Supporting Information for Manuscript: Efficient approach for calculating Pareto boundaries under uncertainties in chemical process design

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Reoptimization scheme

Reoptimization without uncertainties

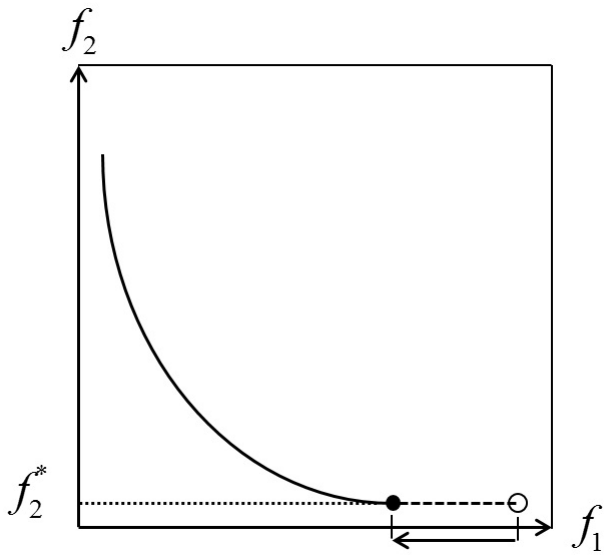

Figure 1: Reoptimization with two objectives, illustrated for the objective f_1 on the horizontal axis. The open circle indicates the point found without reoptimization; the full circle denotes the reoptimized point.

When calculating the nominal Pareto boundary, it can happen that the design parameters for the extreme compromises are not unique, since the optimal value of one objective function does not need to depend on all design parameters. Then, changing those parameters which do not influence that optimal value can only influences the values of the other objectives. Thus, these can be chosen such that the other objectives are as close to their optimal values as possible, while not increasing the value of the optimized objective function above the value found for its minimum. We call this algorithm "reoptimization"and perform it by default after each run for an extreme compromise. It is sketched in figure 1 for the case with two objectives.

Mathematically, this is expressed as follows: Suppose all objective functions $f_{k=1,\ldots,N_{\mathrm{obj}}}$ ($N_{\mathrm{obj}} = 2$ in figure 1) are to be minimized as functions of the free design parameters $x_{i=1,\ldots,N_{\mathrm{var}}}$. We consider the k-th objective f_k ($k = 2$ in Fig. 1). Assume that the minimum for the corresponding extreme

compromise was found as solution of

$$\min_{\mathbf{x}} f_k = f_k^* \tag{1}$$

$$\text{s.t.} \quad \mathbf{g}(\mathbf{x}) \geq 0 \,, \tag{2}$$

where $\mathbf{x} = (x_1, x_2, \ldots, x_{N_{\text{var}}})^T$, and inequality conditions are lumped in a vector $\mathbf{g}$. This leads to a design $\mathbf{x}^*$ and objectives $f_j(\mathbf{x}^*) =: f_j^*$. Then, the reoptimization step consists in

$$\min_{\mathbf{x}} \sum_{j \neq k}^{N_{\text{obj}}} f_j(\mathbf{x}) \tag{3}$$

$$\text{s.t.} \quad f_k(\mathbf{x}) \leq f_k^* \tag{4}$$

$$\mathbf{g}(\mathbf{x}) \geq 0 \,, \tag{5}$$

leading to reoptimized values of the objective functions $f_{j,\text{reopt}}^* \leq f_j^*$. The minimization in Equation (3) is done with respect to all free design parameters, the sum therein carries over all objectives except the k-th. The equal weighting of the objectives in equation (3) is chosen here arbitrarily; for example, if the numerical values of the objectives differ significantly, then, instead of the equal weighting in Equation (3), one could choose more appropriate weights.

After the determination of the reoptimized reference points, the calculation of Pareto points continues as described in.[1]

Reoptimization under uncertainties

A typical situation that occurs when calculating an extreme compromise under uncertainties is sketched in figure 2. For simplicity, suppose the multicriteria problem consists of minimizing two objective functions f_1, f_2, and only two scenarios $\mathbf{p}^{(1)}$, $\mathbf{p}^{(2)}$ are considered. The goal is to find the robust minimum, i.e. the worst minimal case, of the objective functions f_1 and f_2.

