

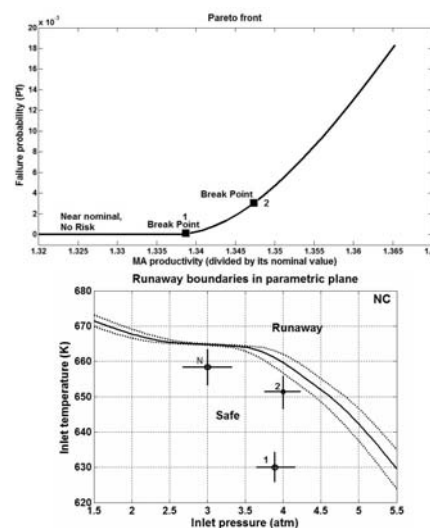
PARETO OPTIMAL OPERATING SOLUTIONS FOR A CATALYTIC REACTOR FOR BENZENE OXIDATION BASED ON SAFETY INDICES AND AN EXTENDED PROCESS KINETIC MODEL

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The importance of process safety in every life cycle stage of a (petro)chemical plant is in continuous growth nowadays. The ability of handling highly exothermic reactions conducted in the presence of parametric uncertainty is related to rules and algorithms to find optimal operating policies of the chemical reactor by simultaneously considering several objectives of sustainability: the contrary process optimization objectives involve, besides economic aspects (process yield, reactor productivity), safety characteristics, such as controllability, stability, and runaway risk. During reactor optimization, the safety aspects must always prevail, without disregarding economic aspects. This paper exemplifies an original methodology to generate the Pareto optimal operating policies of a hazardous chemical reactor, when reactor productivity and safety objectives (expressed in probabilistic terms) are simultaneously considered by using the process and reactor model in a simple way, in the presence of technological constraints, uncertainty in safety boundaries, and random fluctuations in control variables. An example is provided for an industrial fixed-bed tubular reactor, of high thermal sensitivity, used for the catalytic oxidation of benzene to maleic anhydride in vapour phase. Extended process kinetics allows a more accurate determination of the acceptable trade-off between reactor productivity and its safe operation.



INTRODUCTION

In most chemical plants, the reactor is representing the core and usually the riskiest equipment in terms of safety operation. Therefore, the plant optimization efforts are usually focused 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 to the economical process aspects. Optimization procedures are usually

employed to set the reactor nominal operating conditions (set-point) within the parametric space by accounting for the economic criteria, under technological constraints (often empirically determined), followed by elaborated control schemes implemented to keep the reactor operation within the safety limits.¹ Setting of the optimal operating policy for such high sensitive chemical reactors conducts to laborious engineering calculations if process complex models are employed with considering the “parametric uncertainties” (statistically characterized).²

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The engineering calculations start with i) the development of a mathematical model of the process, with a certain detailing degree to offer accurate predictions with a moderate computational effort.

Then, ii) it has to be evaluated the random fluctuation of the operating parameters/control variables around the set-point due to limited performances of the control system (by evaluating the variable standard deviation).

And finally, iii) the parametric uncertainty and plant operation safety have to be considered during optimization of the reactor operation by accounting for the technological constraints, which often are subjected to significant uncertainties associated with other process variables or as a result of the simplified formulations. Random disturbances that can occur in the operating parameters make the implementation accuracy of the optimal operating policy be even more complicated. However, optimization is always defined as a trade-off between economic and safety objectives.

This goal can be reached by using a “safety operation criterion” developed by Maria and Dan³⁻⁶, based on minimizing a “failure probability index P_f ” due to “uncertainty in the reactor runaway boundaries” and “random disturbances in the operating parameters”.⁵ Thus, “a multi-objective optimization can be formulated by simultaneously considering economic, and safety objectives together with technological constraints”.⁴

“The classical deterministic approach resides in searching for optimal nominal values of the control variables of the chemical reactor” (*for instance* feed flow rate, feeding composition and temperature, overall pressure, cooling agent temperature) that guarantee minimization/maximization of a suitable objective function (usually an economic objective in engineering or financial terms), “by fulfilling the differential heat, mass and momentum balance equations, and the technological-safety constraints”.^{2,7}

