

The Reactor Size Influence on the Optimal Operating Setpoint Choice for a Fixed-Bed Multi-Tubular Catalytic Reactor

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Optimal operation of chemical reactors of high thermal sensitivity is a central engineering problem of very high current interest. One elegant alternative to choose the optimal setpoint when at least two contrary (opposite) objectives are considered is based on the so-called Pareto-optimal front technique. This paper exemplifies how to generate Pareto optimal operating policies when reactor productivity and safety objectives (expressed in probabilistic terms) are simultaneously considered in the presence of technological constraints, uncertainty in safety boundaries, and random fluctuations in control variables. Beside the operating control variables, one important design variable is the reactor pipe diameter because it is directly related to the reaction heat removal. This paper exemplifies the influence of this design variable on the setpoint choice when applying the Pareto-optimal front method with computing the runaway-boundaries by using the generalized sensitivity criterion of Morbidelli and Varma (MV-criterion). An example is provided for an industrial fixed-bed tubular reactor used for the catalytic oxidation of benzene to maleic anhydride (MA) in vapour phase.

Keywords: runaway boundaries; Pareto front; catalytic reactor; benzene oxidation; reactor size influence

Setting the optimal operating conditions to fully satisfy the safety requirements for a catalytic chemical reactor of high thermal sensitivity is one of the major engineering challenging problems. The ability of handling highly exothermic reactions in the presence of parametric uncertainty has a high impact on defining the optimal operating conditions of the chemical reactors [1]. In the case of a multi-tubular catalytic reactor (fig. 1-left), the set-point choice of the operating parameters that control the process, that is the control variables, such as: inlet pressure (p_0), and temperature (T_0), inlet gas composition ($y_j =$ molar fractions of the j chemical species; the most important in the approached case study being the benzene inlet molar fraction y_{B_0}), the cooling agent temperature (T_a), etc., is a multi-objective optimization problem to be solved for each case study [2-6].

An elegant option to choose the operating setpoint based on the *multi-objective optimization* of the chemical reactor is to get the set of *Pareto optimal* operating policies, also called Pareto-front for the case of two adverse (opposite) objectives. A Pareto solution is one where any improvement in one objective can only take place at the cost of the other objective.

Such a Pareto-front was generated in the approached reactor case study (i.e. the industrial fixed-bed tubular reactor, of high thermal sensitivity, used for the catalytic oxidation of benzene to maleic anhydride in vapour phase) by [6] for the nominal running conditions of table 3, and a multi-tubular fixed-bed reactor of 24mm pipe diameter. The obtained Pareto-front of figure 2-left reveal that, for continuous variable models, infinity of Pareto-optimal solutions can exist, and the final solution choice is subjective and case-dependent [2]. Also, the runaway risk is exponentially increasing with the reactor productivity. This is why, Muscalu & Maria [6] recommended to choose the setpoint at the Pareto-curve lowest *break-point* (that is point 1 in the fig. 2). Thus, the optimal values of the control variables (u) are kept far away from the runaway boundaries $u_c(\phi)$ [index c denotes the critical value, that is the runaway boundary; $f =$ operating parameters], but also from their confidence region $u_c(\phi) \pm \sigma_{u_c}$ in order to get a prudent operation of this very sensitive tubular reactor (s denotes the standard deviation). The correct choice of the setpoint is also confirmed by also inspecting its location in the parametric space (fig. 1-right).

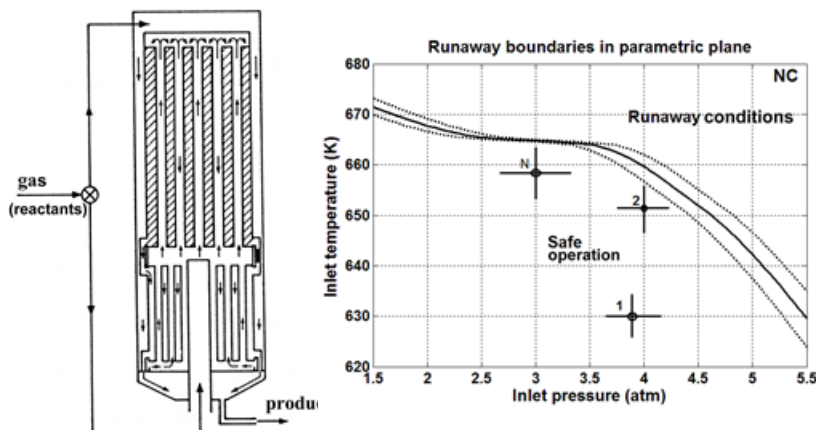


Fig.1. (left) The multi-tubular catalytic reactor schemes. (right) Location of several optimal-Pareto set-points of figure 2 in the parametric [inlet temperature vs. inlet pressure] plane for the benzene oxidation tubular reactor of 24 mm reactor pipe diameter (adapted from [6]); NC= nominal operating conditions

