PARETO OPTIMAL OPERATING SOLUTIONS FOR A CATALYTIC REACTOR FOR BUTANE OXIDATION BASED ON SAFETY INDICES

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Safe operation of a catalytic reactor remains a challenge, especially when exothermic/hazardous reactions are conducted in the presence of a significant parametric uncertainty. Recently, Maria and Dan ([3], [4]) introduced a new failure probability index that characterizes the operation of chemical reactors with high thermal sensitivity. The current paper exemplifies the application of the risk analysis methodology proposed by Dan and Maria ([2]) to generate the Pareto optimal operating solutions accounting for reactor productivity maximization and probabilistic risk minimization. An example is provided for an industrial fixed-bed tubular reactor, of high thermal sensitivity, used for the catalytic oxidation of butane to maleic anhydride in vapour phase.

Keywords: chemical reactor operation; failure probability; Pareto optimal solutions; safety limits; uncertainty

1. Introduction

Trying to determine the optimal operating policy for a highly sensitive chemical reactor can be a difficult work, especially when the whole process complexity is accounted for together with the parametric uncertainties.

The engineering calculations begin with the development of a mathematical model for the process, by accounting for multiple sources of process uncertainty, such as [1,2]: model inaccuracies in both structure and parameters, due to the used experimental data noise; used simplifying hypotheses to define transport limitations; variability in raw-material purity and catalyst characteristics; measurement errors; the simplificatory hypotheses used to represent the complex kinetics of the main and side reactions, etc. The system dynamic behaviour, including the chemical reaction and heat transfer inside the chemical reactor (batch, semi-batch, or tubular operated continuously) is time varying and of nonlinear characteristics.

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Optimization of the reactor operation involves a large number of constraints, which often are subject to significant uncertainties, as a result of the simplified formulations and due to the uncertainties associated with other process variables. Random disturbances occurring in operating parameters make the accurate implementation of the optimization solution even more complicated.

On the other hand, optimization is always a trade-off process between economic, ecologic, and safety objectives. Recently, Maria and Dan [3] introduced a new “safe operation criterion” based on minimizing the sum of two failure probability indices related to uncertainty in the reactor runaway boundaries and random disturbances in the operating parameters. Based on these theoretical considerations, multiple objective criteria of sustainability can be formulated when deriving the optimal operating solution, by simultaneously considering technological, economic, and safety constraints (minimum failure probability and limited accident consequences).

The classical deterministic approach consists in searching for the optimal nominal values of the input or manipulated / control variables of the chemical reactor (e.g. the feed flow rate, the feeding composition, the cooling agent temperature, overall and partial pressures) that ensure extremization of a suitable objective function (i.e. the performance objective, or ‘cost’ function in financial or engineering terms), by fulfilling the differential mass, heat, and momentum balance equations, and the technological-safety constraints [14,15].

Based on an overall failure probability index recently introduced [1,2], the thermal runaway risk during reactor operation can be quantified, and included in the multi-criteria optimization function.

One alternative to obtain the multi-criteria problem solution is to derive the Pareto front that includes the all-optimal trade-off solutions [2]. The proposed step-by-step methodology by Maria & Dan [1,3,5] includes: derivation of the process and reactor model; formulation of the technological constraints; evaluation of the safety limits for the control variables and their confidence (uncertainty) in the parametric space (based on a generalized sensitivity procedure proposed by Morbidelli-Varma [16]); approximation of the safety limits by means of simple algebraic correlations to facilitate the further reactor optimization; evaluation of the joint failure probability index by considering both parametric and safety limit uncertainty; formulation of the multi-criteria objective function, and derivation of the Pareto front solution. Finally, a trade-off optimal solution is selected by eventually including other criteria in the decisional step.

The present paper is aiming at exemplifying the application of this step-by-step optimization methodology based on the generation of the optimal Pareto operating policies for the case of an industrial fixed – bed tubular reactor used for the catalytic oxidation of butane to maleic anhydride in vapour phase.
2. Butane oxidation – process and reactor characteristics

The industrial pilot reactor approached in the present study has been used by Sharma et al. [6] to study the process kinetics and to determine the feasible operating condition region.

The industrial product resulted in this process is maleic anhydride (MA). In the past, the MA was produced on a large scale mostly by the catalytic oxidation of benzene in vapour phase. Today, MA is obtained rather by catalytic oxidation of n-butane in a fixed-bed or a fluidized-bed tubular reactor [7], in order to avoid the use of the more toxic benzene. The reactions taking place in the reactor tubes are very exothermic, which brings about the need for a cooling agent to remove the generated heat, by circulating it across the tubes filled with catalyst (vanadium-phosphor oxide, of commercial grade).

