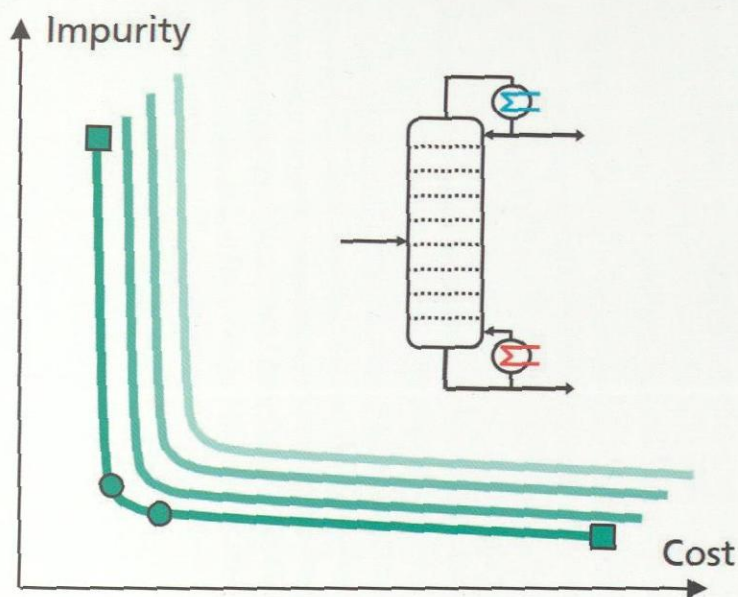


Michael Bortz

Pareto Optimization and Decision Making in Process Design



Fraunhofer-Institut für
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Pareto Optimization and Decision Making in Process Design

Dem Fachbereich Maschinenbau und Verfahrenstechnik
der Technischen Universität Kaiserslautern
zur Erlangung der

Lehrbefugnis

auf dem Gebiet der mathematischen Modellierung und Simulation in der
Verfahrenstechnik vorgelegte

Habilitationsschrift

von

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aus Dortmund

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Bonus vir semper tiro.

Martial

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Abstract

Model-based process design makes it possible to obtain insight into design alternatives. Since the number of alternatives can be huge and the evaluation criteria to sort out the most relevant alternatives are conflicting, identifying the most favorable ones can be a formidable task. In this work, it is demonstrated that adaptive Pareto optimization techniques can be used to address this task efficiently and reliably. Once a sufficient number of Pareto points that represents the Pareto boundary to a required accuracy is found, an interactive decision support scheme allows to explore correlations and trade-offs between the different quality criteria. This work describes the introduction and realization of this scheme in industrially relevant contexts. Examples for significant process improvements that were achieved are given.

Furthermore, since mathematical optimization requires many model evaluations, the challenge of shaping the model structure such that it meshes with the optimization requirements is addressed. Therefore, structural reformulations of the equilibrium stage model and asymptotic simplifications are proposed. Additionally, a hybrid modeling approach is presented in which physical models are augmented with statistical elements in order to obtain models of entire chemical processes suitable for optimization.

Inimately related to data-driven model approaches is the task to estimate reliability of model predictions and, if necessary, to plan new experiments in order to obtain additional data. The optimal design of experiments is put in a multicriteria optimization context as well in this work.

This is a cumulative thesis which is based on twelve scientific publications. An overview of this work is given and the original papers are included in the appendix.

Kurzfassung

Modellbasiertes Prozessdesign ist ein wichtiges Werkzeug, um einen Überblick über mögliche Designalternativen zu gewinnen. Da es eine große Anzahl von Alternativen geben kann und die Qualitätskriterien, mit denen die relevantesten erkannt werden, miteinander im Konflikt stehen, ist die Aufgabe, die besten Alternativen zu finden, kaum zu unterschätzen. In dieser Arbeit wird demonstriert, dass der Einsatz von adaptiver Paretooptimierung diese Aufgabe effizient und verlässlich löst. Sind einmal hinreichend viele Paretopunkte, die die Paretogrenze mit der geforderten Genauigkeit darstellen, gefunden, erlaubt ein interaktives Entscheidungsunterstützungssystem, Korrelationen und Trade-Offs zwischen verschiedenen Qualitätskriterien zu explorieren. Diese Arbeit beschreibt die Einführung und die Realisierung dieses Zugangs in industriell relevanten Kontexten. Beispiele, wo erhebliche Prozessverbesserungen erreicht werden konnten, werden genannt.