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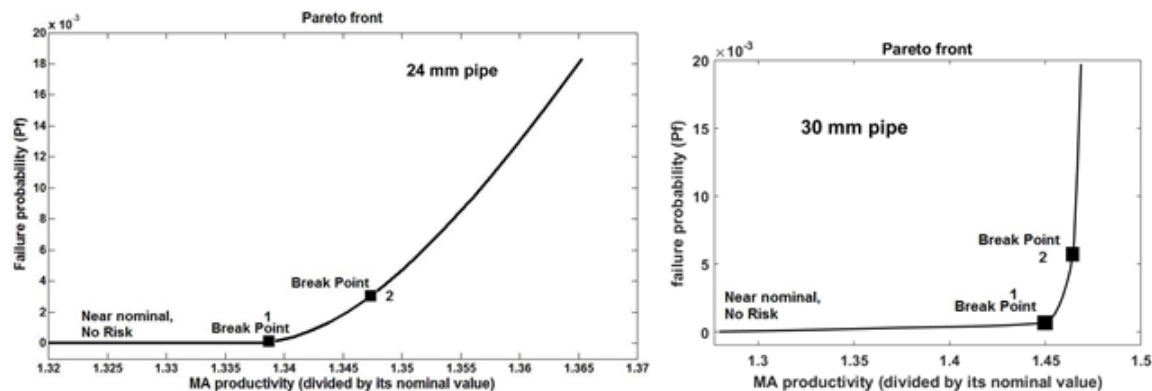


Fig. 2. The Pareto-optimal front of the optimal operating policies of the benzene oxidation tubular reactor of 24 mm reactor pipe diameter (left; adapted from [6]), and for those of 30 mm pipe diameter (right)

Beside the mentioned operating control variables, vector $u = [T_o, p_o, y_{B,0}, T_a]$, one important design variable is the reactor pipe diameter (denoted by dt and determining the reactor pipe cross-section in the reactor model of table 2) because it is directly related to the reaction heat removal. This paper exemplifies the influence of this design variable on the setpoint choice when applying the Pareto-optimal front method [6] with computing the runaway-boundaries (fig. 1-right) by using the generalized sensitivity criterion of Morbidelli and Varma [1].

By using the methodology of Dan and Maria [2], this paper is aiming at comparing the setpoints for two alternatives of the reactor pipe diameter (24mm and 30mm). The setpoints have been selected using the Pareto-optimal front methodology. The Pareto-optimal operating policies are generated for the highly sensitive approached multi-tubular catalytic chemical reactor (fig. 1-left), by simultaneously considering the reactor productivity and safety objectives (expressed in probabilistic terms), in the presence of technological constraints, uncertainty in safety boundaries, and random fluctuations in the mentioned control variables. The example refers to the industrial fixed-bed tubular reactor analyzed by Muscalu and Maria [3-6] for the catalytic oxidation of benzene to maleic anhydride in vapour phase, by using a complex process kinetic model from literature. This paper proves the validity of the Muscalu & Maria [6] concept of choosing the operating setpoint at the lowest *break-point* in the Pareto-front (fig. 2-left).

Benzene oxidation - process kinetic model and reactor model

The multi-tubular reactor (heat exchanger type, fig. 1-left) for benzene oxidation to maleic anhydride includes the catalytic fixed bed inside pipes of small diameters (below 3-4 cm), which are continuously cooled by a good circulation of a molten salt cooling liquid in which the pipes are immersed [7].

The reaction temperature is kept under a permissible limit (450 °C) by quickly dissipating the heat of reaction through reactor inter-tubular space where the cooling liquid

is vigorously recirculated. The benzene/air mixture (in a concentration below the lower explosion limit, of 1.5%vol.) is fed into the reactor at approx. 385 °C where the oxidation to maleic anhydride takes place (see the reactor nominal operating conditions in the table 3). *The catalyst used for the reaction is a mixture of vanadium/chrome oxides on a silica bed* [8]. *The oxidation reaction is complex, with successive and parallel reactions* [4,8], involving a relatively large number of intermediate products. For a more accurate representation of the industrial reactor behaviour, an extended kinetic model of the process was adopted, by accounting for the reactions R1-R9 presented in the table 1 with the reaction enthalpies evaluated using Aspen Hysys software.

For a relatively quick reactor operation optimization, a simplified mathematical model of the reactor was used by considering a pseudo-homogeneous, and one-dimensional plug-flow reactor hypotheses. The model main equations are presented in the table 2 in terms of species mass, heat and momentum balances. The Arrhenius type rate constants are given by Muscalu and Maria [6].

An important characteristic of the reactor represents its high thermal sensitivity and associated operating risk. This is one of the reasons why employing a tight control of the operating parameters is required. This procedure needs to include the suitable choice of the control variable (u) setpoint, that is the reactor inlet conditions (*i.e.* inlet temperature $u_1 = T_o$, inlet benzene concentration $u_2 = T_o = y_{B,0}$, and inlet pressure $u_3 = p_o$), as well as the choice of the suitable cooling agent temperature $u_4 = T_a$ in order to avoid the proximity of critical conditions $u_{j,c}$ leading to the process runaway. In order to do this, a sophisticated reactor control is usually implemented. Another aspect that needs to be considered during the reactor optimization is the impossibility to recover the benzene in an economically way, leading to impose some technological constraints during the process optimization (table 3). The reactor nominal operating conditions are presented in the table 3.