The gaseous reactants are fed into the reactor together with a large excess of air, needed to maintain a low concentration of butane so as not to exceed the lower flammability limit of the mixture (ca. 3 % mol).

One important characteristic of the reactor is its high thermal sensitivity and involved risk of operation. This is the reason for employing a tight control of the adopted operating conditions. This procedure includes choosing the suitable inlet conditions of the reactor (in the form of mixture inlet temperature, butane concentration and pressure), as well as the suitable temperature of the cooling agent 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 to be considered during reactor optimization is the impossibility to economically recover the butane, leading to some technological constraints to be imposed during the optimization process. As recommended by Sharma et al. [6], the nominal operating conditions need to ensure a high butane conversion (85-90%) and a reasonable MA selectivity (ca. 60-70%), that is ca. 50% yield.

It is also to mention that, beside the reaction product MA, various by-products are also produced from direct and consecutive oxidation reactions, the final product thermodynamically favoured being the CO₂. The kinetic model proposed by Sharma et al. [4] accounts for only three main reactions, of hyperbolic kinetics type, with the stoichiometric coefficients and Arrhenius rate constants specified in Table 1.

To quantitatively characterize the potential hazard of the chemical reactions, some risk indices were calculated. The very exothermic reactions, with enthalpies in the range of 215-2100 kJ mol⁻¹ can lead to significant adiabatic temperature rises $\Delta T_{ad}$ of 120-1150 K, which largely outruns the limit of 50 K for out-of-risk reactions [8]. The reaction violence index $B$ of 6-33 is larger than the threshold $B = 5$ for dangerous reactions [2,8] (see its calculation formula in the
notation list). The low values obtained for the contact time to get the maximum rate under adiabatic conditions (not presented here) indicate the section located near the reactor inlet as being that of the “hot-spot” \( (T_{\text{max}} - T_o) \) and of highest thermal sensitivity to parametric changes. As expected, the most risky reaction is the butane partial oxidation to CO and CO\(_2\), being competitive with the butane transformation to MA, of comparable activation energy and not inhibited by the presence of MA.

Since the thermal sensitivity is one of the most important issues to be considered during reactor optimization, the fixed-bed constructive alternative employing thin tubes [9] is intended to rapidly dissipate the generated heat as fast as possible. The tubes filled with catalyst are immersed in the cooling agent, which rapidly circulates across the tubes, efficiently taking over the reaction heat. Still, the limiting step of the heat transfer is located on the catalyst side, which means that the thermal control needs to address the inlet conditions rather than the cooling agent. The parametric sensitivity regime of this process at the nominal conditions corresponds to slow reactions [10], with an effectiveness factor \( \eta \) for the solid particle very close to 1 (catalyst characteristics are given in Table 1).

For optimization and risk analysis purposes, a relatively simple one-dimensional model was adopted for the tubular reactor, of pseudo-homogeneous type, without radial gradients and of plug-flow fluid circulation [11]. The considered mass, heat and momentum differential balance equations assume a constant temperature of the cooling agent and overall heat transfer coefficient, and the intra-particle mass transfer resistance through an isothermal effectiveness factor. The gas properties are approximated with those of the air due to the butane small fraction (lower than 3% mol.). The industrial tubular reactor has a length \( L = 3 \) m, and an inner diameter \( d_t = 24 \text{ mm} \).

The reactor model has been solved with a low-order stiff integrator to also cope with the operation in the vicinity of critical conditions (exhibiting higher reaction rates). The analysis starts with determining the most influential parameters vs. the process performance, which were found to be the cooling agent absolute temperature \( T_a \), the inlet butane molar fraction \( y_{Bu.o} \), the inlet pressure \( p_o \), and the absolute inlet temperature \( T_o \) (generically denoted by control variable vector \( \phi \)). The next step of the sensitivity analysis consists in evaluating the safety limits for the control variables \( u_c(\phi) \) in the parametric space \( (\phi) \), using the generalized sensitivity criterion of Morbidelli and Varma [13] (see [2] for the computational details).
Pareto optimal operating solutions for a catalytic reactor for butane oxidation based on safety… 39

Table 1

Reaction schema, process kinetics and catalyst characteristics [6]

<table>
<thead>
<tr>
<th>Reaction schema:</th>
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<tbody>
<tr>
<td>(R1): Bu(C₄H₁₀) + 3.5 O₂ → MA(C₄H₂O₃) + 4 W(H₂O)</td>
</tr>
<tr>
<td>(R2): MA(C₄H₂O₃) + p O₂ → (6-2p)CO + (2p-2) CO₂ + W(H₂O)</td>
</tr>
<tr>
<td>(R₃): Bu(C₄H₁₀) + n O₂ → (13-2n)CO + (2n-9) CO₂ + 5 W(H₂O)</td>
</tr>
</tbody>
</table>

Stoichiometric coefficients: n = 5.5; p = 1 (experimentally determined).

