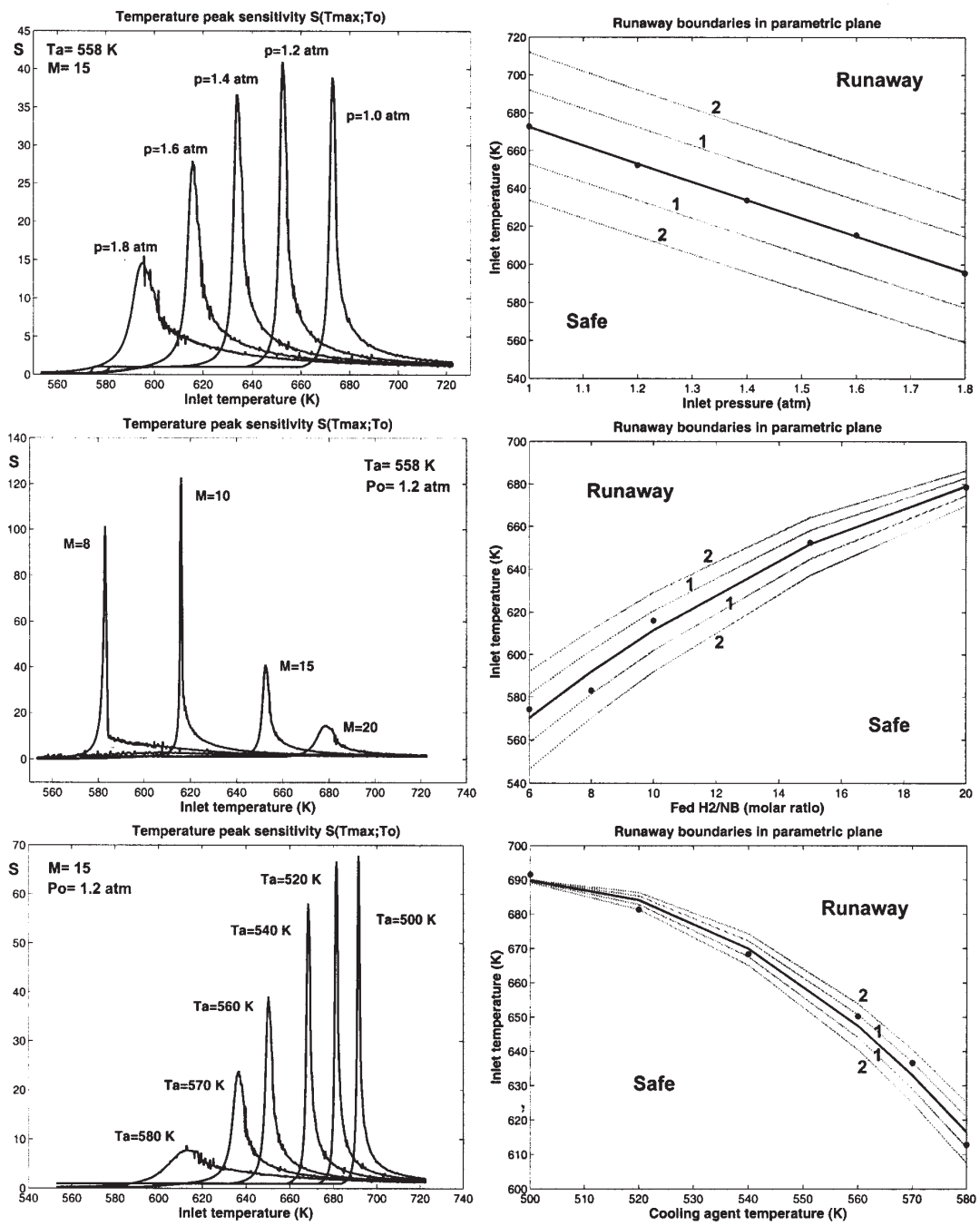

Fig. 2. (Left) Sensitivity of the temperature maximum in the fixed-bed reactor vs. the inlet temperature $S(T_{max}; T_o)$ for different operating parameters (p, M, T_a). (Right) Runaway boundaries (–) in the parametric planes [To vs. P_o](up), [T_o vs. M](centre), [T_o vs. T_a](down) and its confidence band for parametric deviations $\phi_j \pm \delta\phi_j$ of δP_o = 0.2 atm (1---), δP_o = 0.4 atm (2---), δM = 1 mol/mol (1---), δM = 2 mol/mol (2---), δT_a = 2.5 K (1---), δT_a = 5 K (2---).