Table 1

THE REACTION SCHEME OF 9 REACTIONS (R1-R9) FOR THE BENZENE OXIDATION PROCESS BY USING A VANADIUM/CHROME OXIDE ON A SILICA SUPPORT CATALYST [8]. THE ARRHENIUS RATE CONSTANTS, AND REACTION ENTHALPIES ARE GIVEN BY [6].

(R1) $C_6H_6 + \frac{1}{2}O_2 \xrightarrow{k_1} C_6H_5OH$	(R6) $C_6H_4O_2 + 3O_2 \xrightarrow{k_6} C_4H_2O_3 + 2CO_2 + H_2O$
(R2) $C_6H_6 + \frac{3}{2}O_2 \xrightarrow{k_2} C_6H_4O_2 + H_2O$	(R7) $C_4H_2O_3 + 3O_2 \xrightarrow{k_7} 4CO_2 + H_2O$
(R3) $C_6H_6 + \frac{9}{2}O_2 \xrightarrow{k_3} C_4H_2O_3 + 2CO_2 + 2H_2O$	(R8) $C_6H_5OH + 4O_2 \xrightarrow{k_8} C_4H_2O_3 + 2CO_2 + 2H_2O$
(R4) $C_6H_6 + \frac{15}{2}O_2 \xrightarrow{k_4} 6CO_2 + 3H_2O$	(R9) $C_6H_5OH + 7O_2 \xrightarrow{k_9} 6CO_2 + 3H_2O$
(R5) $C_6H_5OH + O_2 \xrightarrow{k_5} C_6H_4O_2 + H_2O$	

Table 2

DIFFERENTIAL BALANCE EQUATIONS OF THE FIXED BED MULTI-TUBULAR REACTOR MODEL USED TO SIMULATE THE BENZENE OXIDATION TO MALEIC ANHYDRIDE PROCESS. THE AUXILIARY RELATIONSHIPS ARE GIVEN BY [6]. NOTATIONS: B = BENZENE, F = PHENOL, Q = QUINONE, AM = MALEIC ANHYDRIDE. THE PSEUDO-HOMOGENEOUS ONE-DIMENSIONAL MODEL HYPOTHESES ARE GIVEN BY [6]

Mass balance (index j denotes species): $\left. \begin{aligned} \frac{dD_{M_j}}{dz} &= -\eta_j v_{P,j} S \\ v_{P,j} &= \sum_{i=1}^9 v_{i,j} \cdot v_{R,i} \\ v_{R,i} &= v_{r,i} \rho_{SC} \\ v_{r,i} &= k_i p_j \end{aligned} \right\} \Rightarrow \frac{dD_{M_j}}{dz} = -\eta_j \rho_{SC} S \sum_{i=1}^9 v_{i,j} k_i p_j$	
Inlet conditions (at $z = 0$, index "0"): $y_j = y_{j,0}, T = T_0, P = P_0$ (from Table 3). $i =$ chemical reaction index (R1-R9); $j =$ species index (B, F, Q, AM) D_{M_j} - molar flow rate of " j " species, kmol/s; S - cross-sectional area of the pipe; m^2 $v_{P,j}$ - volumetric specific reaction rate of species " j ", $\frac{\text{kmol}}{m^3 \cdot s \cdot atm}$; $v_{R,i}$ - volumetric specific reaction rate of reaction " i ", $\frac{\text{kmol}}{m^3 \cdot s \cdot atm}$; $v_{r,i}$ - mass specific reaction rate of reaction " i ", $\frac{\text{kmol}}{\text{kg}_{cat} \cdot s \cdot atm}$ (pseudo first-order reaction); ρ_{SC} - density of the catalytic bed, $\frac{\text{kg}_{cat}}{m^3_{reactor}}$; $\rho_{sc} = (1 - \varepsilon) \cdot \rho_p$, ρ_p - density of catalyst partide, $\frac{\text{kg}_{cat}}{m^3_{cat}}$; ε - void fraction; $v_{i,j}$ - stoichiometric coefficient of species " j " in reaction " i "; p_j - the partial pressure of species " j ", atm; $y_j =$ molar fractions of chemical species η_j - the total effectiveness factor of the catalyst particle, k_i - pseudo-order 1 kinetic constant of reaction " i ", $\frac{\text{kmol}}{\text{kg}_{cat} \cdot s \cdot atm}$; $k_i = k_i \cdot \exp(-E_n / RT)$ [values of [6]]; R - universal gas constant	
Heat balance: $\frac{dT}{dz} = \frac{\sum_{i=1}^9 (-\Delta H_{R,i}) v_{r,i} \rho_{SC} S - K_T \pi d_i (T - T_a)}{D_{m,t} \cdot \bar{c}_p}$	
T - gas temperature, K; z - reactor length, m; $(-\Delta H_{R,i})$ - heat of reaction " i ", kJ/kmol; K_T - overall heat transfer coefficient, $\frac{W}{m^2 K}$; d_i - pipe diameter, m; T_a - cooling agent temperature, K; $D_{m,t}$ - mass flow rate of the feed mixture, kg/s; \bar{c}_p - average mixture specific heat $\frac{\text{kJ}}{\text{kg}_{sm} K}$.	
Momentum balance: $\frac{d\bar{p}}{dz} = -f \left(\frac{D_{m,t}}{S} \right) \frac{1}{\rho_G d_p} = -f \frac{u^2 \rho_G}{d_p}$; f - friction coefficient [12]: $f = \begin{cases} \frac{1-\varepsilon}{\varepsilon^3} \left[1.75 + 150 \frac{1-\varepsilon}{\text{Re}_p} \right], & \frac{\text{Re}_p}{1-\varepsilon} < 500 \\ 6.8 \frac{(1-\varepsilon)^{1.2}}{\varepsilon^3} \text{Re}_p^{-0.2}, & \frac{\text{Re}_p}{1-\varepsilon} > 500 \end{cases} ; \varepsilon = 0.38 + 0.073 \left[1 - \frac{(\alpha_i / \alpha_p - 2)^2}{(\alpha_i / \alpha_p)^2} \right] = \text{bed void fr.}$	

