

Setting Correlated Runaway Boundaries of the Catalytic Reactor for Benzene Oxidation Using a Parametric Sensitivity Analysis and a Detailed Kinetic Model

CONSTANTIN MUSCALU, GHEORGHE MARIA*

University Politehnica of Bucharest, Department of Chemical and Biochemical Engineering, 1-7 Polizu Str., 011061, Bucharest, Romania

The safety concerns in the operation of chemical and petrochemical plants are growing more and more nowadays. The contrary process optimization objectives involve not only economic aspects, but also safety characteristics, such stability, controllability and runaway risk, all being necessary to be considered and somehow optimized to result an optimised reactor operation, when the safety aspects must always prevail. One example is the operation of a fixed bed catalytic reactor, when a highly exothermic reaction is conducted. The nominal operating conditions need to be set at a certain distance from the safety operating limits in order to achieve a certain control on the hot spot into the tubular reactor and to avoid excessive thermal sensitivity to random variations in the process parameters. In this paper, a precise and robust sensitivity criterion, i.e. the model-based generalized criterion of Morbidelli & Varma, is used to determine the runaway boundaries in the operating variable space for the catalytic reactor used for benzene oxidation to maleic anhydride in vapour phase using a detailed kinetic model in order to increase the results precision. The used method sets the global runaway conditions corresponding to the maximum increase of the temperature peak inside the reactor versus operating parameters.

Keywords: runaway boundaries; benzene oxidation; maleic anhydride production, catalytic reactor

In most of chemical plants, the reactor is representing the core equipment and usually the most risky in terms of safety operation. Therefore the plant optimization efforts are usually focus on the reactor due to its high sensitivity to operating conditions, stability, and risk issues, and due to the high value of the products and raw materials related the process economical aspects. Optimization procedures are usually employed to set the reactor nominal operating conditions within the parametric space by accounting for the economic criteria, under technological constraints, followed by elaborated control schemes implemented to keep the reactor operation within the safety limits [1]. For the cases of tubular reactors, safety operation tries to limit the hot spot generated by the exothermic reactions inside tubes during operation by avoiding the excessive reactor sensitivity to random variations in the process parameters. However, calculation of such safety limits is not necessarily an easy task, not only due to the complexity of the numerical algorithms, but also they should be periodically updated due to fluctuations in the process characteristics, raw materials, impurities and catalyst activity modifications [2].

Model-based evaluation of the critical operating conditions of the reactors uses a large variety of methods trying to detect the operating regions of high thermal sensitivity, system stability failure, or situations when the rate of heat generation exceeds the rate of heat removal by the designed cooling system [3]. Because of the exponential dependence of the reaction rate in relation to the temperature, any sudden temperature increase in the feeding or cooling system can conduct to an intensive rise of reaction rates, which in turn leads to a continuous rise in the reactor temperature until the cooling system becomes ineffective, eventually resulting in a reactor explosion.

On way to realize the risk assessment is the use of the approximate and explicit methods, based on simple explicit engineering numbers (such as Damköhler - Da,

Staton - St or Lewis - Le) or safety indices that replace the systematic model-based safety analysis process with a combination of inequalities and engineering numbers [4-7]. These methods were demonstrated to be insufficiently accurate for an advanced optimization of the process, being a practical approach (but not the most efficient one), which is providing sufficient overdesign of the system [9]. For a tubular reactor, including the catalytic fixed-bed operated with a hot spot (HSO) or pseudo-adiabatically (PAO), thermal sensitivity conditions can be identified using mainly three types of methods [8]: geometry-based methods, sensitivity-based methods, and the loss of stability analysis. Geometry-based methods (GM) analyze 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 *temperature - contact time/reactor length 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 (y) with respect to operating parameters ϕ , i.e. $s(y; \phi) = \partial v(z) / \partial \phi$ (in absolute terms), or $S(y_i; \phi_j) = (\phi_j^* / y_i^*) s(y_i; \phi_j)$ (in relative terms with respect to a nominal operating point ϕ_j^*), that is where *the reactor performance becomes unreliable and changes sharply with small variations in parameters* [9].

This paper is aiming at exemplify i) how the runaway boundaries can be evaluated by using the generalized MV (Morbidelli & Varma) generalized criterion in the case of a very sensitivity catalytic reactor using an extended kinetic model of the process and, ii) how these safety limits are correlated in a simple manner with the operating parameters to be of use for a further model-based optimization of the reactor operation; iii) how important is