According to Maria and Dan⁴, the risk corresponding to the thermal runaway during reactor operation can be quantified and included in a multi-criteria optimization function by using an “overall failure probability index”⁵⁻⁶, by evaluating the safety limits for the control variables/operating parameters in the parametric space and “by considering their random fluctuations around the nominal set-point”.^{5-6,8} Approximation of the critical variety with simple algebraic correlations will then facilitate further reactor optimization

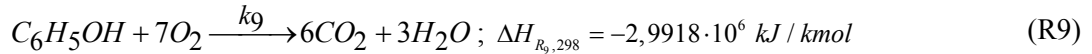
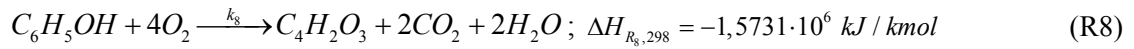
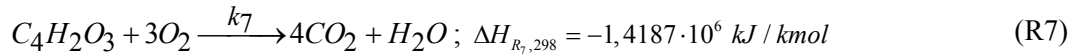
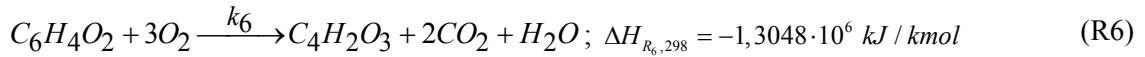
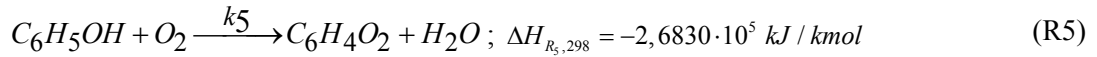
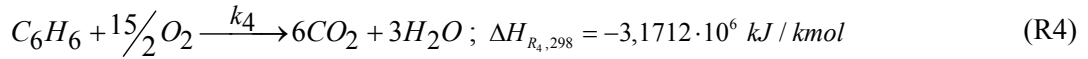
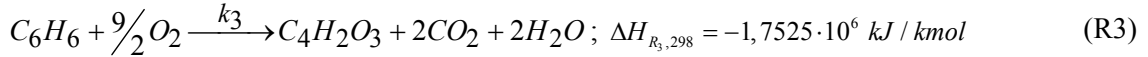
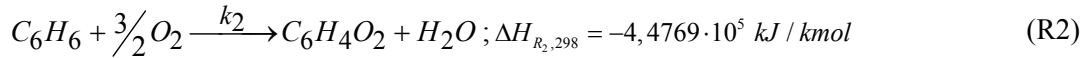
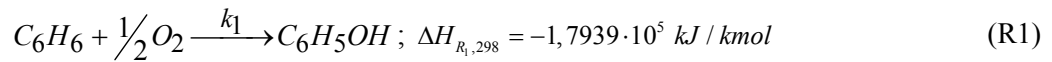
rule. Evaluation of the joint failure probability index P_f takes into account “uncertainty in both parametric safety limits and in maintaining the set-point”⁴, followed by the formulation of the multi-criteria objective function and by derivation of the optimal-Pareto front solution. The next step of Maria and Dan⁴ rule is to determine the Pareto-front of the optimal operating policies “by simultaneously considering the both economic and safety objectives”⁶, and then to select a trade-off optimal solution based on a direct evaluation of the Pareto-front in connection with the runaway boundary plots.

The present paper is aiming at exemplifying an application of this multi-objective optimization methodology consisting in the generation of the optimal Pareto operating policies for the case of an industrial fixed – bed tubular reactor used for the catalytic oxidation of benzene to maleic anhydride in vapour phase, followed by the selection of the most suitable optimal operating policy. The study highlights the importance of using of an extended kinetic model of the process in this final decision.

BENZENE OXIDATION – PROCESS AND REACTOR CHARACTERISTICS

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 good circulation of a molten salt cooling liquid in which the tubes are immersed”.⁹

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, 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 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”¹⁰⁻¹¹, 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 below presented, 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. Model equations are presented in Table 1 in terms of species mass, heat and momentum balances. The Arrhenius type rate constants are given in Table 2.

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 reactor inlet conditions (*i.e.* inlet temperature, benzene concentration, and pressure), as well as the choice of the suitable cooling agent temperature in order to avoid the proximity of critical conditions 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 reactor optimization is the impossibility to recover the benzene in an economical way, leading to imposing some technological constraints during the process optimization.