$Re_g = \frac{u \rho_G d_p}{\mu_G}$ - Reynolds number for flow through the catalytic bed. p_j = Partial pressure of species "j"; p = overall pressure; μ_G - gas viscosity, Pa·s . d_p - catalyst particle diameter, m; u - gas flow velocity, m/s; ρ_G - gas density, $\frac{kg_G}{m^3}$
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 pipe length. For temperatures below 400 °C radiation heat transfer was neglected. The approximate value of K_T at the feed conditions is $K_T = 119.4 \frac{W}{m^2 K}$
Transport resistance inside the particle is represented by overall effectiveness factor: $\eta_h = \frac{3}{\Phi_i} \left(\frac{1}{th(\Phi_i)} - \frac{1}{\Phi_i} \right)$ Thiele modulus, Φ_i is evaluated for a pseudo- first order kinetics for large air/ Benzene inlet ratios [13]: $\Phi_i = \frac{d_p}{6} \sqrt{k_1 \rho_p \frac{1-\varepsilon}{\varepsilon} \frac{RT}{D_{ef}}}$ Effective diffusion coefficient evaluated based on the molecule diffusion coefficient of benzene in air, $D_{ef} \approx \varepsilon D_m / \tau$, calculated using the relationships of [6]; ε = fixed-bed void fraction; d_p = Catalyst particle diameter; D_m = molecule diffusion coefficient of benzene in air; τ = tortuosity; k_1 = Pseudo-order 1 kinetic constant of reaction "i" Ideal plug-flow reactor hypothesis have been applied with concentration, temperature and pressure gradients only in the axial flow direction, $\partial(c_j, T, p) / \partial R_T = 0$; c_j - species concentrations; R_T - pipe radius; L - pipe length.
Axial dispersion coefficient is neglected, $D_z = 0$ [because $L / d_t > 50$]
Isothermal spherical catalyst particles, $\partial T_p / \partial R_p = 0$; Uniform catalyst particles of an average diameter d_p ; inter-granular transport resistances are neglected.

Table 3
THE CHARACTERISTICS AND THE NOMINAL OPERATING CONDITIONS OF THE FIXED-BED CATALYTIC REACTOR FOR BENZENE OXIDATION, ACCORDING TO [4,6]

Catalyst composition= V-Cr/support	Tortuosity, $\tau = 2.01$		
Catalyst density (bulk), $\rho_c = 1260 \text{ kg/m}^3$	Pipe inner diameter (6000 pipes): $d_t = 24\text{mm}$ [6], or 30mm (this paper)		
Catalyst avg. diameter, $d_p = 5 \text{ mm}$	Reactor pipe thickness, $\delta_t = 2 \text{ mm}$		
Catalyst porosity, $\varepsilon = 0.48$	Reactor length, $L = 4 \text{ m}$		
Fixed-bed void fraction, 0.48	Gas velocity(void pipe 24mm), $u_o = 1.68 \text{ m/s}$		
Fed Benzene flow-rate (per reactor pipe)	$F_{B,o} = 0.1 \text{ kg/h}$		
Operating conditions and technological constraints:	Minimum	Nominal	Maximum
Inlet total pressure (Po, atm)	1.6	3	4
Inlet gas temperature (To, °C)	305	385	405
Benzene inlet molar fraction (yB,o)	0.007	0.014	0.018
Cooling agent average temperature (°C)	300	380	400

Derivation of the Pareto-optimal front for the benzene oxidation reactor

To derive the Pareto-optimal front of the benzene oxidation reactor, several computational steps should be followed.