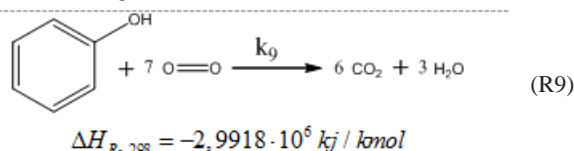
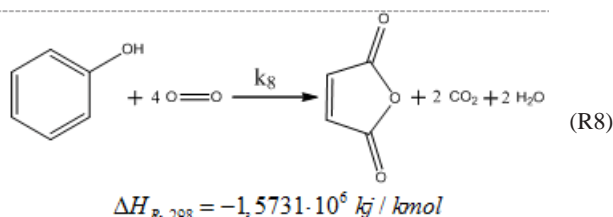
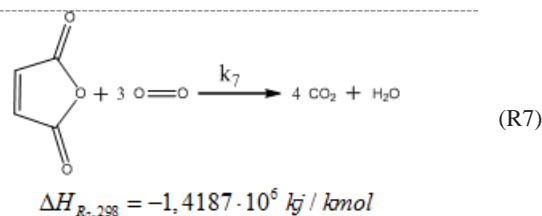
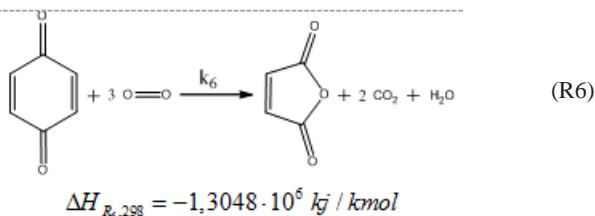
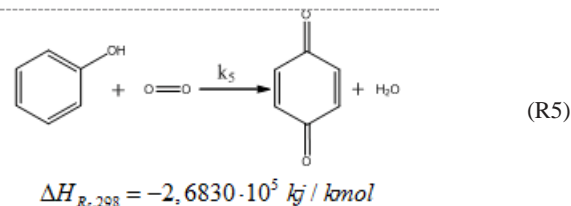
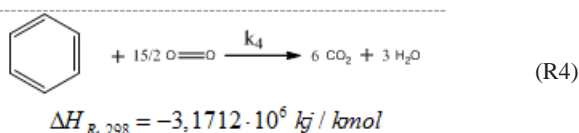
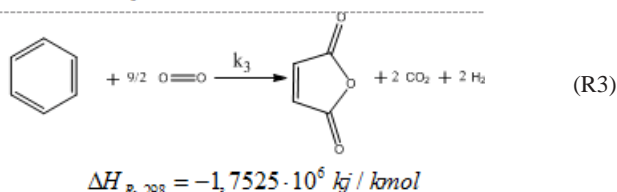
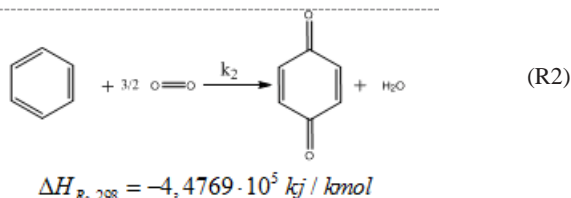
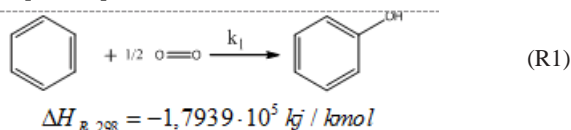
* email: gmaria99m@hotmail.com

the use of a detailed kinetic model of the process, as underlined by Stefan and Maria [19].

Exemplification is made for the case of the fixed-bed multi-tubular reactor for catalytic oxidation of benzene to maleic anhydride in vapour phase [10].

Process kinetics, catalytic reactor model and preliminary process sensitivity

The multi-tubular reactor (heat exchanger type) for benzene oxidation includes the catalytic fixed bed inside tubes of small diameters (under 3 - 4 cm), which are continuously cooled by a molten salt mixture (nitrates, nitrites mixture; Nenitescu, 1954, citation under [5]) circulated outside and among rows of pipes. The reaction temperature is kept under a permissible limit (450 °C) by quickly dissipating the heat of reaction through reactor inter-tubular space molten salt heavy circulation. The benzene/air mixture (concentration below the lower explosion limit, 1.5%vol.) is fed into the reactor at approx. 385°C where the oxidation to maleic anhydride takes place (the reactor nominal operating conditions in table 3. The catalyst used for the reaction is a mixture of vanadium/chrome oxides on a silica bed [10]. The oxidation reaction is complex, with successive and parallel reactions, involving a relatively large number of intermediate products. To realise this study objectives, a complex kinetic model was adopted for a more accurate representation of the industrial reactor behaviour. The involved reactions R1-R9 in the oxidation of benzene and their enthalpies (evaluated using Aspen Hysys software) are displayed below [10, 11]:



In order to quickly derive the reactor safety 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 species mass, heat and momentum balances. The Arrhenius type rate constants are given in table 2.

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

To precisely derive the runaway boundaries and their associated region of confidence in the operating variable plans for a risky fixed-bed catalytic reactor an effective Morbidelli & Varma generalized sensitivity criterion (MV) was used along with an extended kinetic model of the process taken from literature [10].

This criterion associates the critical operating conditions with the maximum of sensitivity of the hot spot ($T_{\max} - T_0$) in the reactor, evaluated over the reactor length, in respect to a certain operating parameter ϕ . In other words, critical value of a parameter $\phi_{j,c}$ corresponds to:

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

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

[where: $S(T_{\max}; \phi_j) = s(T_{\max}; \phi_j) \phi_j^* / T_{\max}^*$ = relative sensitivity function of T_{\max} vs. parameter ϕ_j = operating parameter or control variable; * = nominal operating conditions (set point) in the parameter space]. 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 $x_i(z)$ (including the reactor temperature) can be evaluated by using the so-called sensitivity equation' solved simultaneously with the reactor model [8, 9]:

$$\frac{ds(x; \phi_j)}{dt} = \frac{\partial g}{\partial x} s(x; \phi_j) + \frac{\partial g(t)}{\partial \phi_j}; s(x, \phi_j) \Big|_{z=0} = \delta(\phi_j - x_0)$$

$$dx/dt = g(x, \phi, t), x \Big|_{z=0} = x_0, \text{ (reactor model)} \quad (2)$$

(where the Kronecker delta function $\delta(\phi_j - x_0)$ takes the value 0 for $\phi_j \neq x_0$, or the value 1 for $\phi_j = x_0$); $t = z/u$ = the reactant contact time in the reactor; z = reactor length; u = gas superficial velocity. Evaluation of derivatives in (2) can be precisely performed by using the analytical