Table 1

The fixed bed multi-tubular reactor model used for benzene oxidation to maleic anhydride (adapted after Muscalu and Maria¹¹).

| |
|---|
| <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>$j = B, F, Q, MA, CO_2, H_2O, O_2, N_2$</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 reaction index; j = species index</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> |
|---|

Table 1 (continued)

| |
|---|
| <p> $v_{R,i}$ - volumetric specific reaction rate of reaction „i”, $\frac{kmol}{m^3 \cdot s \cdot atm}$; $v_{r,i}$ - mass specific reaction rate of reaction „i”, $\frac{kmol}{kg_{cat} \cdot s \cdot atm}$ (pseudo first-order reaction); ρ_{SC} - density of the catalytic bed, $\frac{kg_{cat}}{m^3_{reactor}}$; $\rho_{sc} = (1 - \varepsilon) \cdot \rho_p$, ρ_p - density of catalyst particle, $\frac{kg_{cat}}{m^3_{cat}}$; ε - void fraction; $v_{i,j}$ - stoichiometric coefficient of species „j” in reaction „i”; p_j - the partial pressure of species „j”, atm; η_j - the total effectiveness factor of the catalyst particle; k_i - pseudo-order 1 kinetic constant of reaction „i”, $\frac{kmol}{kg_{cat} \cdot s \cdot atm}$; $k_i = k_{i_0} \cdot e^{-\frac{E_a}{RT}}$ (values in Table 2); R – universal gas constant, $R = 8.314 \frac{kJ}{kmol \cdot K}$ </p> |
| <p> Heat balance: $\frac{dT}{dz} = \frac{\sum_{i=1}^9 (-\Delta H_{R,i}) v_{r,i} \rho_{SC} S - K_T \pi d_t (T - T_a)}{D_{m,t} \cdot \bar{c}_p}$ T – gas temperature, K; z – reactor length, m; $(-\Delta H_{R,i})$ - heat reaction of reaction „i”, kJ/kmol; K_T - overall heat transfer coefficient, $\frac{W}{m^2 K}$; d_t - pipe diameter, m; T_a - cooling agent temperature, K; $D_{m,t}$ - mass flow rate of the feed mixture, kg/s; \bar{c}_p - average mixture specific heat, $\frac{kJ}{kg_{am} K}$. </p> |
| <p> Momentum balance: $\frac{dp}{dz} = -f \left(\frac{D_{m,t}}{S} \right) \frac{1}{\rho_G d_p} = -f \frac{u^2 \rho_G}{d_p}$ - friction coefficient calculated by Ergun and Hicks formula:¹² $f = \begin{cases} \frac{1-\varepsilon}{\varepsilon^3} \left[1.75 + 150 \frac{1-\varepsilon}{Re_p} \right], & \frac{Re_p}{1-\varepsilon} < 500 \\ 6.8 \frac{(1-\varepsilon)^{1.2}}{\varepsilon^3} Re_p^{-0.2}, & \frac{Re_p}{1-\varepsilon} > 500 \end{cases}$ $\varepsilon = 0.38 + 0.073 \left[1 + \frac{(d_t / d_p - 2)^2}{(d_t / d_p)^2} \right] = \text{bed void fraction}^{12}$ $Re_p = \frac{u \rho_G d_p}{\mu_G}$ - Reynolds number for flow through the catalytic bed. d_p - catalyst particle diameter, m; u - gas flow velocity, m / s ; ρ_G - gas density, $\frac{kg_G}{m^3}$; μ_G - gas viscosity, Pa · s . </p> |

Table 1 (continued)