The first computational step consists in model-based evaluation of the reactor sensitivity functions and the runaway boundaries of the operating

parameter, or the runaway boundaries of the control parameters u_j . This is performed by using the so-called *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 or control parameter u_j, ϕ_j . In other words, critical value of a parameter or corresponds to:

$$\varphi_{j,c} = \arg \left(\text{Max}_{\varphi_j} \left| s(T_{max}; \varphi_j) \right| \right), \text{ or } \varphi_{j,c} = \arg \left(\text{Max}_{\varphi_j} \left| S(T_{max}; \varphi_j) \right| \right), \quad (1)$$

$$S(T_{max}; \varphi_j) = (\varphi_j^* / T_{max}^*) s(T_{max}; \varphi_j) = (\varphi_j^* / T_{max}^*) (\partial T_{max} / \partial \varphi_j), \text{ or}$$

$$u_{j,c} = \arg \left(\text{Max}_{u_j} \left| S(T_{max}; u_j) \right| \right), \text{ with } S(T_{max}; u_j) = (u_j^* / T_{max}^*) s(T_{max}; u_j)$$

[where: $S(T_{\max}; \phi_j)_z = s(T_{\max}; \phi_j) \phi_j^* / T^*$ is the relative sensitivity function of maximum temperature T_{\max} in the reactor pipe vs. parameter ϕ_j = operating parameter or control variable u_j ; $*$ = nominal operating conditions (set point) in the parameter space; z = reactor length; index z denotes the dependence on the reactor length].

According to the MV criterion, critical conditions induce a sharp peak of the normalized sensitivity $S(T_{\max}; \phi)$ or $S(T_{\max}; u)$ evaluated over the reactor length and over a wide range of ϕ or u . The sensitivity functions $s(x_i; \phi_j) = (\partial x_i / \partial \phi_j)$ of the state variables x_i (including the reactor temperature, overall pressure, species partial pressures) with respect to the operating parameters ϕ_j (feed composition, cooling agent temperature, etc.), or with respect to the control variables u_j (inlet temperature, pressure, cooling agent temperature, species inlet molar fractions) can be evaluated by using the so-called 'sensitivity equation' solved simultaneously with the reactor model [3-6]. 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 $s(x_i; \phi_j)_z$, or $s(x_i; u_j) = \partial x_i / \partial u_j$, or at

$$\hat{T}_{oc} = b_1 + b_2 \times p_o + b_3 \times y_{Bo} + b_4 \times T_a + b_5 \times y_{Bo}^2 + b_6 \times T_a^2; \quad (2)$$

$$\sigma_{T_{o,c}}^2 = \sum_j \left(\partial T_{o,c} / \partial \phi_j \right)_{\phi}^2 \sigma_{\phi_j}^2 \quad \text{with } \phi = [p_o, y_{Bo}, T_a] \quad (3)$$

$$\ln(\hat{y}_{zcc}) = a_1 + a_2 \times p_o + a_3 \times T_o + a_4 \times T_a + a_5 \times T_o^2 + a_6 \times T_a^2 \quad (4)$$

$$\sigma_{y_{Bo,c}}^2 = \sum_j \left(\partial y_{Bo,c} / \partial \phi_j \right)_{\phi}^2 \sigma_{\phi_j}^2 \quad \text{with } \phi = [p_o, T_o, T_a] \quad (5)$$

$$p_{oc} = c_1 + c_2 \times T_o + c_3 \times y_{Bo} + c_4 \times T_a + c_5 \times T_o^2 + c_6 \times y_{Bo}^2 + c_7 \times T_a^2 \quad (6)$$

$$\sigma_{p_{o,c}}^2 = \sum_j \left(\partial p_{o,c} / \partial \phi_j \right)_{\phi}^2 \sigma_{\phi_j}^2 \quad \text{with } \phi = [T_o, y_{Bo}, T_a] \quad (7)$$

where $\hat{\phi}$ = nominal value of the distributed parameter vector; '^' denotes the estimated value by using the algebraic regression model). The vectors of the correlation coefficients (**a**, **b** and **c** in Eqns. 1, 3, and 5) have been estimated by means of nonlinear regression by using the precisely calculated runaway limits with the MV-criterion. The values of the [(**a**, **b**, **c**)] coefficients are given by Muscalu & Maria [5], being not presented here. The variance $\sigma_{u_j,c}^2$ of the control variable safety limits $u_{j,c}(\phi)$ are obtained by using the well-known error-propagation formula [2]:

$$\sigma_{u_c}^2 = \sum_j \left(\partial u_c / \partial \phi_j \right)_{\phi}^2 \sigma_{\phi_j}^2 \quad (8)$$

with known parameter/control variable random dispersions (σ_{ϕ_j}). Such a runaway limit curve (solid-line) and its confidence band (dash-line) for parametric deviations $\phi \pm \delta \phi$ is presented in the figure 1-right for random deviations of $\delta T_o = 10$ K, and $\delta p_o = 0.2$ atm.