Table 1
THE FIXED BED MULTI TUBULAR REACTOR MODEL USED FOR BENZENE OXIDATION TO MALEIC ANHYDRIDE [11]

<p>Mass balance differential equations:</p> <p>Mass balance (index j denotes species):</p> $\left. \begin{aligned} \frac{dD_{M_j}}{dz} &= -\eta_j v_{p,j} S \\ v_{p,j} &= \sum_{i=1}^9 v_{i,j} v_{R,i} \\ v_{R,i} &= v_{r,i} \rho_{SC} \\ v_{r,i} &= k_i p_j \end{aligned} \right\} \Rightarrow \frac{dD_{M_j}}{dz} = -\eta_j \rho_{SC} S \sum_{i=1}^9 v_{i,j} k_i p_j \quad z = 0$ <p>$j = B, F, Q, AM, CO_2, H_2O, O_2, N_2$</p> <p>$y_j = y_{j,0}, T = T_0, P = P_0$</p> <p>B = Benzene, F = Phenol, Q = Quinone, AM = Maleic anhydride; i = Chemical reactions;</p> <p>D_{M_j} - molar flow rate of „j” species, kmol/s;</p> <p>S - cross-sectional area of the pipe;</p> <p>$v_{p,j}$ - volumetric specific reaction rate of species „j”, $\frac{\text{kmol}}{\text{m}^3 \cdot \text{s} \cdot \text{atm}}$;</p> <p>$v_{R,i}$ - volumetric specific reaction rate of reaction „i”, $\frac{\text{kmol}}{\text{m}^3 \cdot \text{s} \cdot \text{atm}}$;</p> <p>$v_{r,i}$ - mass specific reaction rate of reaction „i”, $\frac{\text{kmol}}{\text{kg}_{cat} \cdot \text{s} \cdot \text{atm}}$ (pseudo-order “1” reaction);</p> <p>ρ_{SC} - density of the catalytic bed, $\frac{\text{kg}_{cat}}{\text{m}^3_{reactor}}$;</p> <p>$\rho_{sc} = (1 - \varepsilon) \cdot \rho_p$, ρ_p - density of catalyst particle, $\frac{\text{kg}_{cat}}{\text{m}^3_{cat}}$;</p> <p>ε - void fraction;</p> <p>$v_{i,j}$ - stoichiometric coefficient of species „j” in reaction „i”;</p> <p>p_j - the partial pressure of species „j”, atm;</p> <p>η_j - the total effectiveness factor of the catalyst particle;</p> <p>k_i - pseudo-order 1 kinetic constant of reaction „i”, $\frac{\text{kmol}}{\text{kg}_{cat} \cdot \text{s} \cdot \text{atm}}$;</p> <p>$k_i = k_{i_0} \cdot e^{-\frac{E_a}{RT}}$ (values in Table 2)</p> <p>R - ideal gas constant $R = 8.314 \frac{\text{kJ}}{\text{kmol} \cdot \text{K}}$, $R = 1.987 \frac{\text{kcal}}{\text{kmol} \cdot \text{K}}$, $R = 0.082 \frac{\text{m}^3 \cdot \text{atm}}{\text{kmol} \cdot \text{K}}$;</p>
<p>Heat balance: $\frac{dT}{dz} = \frac{\sum_{i=1}^9 (-\Delta H_{R,i}) v_{r,i} \rho_{SC} S - K_T \pi d_t (T - T_a)}{D_{m,t} \cdot c_p}$</p> <p>$T$ - gas temperature, K;</p> <p>z - reactor length, m;</p> <p>$(-\Delta H_{R,i})$ - heat reaction of reaction „i”, kJ/kmol;</p> <p>K_T - overall heat transfer coefficient, $\frac{W}{\text{m}^2 \cdot \text{K}}$;</p> <p>d_t - pipe diameter, m;</p> <p>T_a - cooling agent temperature, K;</p> <p>$D_{m,t}$ - mass flow rate of the feed mixture, kg/s;</p>

\bar{C}_p - average mixture specific heat, $\frac{kJ}{kg \cdot K}$.

Momentum balance:

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

- friction coefficient calculated by Ergun and Hicks formula [12]:

$$f = \begin{cases} \frac{1-\varepsilon}{\varepsilon^3} \left[1.75 + 150 \frac{1-\varepsilon}{Re_p} \right], & \frac{Re_p}{1-\varepsilon} < 500 \\ 6.8 \frac{(1-\varepsilon)^{1.2}}{\varepsilon^3} Re_p^{-0.2}, & \frac{Re_p}{1-\varepsilon} > 500 \end{cases}$$

$$\varepsilon = 0.38 + 0.073 \left[1 + \frac{(d_i/d_p - 2)^2}{(d_i/d_p)^2} \right] = \text{bed void fraction [12]}$$

$$Re_p = \frac{u \rho_G d_p}{\mu_G} \text{ - Reynolds number for flow through the catalytic bed.}$$

d_p - catalyst particle diameter, m; u - gas flow velocity, m/s;

ρ_G - gas density, $\frac{kg}{m^3}$; μ_G - gas viscosity, Pa·s. [12]

The model hypotheses:

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

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

$$K_r = \frac{1}{\frac{1}{\alpha_i d_{i,i}} + \frac{\delta_i}{\lambda_{col}} \frac{1}{d_{i,i}} + \frac{1}{\alpha_{ext}}}, \quad \frac{W}{m^2 K}; \quad \alpha_i = \frac{\lambda_G Nu_{g,i}}{d_p}, \quad \frac{W}{m^2 K}$$

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)

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

For temperatures below 400 °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:

$$\delta_G = \delta_{G,2} + (\delta_{G,1} - \delta_{G,2}) \frac{\varepsilon - 0.26}{0.476 - 0.26} \text{ In this equation, } \delta_{G,1}, \delta_{G,2} \text{ represent values of the } \delta_G \text{ parameter which corresponds}$$

to the most rarefied packing ($\varepsilon_1 = 0.476$) and most compact packing ($\varepsilon_2 = 0.260$). 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 [13]).