| |
|---|
| 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: |
| $K_T = \frac{1}{\frac{1}{\alpha_i} \frac{d_{t,ext}}{d_{t,i}} + \frac{\delta_t}{\lambda_t} \frac{d_{t,ext}}{d_{t,i}} + \frac{1}{\alpha_{salt}}}, \frac{W}{m^2 K}; \alpha_i = \frac{\lambda_G Nu_G}{d_p}, \frac{W}{m^2 K}$ |
| α_i - heat transfer partial coefficient gas – reactor pipe wall incorporates the contribution of the heat transfer of both gas and catalyst (conduction and radiation heat transfer) |
| $Nu_{gaz} = \frac{\alpha_i^0 \cdot d_p}{\lambda_G} + 0.33 \cdot Re_p \cdot Pr; \alpha_i^0 = 2.44 \cdot \frac{\lambda_R^0}{d_t^{1.33}}, \frac{W}{m^2 K}$ |
| For temperatures below 400 °C radiation heat transfer can be neglected: |
| $\lambda_R^0 = \lambda_G \left[\varepsilon + (1 - \varepsilon) \cdot \frac{\beta}{\delta_G + \frac{2}{3} \cdot \frac{\lambda_G}{\lambda_s}} \right], \frac{W}{m \cdot K}$ |
| 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: |
| $\delta_G = \delta_{G,2} + (\delta_{G,1} - \delta_{G,2}) \frac{\varepsilon - 0.26}{0.476 - 0.26}$ <p>In this equation, $\delta_{G,1}$, $\delta_{G,2}$ represent values of the δ_G 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)¹⁴</p> |
| 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: $\eta_i = \frac{3}{\Phi_i} \left(\frac{1}{th(\Phi_i)} - \frac{1}{\Phi_i} \right)$ |
| Thiele modulus, Φ_i is evaluated for a pseudo-first order kinetics for large inlet ratios ¹⁴ |
| $\Phi_i = \frac{d_p}{6} \sqrt{\frac{k_i \rho_p \frac{1 - \varepsilon}{\varepsilon} RT}{D_{ef}}}$ |
| Effective diffusion coefficient of the particle is evaluated based on the molecule diffusion coefficient of benzene in air, $D_{ef} \approx \varepsilon D_m / \tau$, calculated using the below equation ¹⁵ |
| $D_m = (1 - y_B) / \sum_{j \neq B} y_j / D_{m,j}; D_{m,j} = 4.3 \times 10^{-7} \frac{T^{1.5}}{p(V_B^{0.33} + V_j^{0.33})^2} \sqrt{\frac{1}{M_B} + \frac{1}{M_j}}, (m^2 s^{-1})$ |
| (surface and Knudsen diffusion were neglected in this case) |
| Ideal plug-flow reactor hypothesis have been applied with concentration, temperature and pressure gradients only in the axial-flow direction, that is $\partial(c_j, T, p) / \partial R_t = 0$ |
| Axial dispersion coefficient is null: $D_z = 0$ (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 |
| One neglects the inter-granular transport resistances (Satterfield criterion). |

Table 2

Kinetics constants for benzene oxidation (given by Ahmad *et al.*¹⁶, and resumed by Lupusor *et al.*¹⁰)

| Kinetic constants, $kmol / (kg_{cat} \cdot h \cdot atm)$ | Frequency factor, $k_{i,o}$ | 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 |

For ensuring a satisfactory accuracy when simulating the severe operation in the vicinity of critical conditions (corresponding to high reaction rates), the reactor model was solved by using a low-order stiff integrator. The analysis starts with determining (by repeated reactor operation simulations) of the most influential parameters for the reactor performance. These parameters, to be further considered in optimization, are split in the parameter vector ϕ , and the control variable vector u , depending on the employed process control scheme. These control parameters are the

following: the cooling agent temperature T_a , the inlet benzene molar fraction $y_{B,o}$, the inlet pressure p_o , and the inlet temperature T_o .

The next step of the sensitivity analysis consists in evaluation of the safety limits for the control variables $u_c(\phi)$ in the parametric space (ϕ) , by using the generalized sensitivity criterion of Morbidelli and Varma⁷ (see Muscalu and Maria¹¹ for the computational details).

Table 3

The nominal operating conditions of the fixed-bed catalytic reactor for benzene oxidation, according to the review of Lupusor *et al.*¹⁰