operating region associated with the random fluctuations in the parameters ϕ_j around the nominal set point within a certain range, $\phi_j \pm \delta\phi_j$. Such a parameter uncertainty is usually dependent on the performance of the process regulatory system. By repeatedly applying the MV-sensitivity method, while considering the parameters at lower or upper bounds, the lower and upper bounds of the critical conditions can thus be obtained. The results are presented in figures 2-3 (with dot lines), the derived confidence band in the parametric plane corresponding to various levels of $\delta\phi_j$, i.e. a 100% confidence level if parameters are uniformly distributed, or a lower confidence level for normal distributed parameters depending on the distribution characteristics (i.e. a 68% confidence level for $\delta\phi_j = \sigma\phi_j$ a 95% confidence level for $\delta\phi_j = 2\sigma\phi_j$ etc.).

Based on the critical values of inlet temperature T_o and pressure p_o evaluated with the MV-criterion (tables 1 and 2), it might be possible to empirically correlate them with the operating parameters. Because of the process nonlinearity, a nonlinear statistical model should be employed in this respect. Indeed, a second order polynomial model has been found to adequately represent the critical reactor conditions vs. the main operating parameters for this type of catalyst:

$$T_{oc} = -2277.6489 - 93.1459 \times p_o + 14.4202 \times M + 11.6506 \times T_a - 0.2554 \times M^2 - 0.0116 \times T_a^2$$
$$p_{oc} = 115.0318 + 0.1057 \times M - 0.3746 \times T_a + 0.0003 \times T_a^2 \quad (1)$$

As indicated in tables 2 and 3, the model prediction standard deviation is very low (0.94 K for the predicted

Table 3

CRITICAL INLET PRESSURE (p_{oc}) PREDICTED BY MEANS OF MV-CRITERION AND BY AN EMPIRICAL CORRELATION: $p_{oc} = 115.0318 + 0.1057 \times M - 0.3746 \times T_a + 0.0003 \times T_a^2$ (model standard deviation = 0.06 atm; average relative residual = 0.49%)

Operating conditions (T_o = 573 K)		p_{oc}(MV-criterion), (atm)	p_{oc} (empirical correlation), (atm)	Relative deviation, (%)
M, (mol/mol)	T_a, (K)			
15	520	3.75	3.75	0.05
15	540	2.67	2.68	-0.33
15	560	1.84	1.85	-0.65
15	570	1.52	1.53	-0.62
15	580	1.27	1.27	0.20
8	558	1.20	1.18	1.36
10	558	1.39	1.40	-0.37
15	558	1.92	1.92	-0.19
20	558	2.47	2.45	0.72