The approximate value at the feed conditions: $K_r = 119.4 \frac{W}{m^2 K}$

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 [14].

$\Phi_i = \frac{d_p}{6} \sqrt{\frac{k_i \rho_s \frac{1-\varepsilon}{\varepsilon} RT}{D_e}}$
<p>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 [15]:</p> $D_m = (1 - y_B) / \sum_{j=B} y_j / D_{m,j}; D_{m,j} = 4.3 \times 10^{-7} \frac{T^{1.5}}{P(V_B^{0.33} + V_j^{0.33})^2} \sqrt{\frac{1}{M_B} + \frac{1}{M_j}} \text{ (m}^2\text{s}^{-1}\text{)}$ <p>(surface and Knudsen diffusion can be neglected in this case) [13]</p>
<p>Ideal plug-flow reactor with concentration, temperature and pressure gradients variation only in the axial direction</p> $\partial(c_j, T, p) / \partial R_t = 0$ <p>- for the case $L / d_t > 50; d_t / d_p > 10$</p>
<p>Axial dispersion coefficient is null: $D_z = 0$ (because $L / d_t > 50$)</p>
<p>Isothermal spherical catalyst particle, $\partial T_p / \partial R_p = 0$</p> <p>- Catalyst particle average diameter, d_p</p>
<p>One neglects the resistance to inter-granular property transport (Satterfield criteria) because $L / d_p > 100$</p>

Kinetic constants, $kmol / (kg_{cat} \cdot h \cdot atm)$	Frequency factor, $k_{i,0}$	E_a , $kcal / mol$
k ₁	$2.00 \cdot 10^{-3}$	2.448
k ₂	$3.28 \cdot 10^{-3}$	2.530
k ₃	0.106	2.410
k ₄	0.129	2.454
k ₅	65.31	12.059
k ₆	0.176	2.401
k ₇	0.388	5.882
k ₈	73.7	12.059
k ₉	13.8	12.085

Table 2
KINETICS CONSTANTS FOR BENZENE
OXIDATION [10]

derivation or, being less laborious, by means of numerical derivation. A worthy alternative, also used in the present study, is the application of a numerical finite difference method, which implements a simple differentiation scheme to estimate the derivatives of $s(x_i; \phi_j)$ at various reactor lengths z , of the type $s(x_i; \phi_j) = \Delta x(z) / \Delta \phi_j$ [16].

In the present study, the considered control variables are: the inlet molar fraction of benzene (y_{Bo}); the inlet gas temperature (T_o), and the inlet gas pressure (p_o). The following operating parameters ϕ_i subjected to random fluctuations are included in the analysis: cooling agent temperature (T_c), the inlet gas temperature (T_o), inlet gas pressure (p_o), the inlet molar fraction of benzene (y_{Bo}). Because a finite difference method has been applied in order to obtain 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 $s(y; \phi_j) = \Delta y(z) / \Delta \phi_j$. 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 1 (left) for various ϕ_j 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 $[T_o$ vs. $\phi_i]$, as represented in figure 1 (right), by successively using $\phi_j = p_o$, $\phi_j = y_{Bo}$, and $\phi_j = T_c$. From the analysis of these results, it clearly appears that more severe operating conditions are (leading to an increase in maleic anhydride production), more restrictive runaway boundaries exist.

Another aspect to be investigated is related to the uncertainty in evaluating such safety limits of the operating region associated with the random fluctuations in the parameters ϕ_i around the nominal set point within a certain range, $\phi_j \pm \delta \phi_j$ [2]. 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 figure 1 (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