| Catalyst characteristics: | Value (Observations): |
|---|--------------------------------|
| Chemical composition | V-Cr/support |
| Catalyst density (bulk) ⁴ | $\rho_c = 1260 \text{ kg/m}^3$ |
| Catalyst particle average diameter ⁴ | $d_p = 5 \text{ mm}$ |
| Catalyst porosity | $\varepsilon = 0.48$ |
| Catalyst tortuosity ¹⁹ | $\tau = 2.01$ |
| Reactor characteristics: | |
| Reactor inner diameter | $d_t = 24 \text{ mm}$ |
| Reactor tube thickness | $\delta_t = 2 \text{ mm}$ |
| Reactor length | $L = 4 \text{ m}$ |
| Nominal operating conditions: | |
| Inlet overall pressure | $p_o = 3 \text{ atm}$ |
| Inlet gas temperature | $T_o = 658 \text{ K}$ |
| Feed benzene molar fraction | $y_{B,o} = 0.014$ |
| Fed Benzene flow-rate (per reactor tube) | $F_{B,o} = 0.1 \text{ kg/h}$ |
| Gas superficial velocity (related to void tube) | $u_o = 1.68 \text{ m/s}$ |
| Cooling agent average temperature | $T_a = 653 \text{ K}$ |

An important premise of this study is represented by the uncertainty in evaluating the safety limits of the operating region associated with the random fluctuations ($\delta\phi_j$) in the parameters around the nominal set-point, $\phi_j \pm \delta\phi_j$ used in such runaway boundary assessments. By repeatedly applying the MV-sensitivity method, with successively considering the control variables or influential process parameters at lower and upper bounds, the lower and upper bounds of the critical operating conditions are thus obtained, as represented in Fig. 1 by the dash lines. To reduce the computational effort during the reactor optimization analysis, simple algebraic correlations

$$\hat{T}_{oc} = b_1 + b_2 \times p_o + b_3 \times y_{Bo} + b_4 \times T_a + b_5 \times y_{Bo}^2 + b_6 \times T_a^2; \quad (1)$$

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

$$\ln(\hat{y}_{Boc}) = a_1 + a_2 \times p_o + a_3 \times T_o + a_4 \times T_a + a_5 \times T_o^2 + a_6 \times T_a^2 \quad (3)$$

$$\sigma_{y_{Bo,c}}^2 = \sum_j \left(\frac{\partial y_{Bo,c}}{\partial \phi_j} \right)_{\bar{\phi}}^2 \sigma_{\phi_j}^2 \quad \text{with } \phi = [p_o, T_o, T_a] \quad (4)$$

$$p_{oc} = c_1 + c_2 \times T_o + c_3 \times y_{Bo} + c_4 \times T_a + c_5 \times T_o^2 + c_6 \times y_{Bo}^2 + c_7 \times T_a^2 \quad (5)$$

$$\sigma_{p_{o,c}}^2 = \sum_j \left(\frac{\partial p_{o,c}}{\partial \phi_j} \right)_{\bar{\phi}}^2 \sigma_{\phi_j}^2 \quad \text{with } \phi = [T_o, y_{Bo}, T_a] \quad (6)$$

(where $\bar{\phi}$ = nominal value of the distributed parameter vector; ‘^’ denotes the estimated value by using the algebraic regression model). The vectors of the correlation coefficients (\mathbf{a} , \mathbf{b} and \mathbf{c} in Eqns. 1, 3, and 5) have been estimated by means of

of the control variable safety limits $u_{j,c}(\phi)$ and of their variance $\sigma_{u_{j,c}}^2$ have been derived, “usually of logarithmic or polynomial form”¹⁷, from bringing together all critical curves obtained by means of the MV criterion. By using the following operating parameters (ϕ): the cooling agent temperature T_a , the inlet benzene molar fraction $y_{B,o}$, the inlet pressure p_o , and the inlet temperature T_o , the MV-critical curves of Fig. 1 can be modelled by means of the following “simple nonlinear correlations”:¹⁷

nonlinear regression by using the precisely calculated runaway limits with the MV-criterion (some of them displayed in the Fig. 1 with solid lines).” The following estimate has been obtained”:¹⁷

$$\hat{\mathbf{a}} = [51.903, -0.18076, -0.14902, -0.010771, 0.00011145, 0.0000066824];$$

$$\hat{\mathbf{b}} = [1656.6, -9.4410, -1682.9, -2.4047, -16933, 0.0014749];$$

$$\hat{\mathbf{c}} = [-92.338, 0.023824, -710.15, 0.16799, -0.00018994, 4827.2, -0.00015608].$$

The accuracy of these runaway boundary correlations for the considered control variables $u = [T_o, \ln(y_{Bo}), p_o]$ is very good, the relative error being less than 1-7 %. The use of an extended process kinetic model allows a better representation in the above critical curve correlations of the temperature influence through the considered secondary reaction rate (R1,R2, R4, R5, R7-R9) dependence on the reaction temperature.