Finally, to get the Pareto-optimal front of the reactor operation, two optimization objectives have been formulated:

i) an economic objective, expressed by maximization of the output maleic anhydride (MA) molar flow rate, G_{MA} (at the reactor length L). To be further compared with the probabilistic safety objective, the chosen G_{MA} objective was

various reactor lengths z . Such a resulted critical curve is displayed in the figure 1-right in terms of (critical inlet temperature vs. inlet pressure), i.e. $T_{o,c} = f(p_o)$.

The MV generalized sensitivity criterion is proved to be very effective and generally applicable irrespectively of the reactor type or process [2,9]. 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 [10]. 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.

In the second computational step, the derived runaway boundaries (i.e. $u_{j,c} = f(u, \phi)$, the critical surfaces in the parametric space) of the considered control variables $u = [T_o, \ln(y_{Bo}), p_o]$ are correlated with simple algebraic functions to facilitate further reactor optimization rule. These correlations, derived by Muscalu & Maria [5] are the following:

normalized by division to its nominal value $G_{MA} = 6.95 \times 10^4$ kmol/h (per reactor pipe, at the nominal conditions of table 3).

ii) A safety objective, expressed by the minimum risk in operation, implemented under the definition of Dan & Maria [2], Maria & Dan [9], in the form of a combined failure probability P_f index (including parametric and safety limit uncertainty). P_f is a stochastic term with values in the range of [0-1]. The failure probability index is derived based on the assumption of a parametric and safety limit uncertainty, and has two components which represent a formulation of the *probability of the reactor runaway*:

$$P_f = P_{f1} + P_{f2} \quad (9)$$

The probability P_{f1} expresses the chance that the chosen control variables will overpass the runaway boundaries

$u_{j,c}(\phi) \sim N(\bar{u}_{j,c}, \sigma_{u_{j,c}}^2)$ as a result of the uncertainty in the safe operation limits. For the normally distributed runaway boundaries, the index reflects the probability that:

$$u_j(\phi) \geq \bar{u}_{j,c}(\phi) \pm \delta u_{j,c}(\phi, \delta \phi) \quad (10)$$

P_{f1} results by summing P_{f1j} over all j control variables.

The runaway probability P_{f2} appears as a result of random fluctuations in the control variables and/or operating parameters, thus determining the running point to enter in

the risky runaway limit confidence region. In other words, by considering normally distributed variables

$u_j \sim N(\bar{u}_j, \sigma_{u_j}^2)$, this risk index reflects the probability that:

$$u_{j,c}(\phi) \leq \bar{u}_j(\phi) \pm \delta u_j(\phi, \delta \phi) \quad (11)$$

[see [2,3,9] for computational details].

The combined failure probability index (9) represents a synthetic quantitative measure of some operating risks, very useful for multi-objective reactor operation optimization that accounts for various sources of solution uncertainty.

At this point, the Pareto-optimal operation set points are obtained by formulating the following optimization problem, accounting for the concomitant maximization of the reactor productivity and minimization of the failure probability (including parametric and safety limit uncertainty), as a stochastic term:

$$[\hat{u}_o, \hat{\phi}] = \arg \text{Max}[G_{MA}(L)/G_{MA,r}(L)] \wedge \arg \text{Min}[Max P_f] \quad (12)$$

with the fulfilment of some supplementary imposed technological constraints (of nonlinear inequalities, $g_i \leq 0$ general form), mentioned in the table 3, that is: inlet benzene concentration below the low explosion and flammability limits (0.007 and 0.018 molar fr.); lower and upper limits for the cooling agent temperature (300, and 400°C), and reactor inlet gas temperature (305, and 405 °C); lower limits for benzene conversion (90%) and maleic anhydride yield (25%); and a maximum level for the hot-spot in the reactor (600 °C); maximum limit of pressure drop (2.8 atm).

Compare the Pareto-optimal fronts for two design alternatives of the benzene oxidation reactor

The optimization problem (12), have been solved by using a genetic algorithm (the routine GAMULTIOBJ) implemented in Matlab™ [15]. Application of this algorithm leads to obtaining the Pareto optimal fronts displayed in the figure 2, under the nominal conditions and constraints of table 3, but in two constructive alternatives: reactor pipes of 24mm (fig. 2-left), and 30mm (fig. 2-right). An examination of the plotted results of fig. 2 leads to the following conclusions.

i) When two antagonist optimization criteria are used, infinity of Pareto-optimal operating solutions can be found for the benzene oxidation tubular reactor, each point of these curves corresponding to a certain operating parameter/control variable vector $[T_o, P_o, y_{Bo}, T_a]$.

ii) For a better interpretation of the Pareto front results, the location of the corresponding solution in the parametric space should be simultaneously investigated. This procedure allows detecting the set-points falling in the safety region, without crossing the confidence band of the safety limits (as the case of the set points *N*, *1*, *2* of the Pareto-front 24mm of figure 2-up, also displayed in the parametric plane of fig. 1-right).