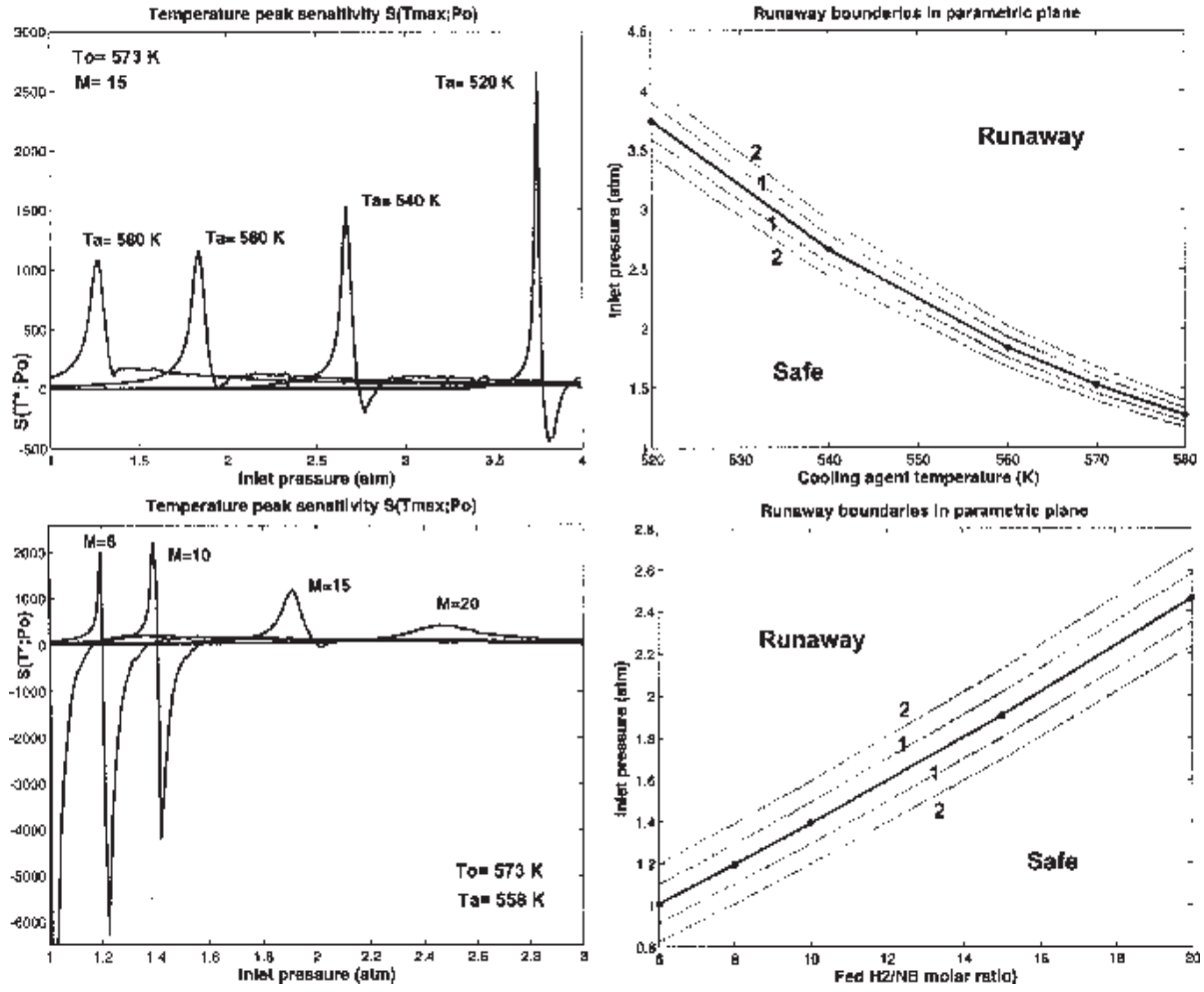

Fig. 3. (Left) Sensitivity of the temperature maximum in the fixed-bed reactor vs. the inlet pressure $S(T_{max}; P_o)$ for different operating parameters (T_a, M) (Right) Runaway boundaries (–) in the parametric planes [P_o vs. Ta](up), [P_o vs. M](down), and its confidence band for parametric deviations $\phi_j \pm \delta\phi_j$ of δM = 1 mol/mol (1---), δM = 2 mol/mol (2---), δT_a = 2.5 K (1---), δT_a = 5 K (2---)

T_{oc} and 0.06 atm for the predicted p_{oc}), while the relative residuals are of low absolute values (ca. 0.5%), being alternatively positive and negative (for more complete model adequacy and parameter inference tests [20, 21]).