For now, let us be interested in the worst minimum of f_1 (i.e. we put a high weight on f_1 and no weight on f_2). The minimum of f_1 for a certain scenario β, $\min_{\mathbf{x}} f_1\left(\mathbf{x}, \mathbf{p}^{(\beta)}\right)$, is named $f_1\left(\mathbf{x}^{(\beta)}, \mathbf{p}^{(\beta)}\right)$

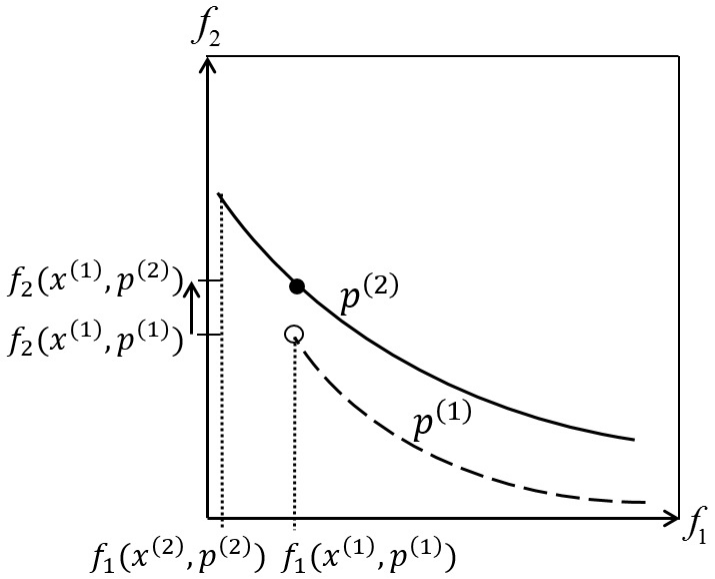

Figure 2: Reoptimization procedure in one objective function for a setting of two objectives and two scenarios in uncertain parameter space. The full (dashed) curves denote the Pareto boundaries for a model parameter fixed to scenario $p^{(2)}$ ($p^{(1)}$). The open circle stands for the reference point found without reoptimization. In the multicriteria setting, the reoptimization procedure is applied, leading to the full circle.

with $\beta \in \{1, 2\}$.

In the example in figure 2 it holds that $f_1\left(\mathbf{x}^{(1)}, \mathbf{p}^{(1)}\right) > f_1\left(\mathbf{x}^{(2)}, \mathbf{p}^{(2)}\right)$, but $f_2\left(\mathbf{x}^{(1)}, \mathbf{p}^{(1)}\right) < f_2\left(\mathbf{x}^{(2)}, \mathbf{p}^{(2)}\right)$. Obviously, the robust, i.e. worst, minimal value for f_1 is $f_1(\mathbf{x}^{(1)}, \mathbf{p}^{(1)})$, cf. the open circle in figure 2. However, in a multi-criteria setting, the objective f_2 has to be considered as well. In scenario $\beta = 2$, the objective function f_2 can take worse values than $f_2(\mathbf{x}^{(1)}, \mathbf{p}^{(1)})$ while the value of f_1 remains at its worst minimal value, cf. the filled circle of scenario 2 in figure 2. This solution is the worst case of the multi-criteria setting.

The corresponding correct value for f_2 is obtained by the following optimization problem:

$$\min_{\mathbf{x}} \max_{\beta=1,2} f_2\left(\mathbf{x}, \mathbf{p}^{(\beta)}\right) \tag{6}$$

$$\text{s.t.} \quad f_1\left(\mathbf{x}, \mathbf{p}^{(\beta)}\right) \leq f_1\left(\mathbf{x}^{(1)}, \mathbf{p}^{(1)}\right) \quad \forall \beta = 1, 2 \tag{7}$$

$$\mathbf{g}\left(\mathbf{x}, \mathbf{p}^{(\beta)}\right) \geq 0 \quad \forall \beta = 1, 2\ . \tag{8}$$