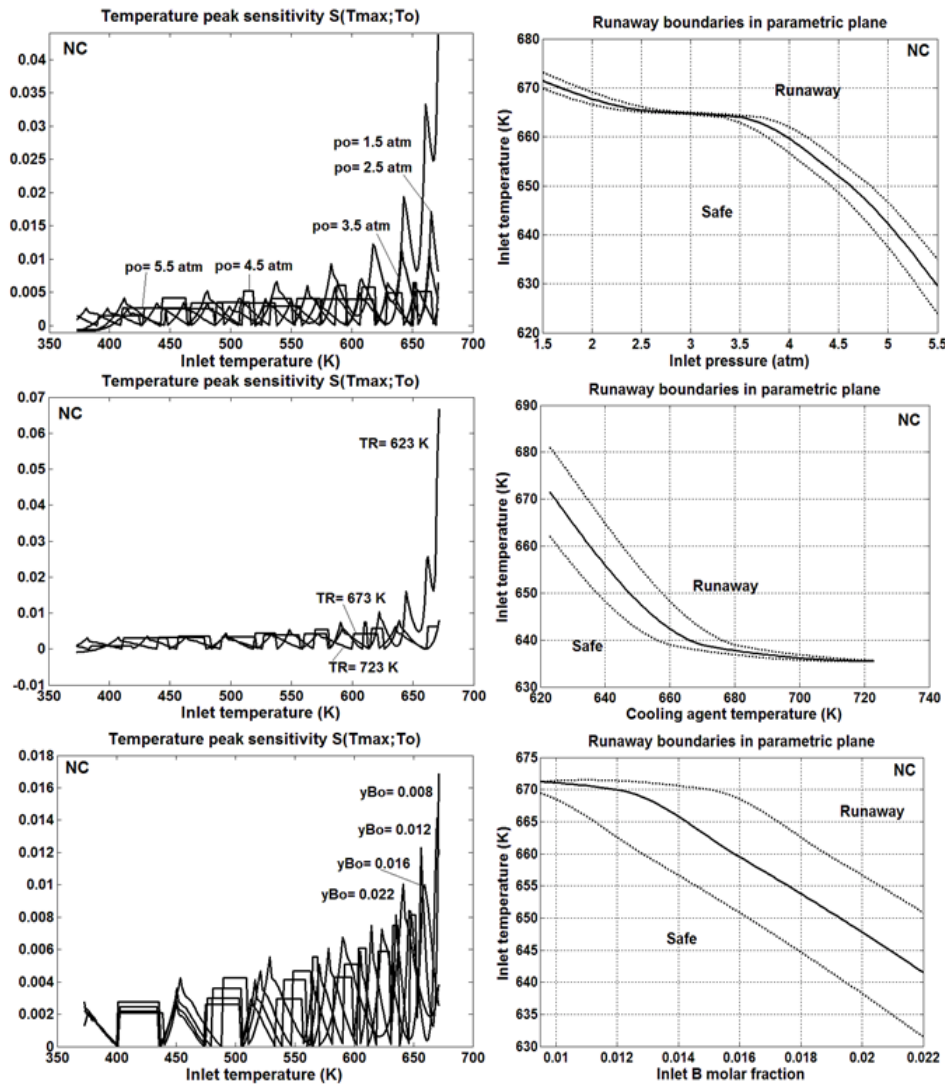


Fig. 1. (Left) Sensitivity of the temperature maximum in the fixed-bed reactor vs. the inlet temperature $S(T_{max}; T_o)$, for different operating parameters: p_o (up), T_a (middle), y_o (down). (Right) Runaway boundaries (\cdot) in the parametric planes $[T_o$ vs. $P_o]$ (up), $[T_o$ vs. $T_c]$ (middle), and $[T_o$ vs. $y_B]$ (down), their confidence band for parametric deviations of ± 0.003 mol fraction ($-$), ± 10 K = ± 10 K. (NC = nominal operating conditions)

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%, a 95% confidence level for $\delta\phi_j = 2\sigma_{\phi_j}$, etc.).

Correlation of runaway boundaries with the running parameters

Based on the critical values of the inlet molar fraction of benzene (y_{Bo}); the inlet gas temperature (T_o), and the inlet gas pressure (p_o), evaluated with the MV-criterion, it is possible to empirically correlate them with the operating parameters. Such a simple correlation can save computing time in the further reactor optimization step.

Because the process presents a deep nonlinearity, a nonlinear algebraic model will be adopted. A second order polynomial model has been found to adequately represent the critical inlet gas temperature with respect to the main operating parameters, of the form:

$$T_{oc} = b_1 + b_2 \times p_o + b_3 \times y_{Bo} + b_4 \times T_a + b_5 \times y_{Bo}^2 + b_6 \times T_a^2 \quad (3)$$

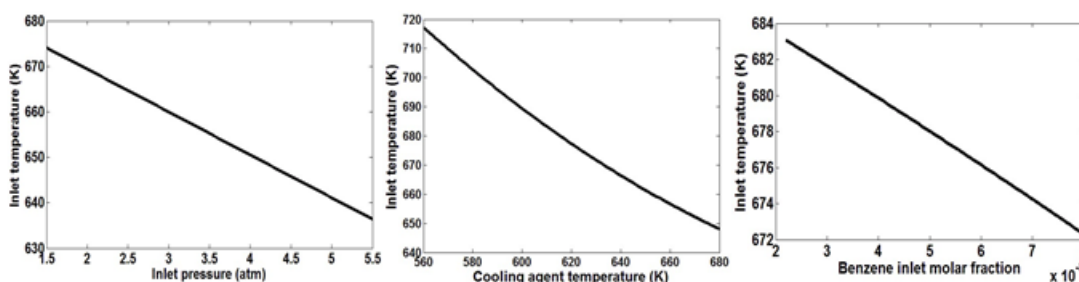


Fig. 2. Dependencies of the of the critical inlet temperature (T_{oc}) on various running parameters predicted by means of MV-criterion vs. various running parameters (plots obtained by means of the empirical correlation of table 4)

Similarly, a simple correlation can be derived for the inlet gas critical pressure with respect to the main operating parameters, of the form:

$$p_{oc} = b_1 + b_2 \times T_o + b_3 \times y_{Bo} + b_4 \times T_a + b_5 \times T_o^2 + b_6 \times y_{Bo}^2 + b_7 \times T_a^2 \quad (4)$$

A simple correlation can be derived also for the inlet benzene critical fraction with respect to the main operating parameters, of the form:

$$\ln(y_{Boc}) = b_1 + b_2 \times p_o + b_3 \times T_o + b_4 \times T_a + b_5 \times T_o^2 + b_6 \times T_a^2 \quad (5)$$

As indicated in the tables 4-6, the proposed algebraic models (3-5) for T_{oc} , p_{oc} , $\ln(y_{Boc})$ are of good quality, the prediction standard deviation being low, while the model relative error vs. the true MV-value is below 1, 5, or 7% respectively. The model residues are small for most of the points, being alternatively positive and negative.