Such a statistical model is useful not only for quickly predicting the safety limits for operating parameters, but also allows a quick determination of their uncertainty. For instance, the standard deviation of the T_{oc} (denoted by σ_{Toc}) can be approximately evaluated by using the error propagation formula for the assumed uncorrelated parameters [19-21]:

$$\dots \quad \sigma^2_{T_{oc}} = \sum_j \left(\frac{\partial T_{oc}}{\partial \phi_j} \right)^2 \sigma^2_{\phi_j} ; \quad \phi_j = M, T_a, p_o, \dots . \qquad (2)$$

The results indicate at nominal conditions of table 1, and parameter dispersions of $\sigma^2_M = 1$ (mol/mol)^2, $\sigma^2_{Ta} = 6.25$ K^2 , $\sigma^2_{po} = 0.04$atm^2, a standard deviation of the critical inlet conditions of $\sigma_{Toc} = 20.1$K , and $\sigma_{poc} = 0.12$ atm.

Such an uncertainty in the operating parameter must be considered in all studies dealing with determining

the optimal nominal operating point. The study also suggests keeping the optimal solution inside the random variation region, without intersecting the confidence band instead of runaway boundaries. Since in many cases the more severe running conditions correspond to a higher productivity, such a modified solution is expected to offer a higher degree of safety in operation with the expense of supplementary computational steps with a precise sensitivity method (such as z-MV) to derive the confidence of the safety limits.

Conclusions

Accurate determination of the safe operating limits for an industrial fixed-bed reactor exhibiting a high thermal sensitivity, especially when nominal operating conditions are often changed according to the process characteristics, is an engineering problem of current interest. The interest is even higher when the safety problem is related to the economic implications of getting a higher productivity by setting the nominal operating point in the vicinity of the safety limits. Even if being more computative and requiring extensive information on the process, the present study proves the advantages of using of a model-based and 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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Notations

ADT_{24} - sample initial temperature for an adiabatic decomposition within 24 h
B - reaction violence index
c_j - molar concentration of species j
$c_{p,j}$ - molar specific heat of gaseous species j
c_{pg} - average specific heat of gas
d_p - particle diameter
d_t - reactor tube inner diameter
$Da = \rho_c k(T_o) c_o^{n-1} L / u_o$ - Damköhler number
D_{ef} - effective diffusivity in the particle
D_m, D_j - ,molecular diffusivity of species j activation energy
E - activation energy
F_m - mass flow rate
F_M - molar flow rate
f - friction factor
G - Green's function matrix of the system
g - model function vector
(-ΔH)- heat of reaction (at local temperature)
h_{fp} - gas-particle heat transfer coefficient
J - Jacobian matrix of the system
k - kinetic constant
k_{fp} - gas-particle mass transfer coefficient
L - reactor length
$Le = h_{fp} / (k_{fp} \rho_g c_{pg})$ - Lewis number
M - molar fed ratio (moles H_2/NB)
n, m - partial orders of reaction
p - overall pressure
p_{oc} - critical inlet pressure
p_j - partial pressure of gaseous component j
r - chemical reaction rate
R_g - universal gas constant
S_t - tubular reactor cross-section
s(y; ϕ) - absolute sensitivity, ∂y(z) / ∂ϕ
S(y; ϕ) - normalized sensitivity, (ϕ* / y*)s(y; ϕ)
$St = 4UL / (u_o \rho_g c_{pg} d_t)$ - Stanton number
T - temperature
T_o - inlet temperature
T_a - average temperature of the external cooling agent
T_{onest} - temperature of the first step change in the recorded heat flux thermograms from a dual scanning calorimeter
T_{oc} - critical inlet temperature
T_{max} - maximum of the temperature in the reactor
TMR_{ad} - time to maximum rate under adiabatic conditions
ΔT_{ad} - adiabatic temperature rise
t - time
U - overall heat transfer coefficient
u_o - gas superficial velocity
X_j - reactant j conversion
y, y_j - state variable, or molar fraction of gas component j
z - reactor axial coordinate
Δ - finite difference
ε - catalyst porosity
ϕ - operating parameter
η- effectiveness factor for solid particle
λ_t, λ_g, λ - ,thermal conductivity of the tube material or of gas; eigenvalue of a matrix
ρ_c - catalyst density (bulk)
ρ_g - gas mixture density
ρ_p - catalyst particle density
σ^2 - variance (σ = standard deviation)
τ - tortuosity factor of the catalyst; contact time
τ_{ad} - adiabatic induction time to explosion
Φ - Thiele modulus

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