iii) For the 24mm reactor pipe alternative, it is to observe that the set-point *1* (the lowest curve break-point) corresponding to a relative maleic anhydride productivity of 1.34 vs. the nominal one (1.00), can be chosen as the setpoint, with a $P_f = 10^{-4}$, being placed in the safety operating region of figure 1-right. Also, in the figure 1 (up-left). It is also to observe that the nominal operating conditions *N*, close to the nominal anhydride productivity (i.e. 100% in relative terms), and with no risk ($P_f \approx 0$) can be chosen anywhere on the Pareto-curve left the point *1*.

iv) By contrast, for the same the 24mm reactor pipe alternative, the upper break-point setpoint *2* corresponding to a relative maleic anhydride productivity of 1.35, corresponds to an unsafe operation (of $P_f = 0.003$), the random fluctuations of this running point crossing the confidence region of the safety limit (fig. 1-right).

v) In the both constructive alternatives, as expected, the failure probability index presents an exponentially-like increase with the maleic anhydride productivity. Consequently, the operating solution selection by only using the Pareto-front plot without considering its location in the parametric space is difficult. This is why, Maria & Dan [2,9,14] recommended to chose the setpoint candidate as being the lowest break-point of Pareto-optimal curve.

vi) It is to observe that the exponentially-like increase of the Pareto-optimal curve $P_f = \text{fct.}(\text{productivity})$ is much more pronounced in the 30mm pipe alternative (fig.2-right) compared to the 24mm pipe alternative (fig.2-left). Such a result can be explained by the higher runaway risk caused by a worse radial heat transfer in thick pipes.

vii) The optimal setpoint involves to keep the control variable values far away from the runaway boundaries

$u_c(\phi)$, but also from their confidence region $u_c(\phi) \pm \sigma_{u_c}$ in order to get a prudent operation of this very sensitive tubular reactor. So, in the 30mm pipe alternative, the *1* setpoint is the right choice, as being the lowest break-point of the Pareto-optimal curve (fig. 2- right), which satisfy all process constraints, and do not cross the runaway boundaries and their confidence region (not presented here).

viii) The tolerated depends of the process and reactor characteristics, and of the process constraints. For the

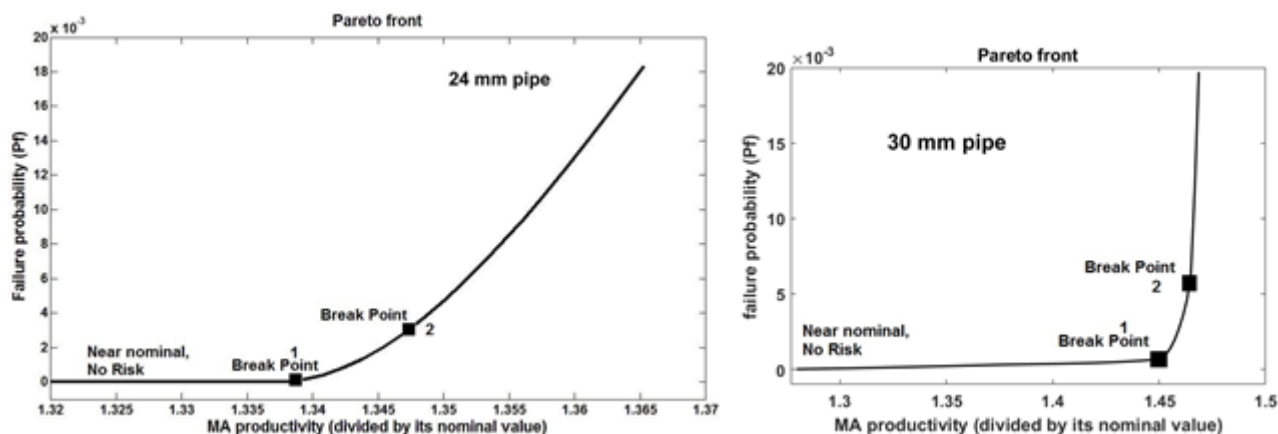


Fig. 2. The Pareto-optimal front of the optimal operating policies of the benzene oxidation tubular reactor of 24 mm reactor pipe diameter (left; adapted from [6]), and for those of 30 mm pipe diameter (right)

studied process and reactor case, the safety operation limit seems to correspond to a failure probability lower than 2% in the 24mm pipe alternative, and of less than 1% in the 30mm pipe alternative.

ix) The operating alternatives can be drastically reduced if a supplementary criterion is considered during optimization (of economic or environmental nature, e.g. costs of the accident consequences using simulated failure scenarios; [7,11]).

Conclusions

Choosing a multi-objective optimal operating policy for a thermally sensitive chemical reactor is a difficult task. Although different optimization methods can be applied in order to determine the problem solution, the final decision also depends on subjective priorities, and on the parametric / model uncertainty level.