<table>
<thead>
<tr>
<th>Reaction rate expressions:</th>
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<tbody>
<tr>
<td>( R_j = k_j P_{Bu} P_{AM} \gamma_j ), ( j = R_1, R_2, R_3 ), (kmol kgcat⁻¹ s⁻¹);</td>
</tr>
<tr>
<td>( k_j = k_{j,r} \exp \left[ -\frac{E_j}{R_T} \left( \frac{1}{T} - \frac{1}{T_r} \right) \right] );</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Kinetic parameters:</th>
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<tr>
<td>( \gamma_1 = (1 + K_2 P_{MA}) ); ( \gamma_2 = (1 + K_2 P_{MA})^2 ); ( \gamma_3 = 1 ).</td>
</tr>
<tr>
<td>( \beta_1 = 0.54; \beta_2 = 0; \beta_3 = 0.54 );</td>
</tr>
<tr>
<td>( \omega_R_1 = \omega_R_3 = 0; \omega_R_2 = 1 );</td>
</tr>
<tr>
<td>( k_{1,r} = 9.6 \cdot 10^{-4}; k_{2,r} = 0.29 \cdot 10^{-3}; k_{3,r} = 0.15 \cdot 10^{-4}, ) (kmol kgcat⁻¹ s⁻¹ atm⁻(β+jω));</td>
</tr>
<tr>
<td>( E_1 = 93100; E_2 = 155000; E_3 = 93100, ) (kJ kmol⁻¹);</td>
</tr>
<tr>
<td>( K_2 = 310 ) (atm⁻¹).</td>
</tr>
</tbody>
</table>

| Catalyst chemical composition: vanadium-phosphor oxide /support |

A very important premise of this study is related to the uncertainty in evaluating the safety limits of the operating region associated to the random fluctuations \( \delta \phi_j \) in the parameters around the nominal set-point, i.e. \( \phi_j \pm \delta \phi_j \).

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 be obtained. To reduce the computational effort during the optimization analysis, simple algebraic correlations of the control variable safety limits \( u_{j,c} (\phi) \) and of their variance \( \sigma_u^2 \) can be derived, usually of logarithmic or polynomial form [5,12], from bringing together all critical curves obtained by means of the MV criterion, that is:

\[
\ln(y_{Bu,o,c}) = a_o + a_1 p_o + a_2 T_o + a_3 T_a + a_4 T_o^2 + a_5 T_a^2; \\
\sigma_{y_{Bu,o,c}}^2 = \sum_j \left( \frac{\partial y_{Bu,o,c}}{\partial \phi_j} \right)^2 \sigma_{\phi_j}^2, \\
\hat{T}_{o,c} = b_o + b_1 p_o + b_2 y_{Bu,o} + b_3 T_a + b_4 y_{Bu,o}^2 + b_5 T_a^2;
\]
\[
\sigma_{T_{o,c}}^2 = \sum_j \left( \frac{\partial T_{o,c}}{\partial \phi_j} \right)^2 \sigma_{\phi_j}^2,
\]
(1)

(where \( \hat{\phi} \) = nominal value of the distributed parameter vector \( \phi = [p_o, T_o, T_a] \), or \( \phi = [p_o, y_{Bu,o}, T_a] \) respectively; "^" denotes the estimated value). The vectors of the correlation coefficients (\( a \) and \( b \) in Eq. 1) have been estimated by means of nonlinear regression and using the precisely calculated runaway limits with the Morbidelli-Varma criterion. The following estimate was obtained:

\[
\hat{a} = [71.867, -0.25262, 8.5038 \times 10^{-2}, -0.27584, -6.8861 \times 10^{-5}, 1.8629 \times 10^{-4}];
\]
\[
\hat{b} = [-1.8799 \times 10^3, -29.046, -1.4257 \times 10^4, 9.9562, 2.6547 \times 10^5, -8.6305 \times 10^{-3}].
\]