Even if such empirical algebraic models includes coefficients with any physical meaning, it is interesting to compare the magnitude of the correlation coefficients with

<i>Catalyst characteristics:</i>	<i>Value (Observations):</i>
Chemical composition [10]	V-Cr/support
Catalyst density (bulk) [17]	$\rho_c = 1260 \text{ kg/m}^3$
Catalyst particle average diameter [17]	$d_p = 5 \text{ mm}$
Catalyst porosity	$\varepsilon = 0.48$
Catalyst tortuosity [18]	$\tau = 2.01$
<i>Reactor characteristics:</i>	
Reactor inner diameter	$d_t = 24 \text{ mm}$
Reactor tube thickness	$\delta_t = 2 \text{ mm}$
Reactor length	$L = 4 \text{ m}$
<i>Nominal operating conditions:</i>	
Inlet overall pressure	$p_o = 3 \text{ atm}$
Inlet gas temperature	$T_o = 658 \text{ K}$
Feed benzene molar fraction	$y_{B,0} = 0.014$
Fed Benzene flow-rate (per reactor tube)	$F_{B,0} = 0.1 \text{ kg/h}$
Gas superficial velocity (related to void tube)	$u_o = 1.68 \text{ m/s}$
Cooling agent average temperature	$T_a = 653 \text{ K}$

Table 3
THE NOMINAL OPERATING CONDITIONS OF THE FIXED-BED CATALYTIC REACTOR FOR BENZENE OXIDATION

P_o , atm	$y_{B,0}$	T_a , K	T_{oc} (MV-criterion), K	T_{oc} (empirical correlation), K	Relative deviation (%)
3	0.012	653	670.00	664.23	0.861
3	0.016	653	659.50	655.60	0.591
3	0.022	653	641.50	641.64	-0.023
1.5	0.014	653	671.50	674.15	-0.394
2.5	0.014	653	665.50	664.70	0.119
3.5	0.014	653	664.00	655.26	1.316
4.5	0.014	653	652.00	645.82	0.947
5.5	0.014	653	629.50	636.38	-1.093
3	0.014	623	671.50	675.67	-0.621
3	0.014	673	638.50	651.00	-1.958
3	0.014	723	635.50	633.71	0.281

Table 4
CRITICAL INLET TEMPERATURE (T_{oc}) PREDICTED BY MEANS OF MV-CRITERION AND BY AN EMPIRICAL CORRELATION (MODEL STANDARD DEVIATION = 1.34 K, AVERAGE RELATIVE RESIDUAL = 0.69%)

Table 5
CRITICAL INLET PRESSURE (p_{oc}) PREDICTED BY MEANS OF MV-CRITERION AND BY AN EMPIRICAL CORRELATION (MODEL STANDARD DEVIATION = 0.547 ATM, AVERAGE RELATIVE RESIDUAL = 4.81%)

T_o , K	$y_{B,0}$	T_a , K	p_{oc} (MV-criterion), atm	p_{oc} (empirical correlation), atm	Relative deviation (%)
643	0.014	653	16.36	16.47	-0.664
673	0.014	653	15.90	16.12	-1.366
703	0.014	653	15.46	15.42	0.234
658	0.012	653	18.99	17.50	7.821
658	0.022	653	10.10	12.04	-19.253
658	0.035	653	7.47	6.39	14.464
658	0.100	653	2.54	2.59	-1.905
658	0.014	643	16.51	16.68	-1.021
658	0.014	678	15.18	15.34	-1.066
658	0.014	703	14.20	14.15	0.332

p_o , atm	T_o , K	T_a , K	$y_{B,oc}$ (MV-criterion)	$y_{B,oc}$ (empirical correlation)	Relative deviation (%)
2.5	658	653	0.0796	0.0797	-0.1253
4.5	658	653	0.0476	0.0555	-16.6397
6.5	658	653	0.0342	0.0387	-13.09
8.5	658	653	0.0259	0.0269	-4.0273
10.5	658	653	0.0211	0.0188	11.0469
3	643	653	0.0794	0.0773	2.6047
3	673	653	0.0770	0.0721	6.3852
3	693	653	0.0756	0.0769	-1.7111
3	658	643	0.0800	0.0744	7.043
3	658	673	0.0743	0.0701	5.6752
3	658	723	0.0648	0.0652	-0.628

Table 6
CRITICAL INLET MOLAR FRACTION OF BENZENE ($y_{B,oc}$) PREDICTED BY MEANS OF MV-CRITERION AND BY AN EMPIRICAL CORRELATION (MODEL STANDARD DEVIATION = 0.16, AVERAGE RELATIVE RESIDUAL = 6.27%)

Table 7

COMPARISON OF EMPIRICAL CORRELATION COEFFICIENTS OF THE CRITICAL INLET TEMPERATURE (T_{oc}) PREDICTED BY MEANS OF MV-CRITERION FOR TWO SIMILAR CATALYTIC FIXED-BED REACTORS FOR BENZENE OXIDATION (PRESENT PAPER), AND NITROBENZENE HYDROGENATION [2]: $T_{oc} = b1 + b2 \times p_o + b3 \times M(y_{Bo}) + b4 \times T_a + b5 \times M^2(y_{Bo}^2) + b6 \times T_a^2$ (observation: in the benzene oxidation reactor case, the M variable (molar fed ratio, moles H_2/NB) has been replaced by y_{Bo} = inlet molar fraction of benzene in the air).