For the sake of completeness, we also note the formulation of the reoptimization problem in the

worst case for an arbitrary number of objectives:

$$\min_{\mathbf{x}} \max_{\beta=1,2} \sum_{j\neq k}^{N_{\mathrm{obj}}} f_j\left(\mathbf{x}, \mathbf{p}^{(\beta)}\right) \tag{9}$$

$$\text{s.t.} \quad f_k\left(\mathbf{x}, \mathbf{p}^{(\beta)}\right) \leq f_k^* \quad \forall \beta = 1, 2 \tag{10}$$

$$\mathbf{g}\left(\mathbf{x}, \mathbf{p}^{(\beta)}\right) \geq 0 \quad \forall \beta = 1, 2 \tag{11}$$

with $f_k^* = \min_{\mathbf{x}} \max_{\beta=1,2} f_k\left(\mathbf{x}, \mathbf{p}^{(\beta)}\right)$ s.t. $f_k\left(\mathbf{x}, \mathbf{p}^{(\beta)}\right) \leq f_k^* \ \forall \beta = 1, 2$. In the sum in (9), all terms are weighted equally. This weighting is arbitrary and can be adjusted if needed.

The best case is treated similarly. Let N_{scen} be the number of scenarios ($N_{\mathrm{scen}} = 2$ in the special case above). Then, the non-reoptimized reference points are obtained from

$$f_k^* = \min_{\mathbf{x}} \min_{\beta=1,\ldots,N_{\mathrm{scen}}} f_k\left(\mathbf{x}, \mathbf{p}^{(\beta)}\right) \tag{12}$$

$$\text{s.t.} \quad \mathbf{g}\left(\mathbf{x}, \mathbf{p}^{(\beta)}\right) \geq 0 \quad \forall \beta = 1, \ldots, N_{\mathrm{scen}} \, . \tag{13}$$

Note that the best case is defined such that the restrictions (13) are fulfilled for each scenario. Similarly, the reoptimization problem reads

$$\min_{\mathbf{x}} \min_{\beta=1,\ldots,N_{\mathrm{scen}}} \sum_{j\neq k}^{N_{\mathrm{obj}}} f_j\left(\mathbf{x}, \mathbf{p}^{(\beta)}\right) \tag{14}$$

$$\text{s.t.} \quad f_k\left(\mathbf{x}, \mathbf{p}^{(\beta)}\right) \leq f_k^* \quad \forall \beta = 1, \ldots, N_{\mathrm{scen}} \tag{15}$$

$$\mathbf{g}\left(\mathbf{x}, \mathbf{p}^{(\beta)}\right) \geq 0 \quad \forall \beta = 1, \ldots, N_{\mathrm{scen}} \, . \tag{16}$$

Here, the situation is again similar to the one sketched in Fig. 1.

One-at-a-time and factorial design sensitivity samplings

In this section, a short account of the one-at-a-time and factorial sampling schemes is given. For simplicity, we assume that the nominal value in the uncertain parameter space is in the origin, and

that the sampling is done on a unit ball with radius 1 around the origin. This situation can always be achieved by a suitable affine transformation.

It is convenient to use a design matrix $\mathbf{D}$ to calculate the N_{scen}-many sample points, where $\mathbf{D}$ is a N_{scen} times N_{unc}-matrix:

$$\mathbf{P} = \mathbf{D} \cdot \mathbb{1}_{N_{\text{unc}} \times N_{\text{unc}}} \,. \tag{17}$$

Here, $\mathbb{1}_{N_{\text{unc}} \times N_{\text{unc}}}$ is the unit matrix in N_{unc} dimensions, and the β-th row of $\mathbf{P}$ contains the sample point $\mathbf{p}^{(\beta)} = [\mathbf{P}]_\beta$. For the one-at-a-time sampling, $N_{\text{scen}} = 2N_{\text{unc}}$, and

$$[\mathbf{D}]_{\beta,k} = \begin{cases} 1, & \beta = k \\ -1, & \beta = k+1 \\ 0, & \text{otherwise} \end{cases} \tag{18}$$