3. Failure probability index under parametric and safety limit uncertainty

To include the double parametric and safety limit uncertainty in the process numerical optimization, a mathematical formulation of the runaway risk has been proposed by Maria & Dan [3,4], in the form of:

\[
P_f = P_{f1} + P_{f2}.
\]
(2)

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

\[
u_{j,c}(\phi) \geq \bar{u}_{j,c}(\phi) \pm \delta u_{j,c}(\phi, \delta \phi)
\]
(3)

The runaway probability \( P_{f2} \) appears as a result of random fluctuations in the operating / control variables. 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:

\[
u_{j,c}(\phi) \leq \bar{u}_j(\phi) \pm \delta u_j(\phi, \delta \phi)
\]
(4)

(see Maria and Dan [1-4] for computational details).

The sum (2) of the two risk indices, that is the joint failure probability, represents a synthetic quantitative measure of some operating risks, very useful for multi-objective reactor operation optimization that accounts for various sources of problem uncertainty.
4. Results and Discussion: Pareto Optimal Operation Policies with Risk Minimization

In order to obtain the optimal operating policy for the investigated tubular reactor used for butane oxidation, two competitive objectives need to be considered simultaneously. One of them consists in the maximization of an economic index, e.g. the reactor productivity, the yield or selectivity in the main product MA, etc. This economic goal was formulated here in deterministic terms by maximizing the productivity in MA, expressed by maximization of the output \( G_{MA} \) molar flow rate (at length \( L \)). To be further compared with the probabilistic safety objective, the \( G_{MA} \) was normalized by division to its nominal value \( G_{MA,r}(L) = 6.489\cdot10^{-4} \text{ kmol h}^{-1} \) (per reactor pipe, at the nominal conditions of Table 1).

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

\[
[\hat{u}, \hat{\phi}] = \arg \max \left[ \frac{G_{MA}(L)}{G_{MA,r}(L)} \right] \land \arg \min \left[ \max P_f \right]
\]  

Optimal operation also means that all the technological constraints imposed need to be fulfilled. This problem constraints (formulated as nonlinear inequalities, \( g_i \leq 0 \)) see [5] have been experimentally determined [6], and they reflect several explicit parametric requirements, such as: physical boundaries limits for the operating parameters (e.g. inlet butane concentration below the low flammability and detonation limits), cooling agent characteristics, imposed low limits for butane conversion and MA selectivity, and a maximum level for the hot-spot in the reactor.

In a previous study [2], optimization of the butane oxidation reactor was performed using the weighting function method, attributing a weight of \( w_{AM} = 1 \) to the economic goal, and several adopted weights \( w_{PF} \) for the risk index, corresponding to different levels of risk assumed. The study revealed that a \( P_f = 3-4\% \) value is a reasonable threshold for the assumed operating risk in this case study. The high importance of precisely assessing the safety limits and their confidence region during the safety analysis was also pointed-out, as they present a strongly nonlinear dependency on the operating conditions, being necessary to be re-evaluated during the reactor optimization for every tried solution.
A more elegant option for the multi-objective reactor optimization is to derive the set of Pareto optimal solutions, also called Pareto-front for the case of two adverse objectives. A Pareto solution is one where any improvement in one objective can only take place at the cost of another objective. For continuous variables, an infinity of Pareto-optimal solutions exists, and the final solution choice is subjective and case-dependent.

In the present study, the applied genetic algorithm implemented in Matlab™ leads to obtaining the Pareto optimal front of the previous mathematical formulation (5). An examination of the results plotted in Fig. 1 (A-C) leads to the following conclusions.

i) When two opposite optimization criteria are used, an infinity of Pareto-optimal operating solutions can be found for the tubular reactor, each one corresponding to certain operating parameters \([T_0, P_0, y_{Bu_0}, T_a]\) and criteria trade-off.

ii) To better interpret the Pareto front results, the location of the corresponding solution in the parametric space should be concomitantly investigated. This allows setting the selected reactor operation in the safety region, without crossing the confidence band of the safety limits (Fig. 1 B-C).

iii) To illustrate the set-point choice, three operating solutions have been selected from the Pareto front: the nominal operating point “N”, corresponding to the nominal MA productivity (i.e. 100% in relative terms); the point “1” corresponding to a relative MA productivity of 1.2 vs. the nominal one; the point “2” corresponding to a relative MA productivity of 1.3. As expected, the failure probability index \(P_f\) increases with the MA productivity, without a clear “break-point”. Consequently, the operating solution selection by only using the Pareto-front plot and without considering its location in the parametric space is difficult.
iv) By analysing the selected three running points in the parametric space, it is to observe that, while the nominal point “N” (with $P_f = 0.1$) and also the point “1” (with $P_f = 0.27$) are placed in the safety region, the solution point “2” (of $P_f = 0.45$) corresponds to an unsafe operation, the random fluctuations of this running point crossing the 68% confidence region of the safety limit.