Da mathematische Optimierung viele Modellauswertungen erfordert, wird darüber hinaus die Herausforderung adressiert, die Modellstruktur in Einklang zu bringen mit den Optimierungserfordernissen. Sowohl strukturelle Umformulierungen des Gleichgewichtsstufenmodells und asymptotische Vereinfachungen werden diskutiert. Darüber hinaus wird ein Modellierungszugang vorgestellt, in dem physikalische Modelle mit statistischen Elementen ergänzt werden, um so Modelle für chemische Gesamtprozesse zu erhalten.

Eng verbunden mit datengetriebenen Modellansätzen ist die Aufgabe, die Modellzuverlässigkeit von Modellvorhersagen zu beurteilen und, falls nötig, neue Experimente zu planen, um zusätzliche Daten aufzunehmen. Die optimale Versuchsplanung wird in dieser Arbeit ebenfalls in einen mehrkriteriellen Kontext gestellt.

Diese Schrift ist kumulativ und basiert auf zwölf wissenschaftlichen Veröffentlichungen. Darüber wird ein Überblick gegeben, wobei die Originalveröffentlichungen im Anhang enthalten sind.

Kurzfassung

Die vorliegende Arbeit ist eine Untersuchung über die Bedeutung der Sprache für die Entwicklung des Denkens. Sie ist in drei Teile gegliedert. Der erste Teil ist eine Einführung in die Problematik der Sprache und des Denkens. Der zweite Teil ist eine Darstellung der verschiedenen Theorien über die Sprache und das Denken. Der dritte Teil ist eine kritische Analyse der verschiedenen Theorien.

Die Sprache ist ein zentrales Element des menschlichen Lebens. Sie ist ein Mittel zur Kommunikation und zur Übermittlung von Wissen. Die Sprache ist auch ein Mittel zur Darstellung der Welt und zur Entwicklung des Denkens. Die Sprache ist ein Spiegelbild der Welt und des Denkens. Die Sprache ist ein Werkzeug zur Erforschung der Welt und des Denkens.

Die Entwicklung des Denkens ist ein Prozess, der von der Sprache beeinflusst wird. Die Sprache ist ein Mittel zur Darstellung der Welt und zur Entwicklung des Denkens. Die Sprache ist ein Spiegelbild der Welt und des Denkens. Die Sprache ist ein Werkzeug zur Erforschung der Welt und des Denkens.

Die verschiedenen Theorien über die Sprache und das Denken sind in drei Hauptgruppen unterteilt. Die erste Gruppe ist die Theorie der Sprache als Werkzeug. Die zweite Gruppe ist die Theorie der Sprache als Spiegelbild. Die dritte Gruppe ist die Theorie der Sprache als Werkzeug und Spiegelbild.

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1 Motivation

The permanent struggle for improvement of actual conditions by scientific and technical means has been a strong driving force in the evolution of mankind. The comprehension of physical laws, skilful craftsmanship and the eager belief in being able to make inventions work were prerequisites for letting industrial revolution take off. Mechanized factories allowed the production of textiles at a quantity and quality impossible until then. A soaring demand lead to the installation of growing production facilities. Society had to learn to deal with the down-sides as well: Mass poverty, nearly unlimited working hours for the employees and life-threatening working conditions.

Today, roughly 250 years after James Watt developed his steam engine, there is a generally accepted understanding that the constant improvement of living conditions and the increase in economic wealth comes with serious global trade-offs like impact on the earth's climate, exploitation of limited natural resources and increasing social imbalances. The ideal solution - wealth for everyone at no cost - does not seem attainable, at least not with today's technical means. The earth's societies are confronted with the task to choose among possible future alternatives the one that they think guarantees the wealth they wish while at the same time not compromising the living conditions on the planet. The Paris agreement to limit global warming to below 2 °C compared to the pre-industrial level is an example.

The essential key ingredient for such a compromise is the knowledge of how different factors - like the quality and quantity of fossil fuels used or the increasing demand *for food of an increasing population* - contribute to the response, which in this case is the global warming. Therefore, models have been built, highly complex models of the earth's climate, on different scales and including most diverse phenomena. Huge amount of climate data from all over the world have been and are being used to find an adequate parametrization of these models to be able to forecast the global warming over the next decades.

The scope of this work is much more modest, but carries all of the above mentioned elements in it: It describes model-based methods to generate alternatives for process designs in order to support the decision on which design is eventually chosen. Furthermore, examples for practical implementations of the method are given.

Obviously, the practical relevance of the alternatives depends on the quality of the model and on the strategy to generate the alternatives. We first comment on the strategy to generate the alternatives.

The key strategy in this work consists in an adaptive calculation of Pareto points. This means that first of all, the problem of choosing alternatives is viewed as a mathematical optimization problem. Therefore, not only a model is needed that is able to make predictions for outcomes not observed so far, but also the model must be manageable computationally, for optimization runs usually require a large number of model evaluations.