For the full factorial design, $\mathbf{D}$ is a $2^{N_{\text{unc}}} \times N_{\text{unc}}$ matrix which can be calculated as follows:

$$2 \cdot \underbrace{\begin{pmatrix} 0 & \dots & 0 & 0 \\ \vdots & \ddots & & \vdots \\ 1 & \dots & 1 & 1 \end{pmatrix}}_{\text{Binary numbers from 0 to } 2^{N_{\text{unc}}}-1} - \begin{pmatrix} 1 & \dots & 1 \\ \vdots & \ddots & \vdots \\ 1 & \dots & 1 \end{pmatrix} = \begin{pmatrix} -1 & \dots & -1 & -1 \\ \vdots & \ddots & & \vdots \\ 1 & \dots & 1 & 1 \end{pmatrix} . \tag{19}$$

Finally, we mention the design matrix for a reduced factorial design of resolution III, which can be constructed as follows. For N_{unc} uncertain parameters, one first calculates the binary representation of N_{unc}, which is assumed to have length n_b. Similarly to Equation (19), one obtains the 2^{n_b} times n_b base matrix as

$$\underbrace{\begin{pmatrix} 0 & \dots & 0 & 0 \\ \vdots & \ddots & & \vdots \\ 1 & \dots & 1 & 1 \end{pmatrix}}_{\text{Binary numbers from 0 to } 2^{n_b}-1} . \tag{20}$$

Obviously, if $\log_2 N_{\text{unc}} = n$ is integer, then $n_b = n + 1$. From the base matrix (20), one obtains, in analogy to Equation (19), a matrix with entries ± 1. To this matrix, called $\mathbf{D}_a$ here, additional columns have to be added in order to obtain the desired design matrix.

To do this, one looks again at the matrix in (20). Each row defines a mask vector if the sum of the elements within this row is larger than one, for example

$$(1 \quad 1 \quad 0 \ldots 0) \,. \tag{21}$$

For each mask vector, one takes those columns from $\mathbf{D}_a$ that correspond to the non-zero entries within the mask vector and multiplies the elements of these columns point-wise. The resulting columns are appended to $\mathbf{D}_a$, resulting in the 2^{n_b} times N_{unc} design matrix. For the special case $\log_2 N_{\text{unc}} = n$ integer, this design matrix encodes $2N_{\text{unc}}$ many sample points, i.e. $N_{\text{scen}} = 2N_{\text{unc}}$. Otherwise, if $N_{\text{unc}} = 2^n + m$ with $0 < m < 2^n$, the number of sample points is $N_{\text{scen}} = 2^{n+1}$.

The advantage of using a design matrix becomes obvious now: As sensitivity measure $S_{j,k}^{(\alpha)}$, averaged difference quotients are defined:

$$\mathbf{s}_j^{(\alpha)} = c\mathbf{D}^T\mathbf{f}_j^{(\alpha)} \,. \tag{22}$$

Now $\mathbf{D}^T$ is a $N_{\text{unc}} \times N_{\text{scen}}$-matrix, and $\mathbf{f}_j^{(\alpha)} := (f_j(\mathbf{x}^{(\alpha)}, \mathbf{p}^{(1)}), \ldots, f_j(\mathbf{x}^{(\alpha)}, \mathbf{p}^{(N_{\text{scen}})}))^T$ contains the N_{scen}-many samples of the j-th objective. Thus $S_{j,k}^{(\alpha)} = \left[\mathbf{s}_j^{(\alpha)}\right]_k$. The normalization constant c is

$$c = \begin{cases} 1, & \text{one} - \text{at} - \text{a} - \text{time} \\ 2^{N_{\text{unc}}-1}, & \text{full factorial design} \\ N_{\text{unc}}/2, & \text{reduced factorial design} \end{cases}$$

Generalizations of these sensitivity measures are possible and may be adequate in different contexts. For example, one can scale the $S_{j,k}^{(\alpha)}$ by some distance measure of the sample points for each parameter p_k. Furthermore, it can be interesting to calculate the uncertainty with respect to the no-

minal point, that is, to take the deviation from the nominal point directly into account. An example to model this is given in.[2]

Thermo-physical properties and sensitivity settings

In the following, some additional information on the thermodynamic model parameters is given. In Table 1 the boiling temperatures at specific pressures, the enthalpy of vaporization and the molar mass of the components are listed.