v) For the studied process, the safety operation limit seems to correspond to a failure probability lower than 40%.
vi) The results obtained using the Pareto front are somewhat different from those obtained from optimizing a semi-batch reactor [5]. In the last case, a clear “break-point” in the Pareto front, where a sharp increase in the failure probability occurred at a small rise in the productivity goal, has been identified. Also, the critical $P_f$ indices present lower values, which could be a consequence of a lower exothermicity of the analysed batch reaction (max. 1400 kJ/mol) compared to max. 2100 kJ/mol for the butane oxidation in the tubular reactor.

vii) The optimal 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 obtain a prudent operation of the sensitive tubular reactor.

viii) 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 simulated accident consequences for various failure scenarios).

6. Conclusions

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

The presented model-based methodology to obtain an operating solution for a tubular reactor accounts for an economic, but also for a probabilistic risk index. The procedure 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 accounts 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 focused on more prudent operating conditions, searching for running points where the parameter disturbances do not lead to crossing the confidence region of the safety limits for all the control and operating variables.

Notations

\[ a, b \]

\[ B = \Delta T_{ad}E/(R_g T_o^2) \] - correlation coefficients

- reaction violence index [8]
\( c_j \) - component \( j \) concentration in the gaseous phase

\( \overline{c}_p \) - specific heat of gaseous phase

\( d \) - distance

\( D_{ef} \) - effective diffusivity in the particle

\( D_{m,j} \) - molecular diffusivity of species \( j \)

\( d_p \) - particle diameter

\( d_t \) - inner reactor tube diameter

\( E \) - expected value, or activation energy

\( f, f \) - model function vector, or friction factor

\( g \) - constraint function vector

\( G_m \) - mass flow rate

\( G_{MA} \) - MA molar flow rate

\( (\Delta H) \) - reaction enthalpy

\( k, K \) - rate constants

\( L \) - reactor length

\( M_j \) - molecular mass of species \( j \)

\( \overline{M} \) - average molecular mass of gas phase

\( n \) - stoichiometric coefficient

\( p \) - overall pressure, or stoichiometric coefficient

\( p_j \) - partial pressure of species \( j \)

\( P \) - probability

\( P_f \) - failure probability

\( R_g \) - universal gas constant

\( R \) - chemical reaction rate

\( S_t \) - tubular reactor cross-section

\( T \) - temperature

\( T_o \) - inlet temperature

\( T_a \) - average temperature of the external cooling agent

\( \Delta T_{ad} = (\Delta H) c_{j,o} / (\overline{p} \overline{c}_p) \) - temperature rise under adiabatic conditions

\( u \) - vector of control / manipulated variables
\( U \) - overall heat transfer coefficient (fixed-bed to external cooling agent)
\( v_j \) - molar diffusion volume of species \( j \) at normal boiling point
\( x, x \) - state variable vector, or butane conversion
\( y_j \) - molar fraction of gas component \( j \)
\( w \) - weights in the joint objective function
\( z \) - reactor axial coordinate

**Greeks**
\( \beta, \gamma, \omega \) - kinetic constants in the rate expression (Table 1)
\( \delta \phi \) - random variation of parameter \( \phi \)
\( \varepsilon \) - catalyst porosity
\( \eta \) - effectiveness factor for solid particle
\( \rho_c \) - catalyst density (bulk)
\( \bar{\rho} \) - gas mixture density
\( \rho_p \) - catalyst particle density
\( \sigma \) - standard deviation
\( \sigma^2 \) - variance
\( \tau \) - tortuosity factor of the catalyst particle
\( \Phi \) - optimization objective function, or Thiele modulus
\( \phi \) - operating parameter vector

**Index**
\( a \) - cooling agent
\( ad \) - adiabatic
\( bu \) - butane
\( c \) - critical
\( f \) - failure
\( max \) - maximum
\( o \) - initial (inlet)
\( p \) - particle
\( r \) - reference

**Superscript**
\(-\) - average value
\(^\wedge\) - estimated value
Pareto optimal operating solutions for a catalytic reactor for butane oxidation based on safety… 47

* reference / nominal conditions

Abbreviations
arg - argument of
Bu - butane
MA - maleic anhydride
W - water
~ - distribution

REFERENCES