FAILURE PROBABILITY INDEX UNDER PARAMETRIC AND SAFETY LIMIT UNCERTAINTY

To include the parametric and safety limit uncertainty in evaluation of the process optimal operating policy, a mathematical formulation of the “probability of the reactor runaway” has been proposed in the form of Maria and Dan⁴:

$$P_f = P_{f1} + P_{f2} \quad (7)$$

The probability P_{f1} expresses the chance that the chosen control variables will overpass the runaway boundaries as a result of the uncertainty in the safe operation limits. For the normally distributed runaway boundaries $u_{j,c}(\phi) \sim N(\bar{u}_{j,c}, \sigma_{u_{j,c}}^2)$, the index reflects the probability that:

$$u_j(\phi) \geq \bar{u}_{j,c}(\phi) \pm \delta u_{j,c}(\phi, \delta\phi), \quad (8)$$

Finally, P_{f1} results by summing $P_{f1,j}$ 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:

$$u_{j,c}(\phi) \leq \bar{u}_j(\phi) \pm \delta u_j(\phi, \delta\phi) \quad (9)$$

(see Muscalu and Maria,¹⁸ and Maria and Dan⁴ for computational details).

The combined failure probability index (7) 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.

RESULTS AND DISCUSSION: PARETO OPTIMAL OPERATING POLICIES WITH RISK MINIMIZATION

In order to obtain the optimal operating policy for the investigated tubular reactor used for benzene oxidation, two antagonistic (contrary) objectives have been simultaneously considered. One of the objectives consists in a maximization of an economic index, for instance the reactor productivity (in the main product), expressed by maximization of the output maleic anhydride G_{MA} molar flow rate (at the reactor length L). To be further compared with the probabilistic safety objective, the chosen G_{MA} objective was normalized by division to its nominal value $G_{MA} = 6.95 \cdot 10^{-4}$ kmol/h (per reactor pipe, at the nominal conditions of Table 3).

The minimum risk in operation objective was implemented in the optimization process through the combined failure probability P_f (including parametric and safety limit uncertainty), as a stochastic term, resulting the following optimization problem:

$$[\hat{u}_o, \hat{\phi}] = \arg \text{Max}[G_{MA}(L) / G_{MA,r}(L)] \wedge \arg \text{Min} [\text{Max } P_f] \quad (10)$$

with the fulfilment of some supplementary imposed technological constraints (of nonlinear inequalities, $g_i \leq 0$ general form), 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 (200 °C, and 500 °C), and reactor inlet gas temperature (205 °C, and 505 °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).

An elegant option to solve the multi-objective optimization problem (10) is to get the set of Pareto optimal solutions, also called Pareto-front for the case of the two contrary objectives. A Pareto solution is one where any improvement in one objective can only take place at the cost of the other objective. For continuous variables, an infinity of Pareto-optimal

solutions can exist, and the final solution choice is subjective and case-dependent.

In the present study, a genetic algorithm (the routine GAMULTIOBJ) implemented in MatlabTM was used to solve the problem (10). Application of this algorithm leads to obtaining of the Pareto-optimal front displayed in the Fig. 1(up-right). An examination of the plotted curve in Fig. 1(up-right) leads to the following conclusions.

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

a) 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 (Fig. 1).

b) To illustrate the set-point choice, two operating solutions have been selected from the Pareto front: the set-point “1” corresponding to a relative maleic anhydride productivity of 1.34 vs. the nominal one (1.00); the point “2” corresponding to a relative maleic anhydride productivity of 1.35. Also, in the Fig. 1 (up-left) it is to observe that the nominal operating conditions “N”, close to the nominal anhydride productivity (i.e. 100% in relative terms) can be chosen anywhere on the Pareto-curve left the point “1”. As expected, the failure probability index P_f increases with the maleic anhydride productivity, without a clear “break-point”. Consequently, the operating solution selection by only using the Pareto-front plot without considering its location in the parametric space is difficult.

c) By analysing the location of the selected three set-points in the parametric space, it is to observe that, while the nominal point “N” (with $P_f \approx 0$) and also the point “1” (with $P_f = 10^{-4}$) are placed in the safety region, the set-point “2” (of $P_f = 0.003$) corresponds to an unsafe operation, the random fluctuations of this running point crossing the confidence region of the safety limit (Fig. 1, down-right).

d) For the studied process, the safety operation limit seems to correspond to a failure probability lower than 2%.

e) The optimal values of the control variables must be kept 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.