The applied model-based methodology of Maria & Dan [2,9] allows obtaining Pareto-optimal operating solutions for the studied tubular reactor that account for both an economic objective, but also for a safety one, expressed in a probabilistic risk index. The procedure, even if computationally intensive, was proved to be simple and robust, being easily implementable on a common computer.

The study also proves that the Pareto-optimal technique is as more valuable as the reactor sensitivity is higher, due to thicker reactor pipes in the present case study.

The selected multi-objective operating solution of the reactor (the so-called Pareto front) is in fact a trade-off between opposite economic (reactor productivity) and safety criteria, but also accounting for the technological constraints, the safety boundary uncertainty, and for the random fluctuations in the control variables. As a conclusion, the recommended optimal operation must be rather focus on more prudent operating conditions, searching for set-points where the parameter disturbances do not lead to crossing the confidence region of the safety limits for all the control and operating variables, while keeping a reasonable small runaway probability (below 0.3-1 % in the studied case).

The right choice of the tolerable safety limit of the failure probability P_f in the reactor design/operation calculus depends, as proved by Dan and Maria (2012), on the reactor type/characteristics, process hazard, and of the magnitude of consequences of a reactor runaway [11]. For instance, this limit is of 3-4 % for a tubular catalytic reactor used for butane oxidation [2], of 0.5-2% for the same tubular catalytic reactor but used for benzene oxidation (this study), or of 3-6 % for a semi-batch reactor used for the catalytic acetoacetylation of pyrrole with diketene in homogeneous liquid phase [2]. Consequently, the study suggests a holistic approach of the reactor safety operation, when deciding what is the acceptable trade-off safety-productivity (economic benefit) eventually by accounting for the costs of possible runaway scenario consequences.

References

1. VARMA, A., MORBIDELLI, M., WU, H. Parametric sensitivity in chemical systems, Cambridge: Cambridge University Press, 1999.
2. DAN, A., MARIA, G., Pareto optimal operating solutions for a semibatch reactor based on failure probability indices, *Chemical Engineering & Technology*, **35**, no. 6, 2012, p. 1098-1103. DOI: 10.1002/ceat.201100706.
3. MUSCALU, C., MARIA, G., Critical variety under parametric uncertainty in an industrial reactor for benzene catalytic oxidation, *Environmental Engineering and Management Journal*, **14**, 2015, p. 2605-2615.
4. MUSCALU, C., MARIA, G., Setting runaway boundaries under parametric uncertainty for the benzene oxidation industrial catalytic reactor, *U.P.B. Sci. Bull., Series B*, **77**, no. 4, 2015, p. 231-246.
5. MUSCALU, C., MARIA, G., Setting correlated runaway boundaries for the catalytic reactor for benzene oxidation using a parametric sensitivity, *Rev. Chim. (Bucharest)* **67**, no. 11, 2016, p. 2266-2275.
6. MUSCALU, C., MARIA, G., Pareto optimal operating solutions for a catalytic reactor for benzene oxidation based on safety indices and an extended process kinetic model, *Revue Roumaine de Chimie*, **61**, no. 11-12, 2016, p. 881-892.
7. MARIA, G., (), Chemical process quantitative risk analysis and modelling of accident consequences, Bucharest: Printech Publ., 2007 (in Romanian).
8. LUPUSOR, G., MERICA, E., GOREA, C., BUCEA-GORDUZA, V., Synthesis of aromatic intermediates engineering, vol. **1-2**, Bucharest: Ed. Tehnica, 1977, 1981. (in Romanian)
9. MARIA, G., DAN, A., Derivation of critical and optimal operating conditions for a semi-batch reactor under parametric uncertainty based on failure probability indices, *Asia-Pacific Journal of Chemical Engineering*, **7**, 2012, p. 733-746. DOI: 10.1002/apj.625.
10. 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**, no. 4, 2010, p. 450-460. DOI: 10.2478/s11696-010-0035-5.
11. MARIA, G., DINCULESCU, D., KHWAYYIR, H.H.S., Proximity risk assessment for two sensitive chemical plants based on the accident scenario consequence analysis, *Asia-Pacific Journal of Chemical Engineering*, **9**, no. 1, 2014, p. 146-158. DOI: 10.1002/apj.1755.
12. FROMENT, G.F., BISCHOFF, K.B., Chemical reactor analysis and design, New York: Wiley, 1990.
13. TRAMBOUZE, P., VAN LANDEGHEM, H., WAUQUIER, J.P., Chemical reactors: Design, engineering, operation, Paris : Edition Technip, 1988.
14. DAN, A., MARIA, G., Pareto optimal operating solutions for a catalytic reactor for butane oxidation based on safety indices, *U.P.B. Sci. Bull., Series B - Chimie*, **76**, 2014, p. 35-48. <http://www.scientificbulletin.upb.ro/>.
15. COLEMAN, T., BRANCH, M.A., GRACE, A., Optimization Toolbox for Use with MATLAB. User's Guide (ver. 6), MathWorks Inc., Natick (MA), 1999.

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