Table 1: Normal boiling temperature (1 bar), enthalpy of vaporization (Δh_V) and molar mass (M) of the pure substances

	t (1 bar) [°C]	Δh_V [kJ/kg]	M [g/mol]d
methyl formate	31.44	462.1	60.1
Methanol	64.27	1173.4	32.0

In table 2 the parameters for the used NRTL model are given.

Table 2: NRTL- parameter used in CHEMASIM; accuracy: 1044 measured points, Standard deviation: 2.041

	A_{12}	B_{12}	A_{21}	B_{21}	C_{12}	D_{12}
MF-MEOH	0.9805	-32.60	-2.233	860.3	0.3	0
MEOH-WA	6.304	-1891.9	3.940	1337.6	0.3	0

The sampling points for the sensitivity analysis using a factorial design are listed below. Each of them represents one scenario. **N** is the center of the cube, standing for the nominal settings.

$$\mathbf{N} := \begin{pmatrix} 8000 \\ 0.2 \\ 1.3420 \end{pmatrix}$$

$$\mathbf{U}_{C1} := \begin{pmatrix} 7960 \\ 0.18 \\ 1.2078 \end{pmatrix} \quad \mathbf{U}_{C2} := \begin{pmatrix} 7960 \\ 0.18 \\ 1.4762 \end{pmatrix} \quad \mathbf{U}_{C3} := \begin{pmatrix} 8040 \\ 0.18 \\ 1.2078 \end{pmatrix} \quad \mathbf{U}_{C4} := \begin{pmatrix} 8040 \\ 0.18 \\ 1.4762 \end{pmatrix}$$

$$\mathbf{U}_{C5} := \begin{pmatrix} 7960 \\ 0.22 \\ 1.2078 \end{pmatrix} \quad \mathbf{U}_{C6} := \begin{pmatrix} 7960 \\ 0.22 \\ 1.4762 \end{pmatrix} \quad \mathbf{U}_{C7} := \begin{pmatrix} 8040 \\ 0.22 \\ 1.2078 \end{pmatrix} \quad \mathbf{U}_{C8} := \begin{pmatrix} 8040 \\ 0.22 \\ 1.4762 \end{pmatrix}$$

The influence of the perturbation in the activity coefficient for both components of the reactive system MF-MeOH in infinite dilution ($\gamma^{\infty,P}_{\text{MF-MeOH}}$ and $\gamma^{\infty,P}_{\text{MeOH-MF}}$) on the NQ curve is shown in the following figure.

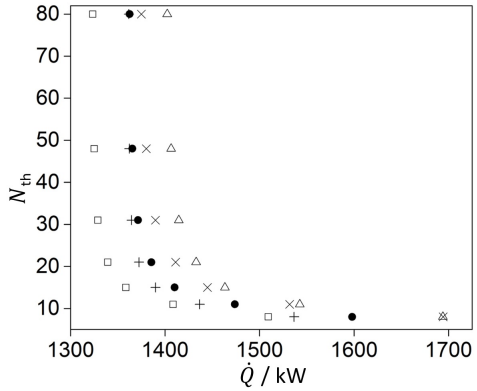

Figure 3: Influence of $\gamma^{\infty,P}_{\text{MF-MeOH}}$ (□: 0.9, △: 1.1) and $\gamma^{\infty,P}_{\text{MeOH-MF}}$ (+:0.9, ×:1.1). ●: Nominal case.

It can be seen that the effect of $\gamma^{\infty,P}_{\text{MF-MeOH}}$ is larger than that of $\gamma^{\infty,P}_{\text{MeOH-MF}}$, especially for lower values of $\dot{Q}$.

References

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(2) Bortz, M.; Maag, V.; Schwientek, J.; Benfer, R.; Böttcher, R.; Burger, J.; von Harbou, E.; Asprion, N.; Küfer, K.-H.; Hasse, H. Decision Support by Multicriteria Optimization in Process Development: An Integrated Approach for Robust Planning and Design of Plant Experiments. *Comp. Aided Chem. Eng.* **2015**, *37*, 2063–2068.