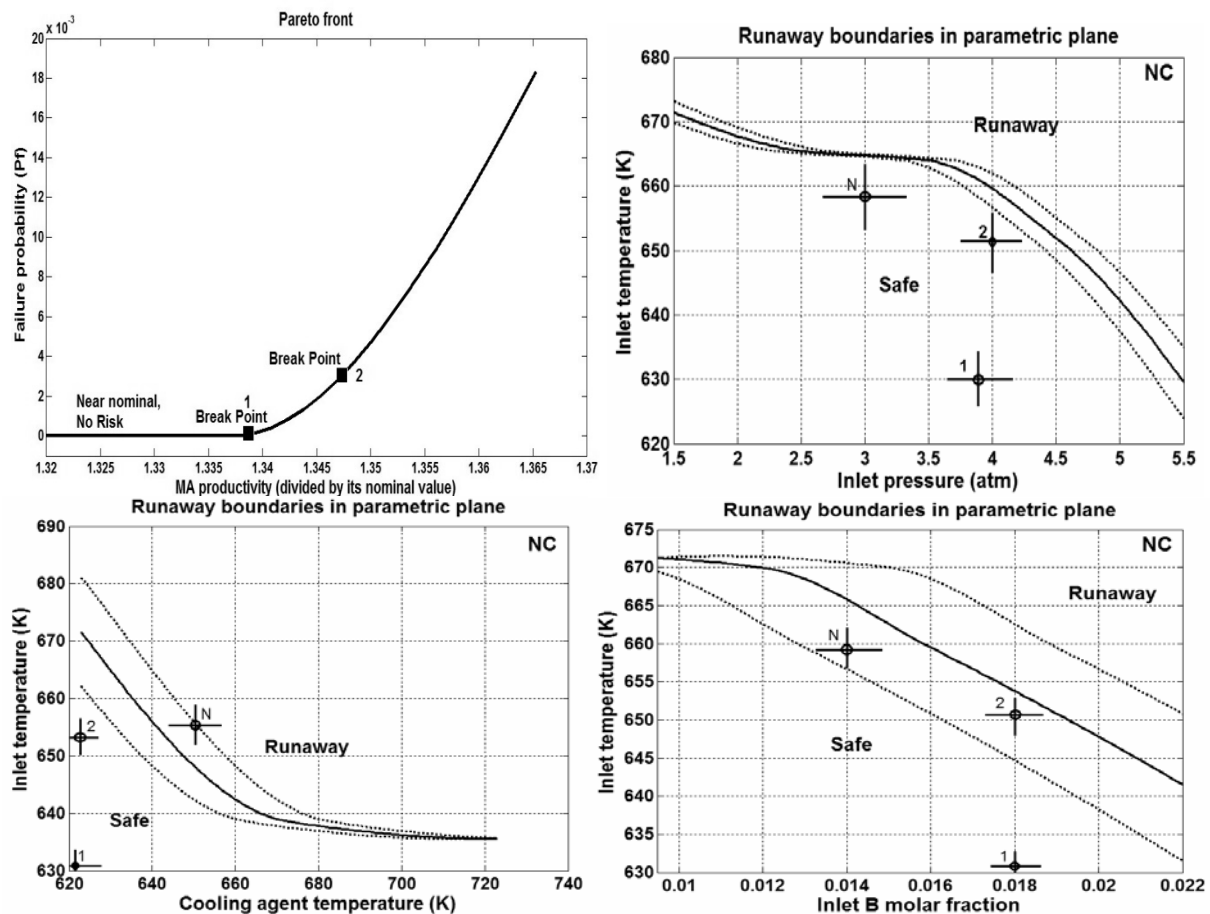


Fig. 1 – Optimal-Pareto operating policies of the tubular reactor (up-left), Location of several optimal-Pareto set-points in the parametric plane plots $[T_o$ vs. p_o] (up-right), $[T_o$ vs. T_a] (down-left), and $[T_o$ vs. $y_{Bo}]$ (down-right) vs. the runaway boundaries (solid lines) and their confidence bands (dash lines).