Coefficient	Reactor	
	Benzene oxidation (this paper)	Nitrobenzene hydrogenation (Stefan and Maria[2])
B1	1656.6	-2277.6489
B2	-9.4410	-931459
B3	-1682.9	14.4202
B4	-2.4047	11.6506
B5	-16933	-0.2554
B6	0.0014749	-0.0116
Empirical model prediction relative error (%)	0.69	0.41

Table 8

COMPARISON OF EMPIRICAL CORRELATION COEFFICIENTS OF THE CRITICAL INLET PRESSURE (p_{oc}) PREDICTED BY MEANS OF MV-CRITERION FOR TWO SIMILAR CATALYTIC FIXED-BED REACTORS FOR BENZENE OXIDATION (PRESENT PAPER), AND NITROBENZENE

HYDROGENATION [2]: $p_{oc} = b1 + b2 \times T_o + b3 \times M(y_{Bo}) + b4 \times T_a + b5 \times T_o^2 + b6 \times M^2(y_{Bo}^2) + b7 \times T_a^2$ (observation: in the benzene oxidation reactor case, the M variable (molar fed ratio, moles H_2/NB) has been replaced by y_{Bo} = inlet molar fraction of benzene in the air)

Coefficient	Reactor	
	Benzene oxidation (this paper)	Nitrobenzene hydrogenation (Stefan and Maria [2])
B1	-92.338	115.0318
B2	0.023824	0.1057
B3	-710.15	-0.3746
B4	0.16799	0.0003
B5	-0.00018994	0
B6	4827.2	0
B7	-0.00015608	0
Empirical model prediction relative error (%)	4.8	0.49

Coefficient	Benzene oxidation Reactor case
B1	51.903
B2	-0.18076
B3	-0.14902
B4	-0.010771
B5	0.00011145
B6	0.0000066824
Empirical model prediction relative error (%)	6.27

Table 9

EMPIRICAL CORRELATION COEFFICIENTS OF THE CRITICAL INLET MOLAR FRACTION OF BENZENE (y_{Boc}) PREDICTED BY MEANS OF MV-CRITERION FOR THE CATALYTIC FIXED-BED REACTOR FOR BENZENE OXIDATION:

$$\ln(y_{Boc}) = b1 + b2 \times p_o + b3 \times T_o + b4 \times T_a + b5 \times T_o^2 + b6 \times T_a^2$$

those similarly obtained by Stefan and Maria [2] for a similar risky multi-tubular catalytic reactor used for aniline production in vapour phase. The comparison of T_{oc} -

correlation coefficients in the table 7, reveals: the great influence of p_o and y_{Bo} on the T_{oc} in both processes. Such individual dependencies are plotted in figure 2. A similar analysis is made in table 8 for the p_{oc} -correlation coefficients. The largest influence on p_{oc} is exercised by the y_{Bo} . Such individual dependencies are plotted in figure 3. A similar analysis is made in table 9 for the y_{Boc} -correlation

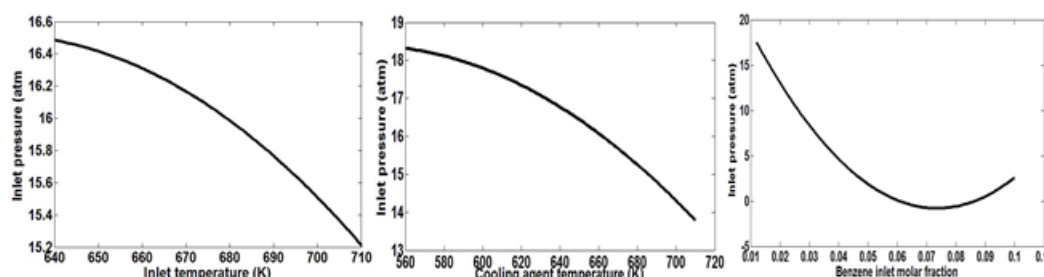


Fig. 3. Dependencies of the critical inlet pressure (p_{oc}) on various running parameters predicted by means of MV-criterion vs. various running parameters (plots obtained by means of the empirical correlation of table 5)

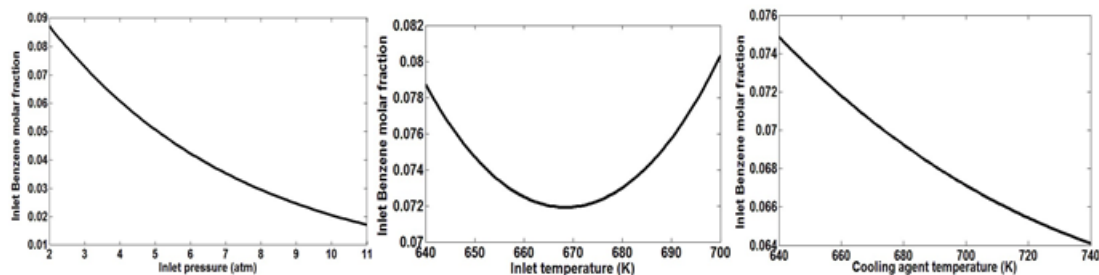


Fig. 4. Dependencies of the critical inlet molar fraction of benzene (y_{Boc}) on various running parameters predicted by means of MV-criterion vs. various running parameters (obtained by means of the empirical correlation of table 6).

coefficients. The largest influence on y_{Boc} is exercised by the p_o and T_a . Such individual dependencies are plotted in figure 4.

It is to remark that such individual dependencies of safety limits of control variables $u_{i,c}$ on running parameters ϕ_j are not linear, which means they are difficult to be extrapolated, and requiring re-evaluation when the nominal operating conditions of the reactor or the catalyst characteristics are changed.