f) 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).^{9,20}

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 and Dan⁴⁻⁶ 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 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 to 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 0.3-2 % 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^{7,21} on the reactor type/characteristics, process hazard, and of the magnitude of consequences of a reactor runaway.²⁰ For instance, this limit is of 3-4 % for a tubular catalytic reactor used for butane oxidation²¹, or of 3-6 % for a semi-batch reactor used for the catalytic acetoacetylation of pyrrole with diketene in homogeneous liquid phase⁷. 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. A model-based analysis as those presented in this study offers the advantage of a rapid identification of the more desirable Pareto-optimal set-points. As the process model is more detailed (as for the present paper case), as the prediction of the failure probability P_f safety limit is more accurate.

SYMBOLS

| | |
|-------------|--|
| \bar{c}_p | - Mixture average specific heat |
| D_z | - Axia dispersion |
| D_M | - Molar flow rate |
| $D_{m,t}$ | - Mass flow rate of the feed mixture |
| D_m | - Molecule diffusion coefficient of benzene in air |
| D_{ef} | - Effective diffusion coefficient |
| d_p | - Catalyst particle diameter |
| d_t | - Catalytic bed diameter (equal with pipe interior diameter) |
| $d_{t,ext}$ | - Pipe exterior diameter |
| $d_{t,i}$ | - Pipe interior diameter |
| E_a | - Activation energy |
| f | - Friction coefficient |
| G | - Molar flow rate |

| | |
|------------------------------|---|
| ΔH | - Heat of reaction |
| K_T | - Overall heat transfer coefficient |
| k_i | - Pseudo-order 1 kinetic constant of reaction „i” |
| L | - Reactor length |
| M | - Molecular weight |
| Nu_{gaz} | - Nusselt number for gases |
| P_f | - Overall failure probability index ⁶ |
| Pr | - Prandtl number |
| p_j | - Partial pressure of species „j” |
| p | - Overall pressure |
| R | - Universal gas constant |
| Re_p | - Reynolds number for flow through the catalytic bed |
| S | - Cross-sectional area of the reactor pipe |
| T_a | - Cooling agent temperature |
| T | - Temperature |
| t | - Time |
| u_j | - Control variables |
| u | - Gas flow velocity |
| $v_{p,j}$ | - Volumetric specific reaction rate of species „j” |
| $v_{R,i}$ | - Volumetric specific reaction rate of reaction „i”, |
| $v_{r,i}$ | - Mass specific reaction rate of reaction „i” |
| V_{TP} | - Pore total volume |
| V | - Molecular volume |
| y_j | - Molar fractions of chemical species |
| z | - Reactor length |
| Greeks | |
| α | - Heat transfer partial coefficient |
| α_i^0 | - Static contribution of the catalytic bed |
| β | - Coefficient that depends on the particle geometry ($\beta = 0.9 \div 1.0$) |
| δ_G | - A measure of gas film thickness, normalized relative to the particle diameter |
| $\delta_{G,1}, \delta_{G,2}$ | - Values of the δ_G parameter which correspond to the most rarefied packing ($\varepsilon_1 = 0.476$) and most compact packing ($\varepsilon_2 = 0.260$) |
| δ_t | - Reactor wall thickness |
| ε | - Void fraction |
| η_j | - The total effectiveness factor of the catalyst particle |
| λ | - Thermal conductivity |
| λ_G | - Gas thermal conductivity |
| λ_R^0 | - Static contribution of the catalytic bed to the thermal conductivity |
| λ_S | - Catalytic bed thermal conductivity |
| μ_G | - Gas viscosity |
| $v_{i,j}$ | - 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_i | - Thiele modulus |
| Index | |
| * | - Nominal operating conditions |
| c | - Critical conditions |
| i | - Chemical reactions |
| j | - Chemical species |
| o | - Initial conditions |
| t | - Reactor wall |
| Abbreviations | |
| AM, MA | - Maleic anhydride |
| B | - Benzene |
| F | - Phenol |
| Q | - Quinone |
| ^ | - and |

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