Conclusions

Even if the systematic model-based evaluation of a risky reactor safety limits is a steady and computational intensive procedure, it is a crucial step in all phases of the process development: design, safe operation, and process optimization. Such a sustainable process development requires the use of detailed kinetic models of the process, and complex but rigorous approaches to determine the safety operation limits of risky chemical reactors, completed with simple but adequate models to correlate all these safety limits to be used in further reactor operation optimization.

The generalized MV criterion has been proved as being a worthy instrument in this respect, followed by simple safety limit correlations to facilitate further reactor operation multi-objective optimization computational steps.

Notation

\bar{c}_p - Average mixture specific heat
 D_z - Axial 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)
 $d_{t,ext}$ - 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
 $s(x_i, \phi_j)$ - Parametric sensitivities

T_a - Cooling agent temperature

T - Temperature

t - Time

u_j - Sensitivity functions of the control variables

u - Gas flow velocity

$v_{p,i}$ - Volumetric specific reaction rate of species i

$v_{r,i}$ - 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_i - Molar fractions of chemical species

z - Reactor length

Greeks

α - Heat transfer partial coefficient

α_i^o - Static contribution of the catalytic bed

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

$\delta_{G,1}, \delta_{G,2}$ - Represent values of the δ_G parameter which correspond to the most rarefied packing ($\epsilon_1 = 0.476$) and most compact packing ($\epsilon_2 = 0.260$)

δ_1 - 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^o - Static contribution of the catalytic bed to the thermal conductivity

λ_s - Catalytic bed thermal conductivity

μ_G - Gas viscosity

$v_{i,j}$ - 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_1 - 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 - Divergent based criteria

F - Phenol

GM - Geometry - based methods

HSO - hot-spot of the temperature axial profile in the tubular reactor

ODE - Ordinary differential equation set

PAO - Pseudo-adiabatic operation

References

1. DIMIAN, C.A., BILDEA, C.S., Chemical process design, Weinheim: Wiley - VCH, 2008;
2. STEFAN, D. N., MARIA, G., Derivation of operating region runaway boundaries for the vapour phase catalytic reactor used for aniline production, *Rev. Chim. (Bucharest)*, **60**, no. 9, 2009, p. 949
3. MARIA, G., STEFAN, D. N., Comparative evaluation of critical operating conditions for a tubular catalytic reactor using thermal sensitivity and loss-of-stability criteria, *Chemical Papers*, **64**, 2010, p. 450-460;
4. GREWER, T., Thermal hazards of chemical reactions, Amsterdam: Elsevier, 1994.
5. MARIA, G., Chemical process quantitative risk analysis and modelling of accident consequences, Bucharest: Printech Publ., 2007, (640 p., in Romanian).
6. STOESSEL, F., Thermal safety of chemical processes. Risk assessment and process design, Weinheim: Wiley-VCH, 2008.
7. NICOLAE, A., MARIA, G., *Rev. Chim. (Bucharest)*, **58**, no. 4, 2007, p. 427
8. VARMA, A., MORBIDELLI, M., WU, H., Parametric sensitivity in chemical systems. Cambridge (MS): Cambridge University Press, 1999.
9. SEIDER, W.D., BRENDEL, D., PROVOST, A., Nonlinear analysis in process design. Why overdesign to avoid complex nonlinearities, *Industrial Engineering Chemical Research*, **29**, 1990, pp. 805-818.
10. LUPUSOR, G., MERICA, E., GOREA, C., BUCEA-GORDUZA, V., *Ingineria sintezei intermediarilor aromatici (Synthesis of aromatic intermediates engineering)*, 1, Ed. Tehnica, Bucharest, (1977); 2, Ed. Tehnica, Bucharest, (1981).
11. MUSCALU, C., MARIA, G., Setting runaway boundaries under parametric uncertainty for the benzene oxidation industrial catalytic reactor, U.P.B. Scientific Bulletin (in press)
12. FROMENT, G.F., BISCHOFF, K.B., Chemical reactor analysis and design, Wiley, New York, 1990.
13. BOZGA, G., MUNTEAN, O., *Reactoare chimice - Vol II - Reactoare eterogene (Chemical Reactors: Heterogeneous Reactors)*, Ed. Tehnica, Bucharest, 2001.
14. TRAMBOUZE, P., Van LANDEGHEM, H., WAUQUIER, J.P., *Chemical reactors: Design, engineering, operation.*, Paris: Edition Technip, 1988
15. GILLILAND, E., BADDOUR, R., PERKINSON, G., SLADEK, K.J., Diffusion on surfaces. 1. Effect of concentration on the diffusivity of physically adsorbed gases, *Industrial & Engineering Chemistry Fundamentals*, **13**, 1974, p. 95-100.
16. ZWILLINGER, D., KRANTZ, S.G., ROSEN, K.H., *Standard mathematical tables and formulae*, CRC Press, Boca Raton, 1996, p. 705.
17. MARIA, G., DAN, A., Setting optimal operating conditions for a catalytic reactor for butane oxidation using parametric sensitivity analysis and failure probability indices, *Jl. Loss Prevention in the Process Industries*, **25**, 2012, p. 1033-1043.
18. SHARMA, R. K., CRESSWELL, D. L., NEWSON, E. J., Kinetics and fixed-bed reactor modelling of butane oxidation to maleic anhydride, *AIChE Journal*, **37**, 1991, p. 39-47.
19. STEFAN, D. N., MARIA, G., A note concerning the risk of using global kinetics instead of detailed kinetic models in evaluating the runaway boundaries of industrial (semi-)batch reactors, *U.P.B. Sci. Bull., Series B*, **73**, 2011, p. 167-180.

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