At this point, a more precise wording is introduced, according to [Bortz et al., 2014]: A “criterion” is henceforth called an objective, and what was called an “alternative” consists of a set of design variables in design space, and of a set of objective values in decision space. An “alternative” will also be called a “solution” in the following. An exemplary sketch is shown in Figure 1.

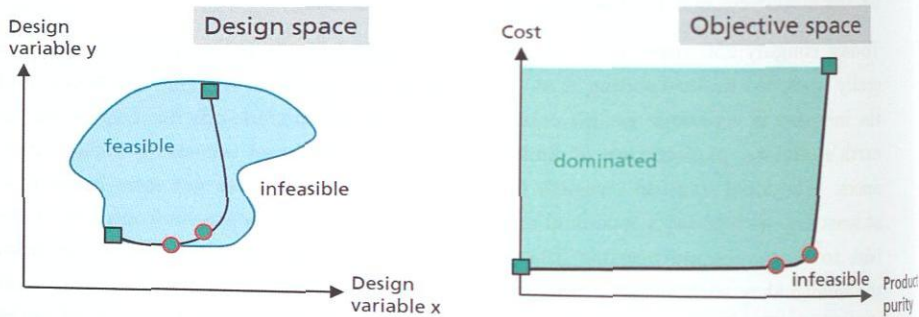


Figure 1: Exemplary view on a two-dimensional objective space and a two-dimensional design space. The Pareto points are located in those regions of the Pareto boundary where the curvature is large. In design space, the feasible range is sketched as well; however, it is generally not necessary to explore it entirely.

Apart from the model, a description of the set of allowed design variables is required, as well as objective functions. Generally, for each process, these objective functions can be grouped into cost and gain functions, which are in conflict. The methods presented in this work suggest alternatives that are Pareto-optimal, meaning that an improvement in one criterion comes with a worsening in at least one other criterion.

From a practical perspective, these are the most interesting alternatives. Any alternative that is feasible, but not Pareto-optimal still has the potential of being improved in all objectives simultaneously, which will be done. Thus the focus of the process engineer

does not need to be on all possible alternatives, but only on the Pareto-optimal ones - which usually is only a tiny subset compared to all feasible alternatives. From a mathematical perspective, the restriction to Pareto optimal alternatives means that one wants to sample a hypersurface in the space of evaluation criteria. In such a situation, adaptive schemes are available [Hernández, 2012, Teichert, 2013], taking care that Pareto points are calculated in regions of the hypersurface where the curvature is large. In flat regions, with small curvature, linear interpolation can be carried out between Pareto points far apart, with a small known error.

In this context, the quality of the model, which was identified above as being responsible for the practical relevance of the generated alternatives, can be viewed as one criteria among many others. Actually, there is no need in having a model which makes perfect predictions in all circumstances. Such a model exists in theory (Schrödinger's equation together with Boltzmann's notion of the entropy), but is computationally intractable except for special situations. What is interesting for the engineer are reliable model predictions for the Pareto optimal alternatives, especially for the most relevant ones. It will be described later on how reliability of a model can be cast into criteria for the optimization, and how to deal with model uncertainties.

The methods described here to generate Pareto optimal alternatives go in hand with the possibility to compare these solutions. In this work, supporting decisions means enabling the ones making the decisions to compare Pareto optimal alternatives interactively, in real time. This involves highly responsive graphical user-interfaces and allows it to distinguish regions with relatively small trade-offs between the criteria from those where the trade-off is significant.

Apart from the algorithmic implementation of the methods in a process engineering context, their integration into real-world industrial design workflows is a major achievement of the work presented here. Thus this work also includes the software development of decision support systems that run stable in industrial applications, being available to several hundred process engineers each day, within the specific software environment of industrial companies. This goes beyond applied mathematics and can be viewed as an example how innovation triggered by a synthesis of methods and applications can lead to significant improvements.

The remainder of this work is organized as follows: In the next section, the scope of the methods included here is sketched. Section three contains a brief account on hybrid modelling as one ingredient to arrive at models suitable for Pareto optimization. The final section of this summary consists of an outlook to future work. A reprint of the author's most important publications dealing with Pareto optimization and decision making in process design can be found in the appendix.

Only few literature references are given in this main text; for further reading, the reader generally is referred to the original papers reprinted in the appendix.

2 Conceptual Scope of Methods and Algorithmic Implementation

Model-based process design is a multicriteria problem with different cost and gain functions as motivated in the preceding section. Additionally, process design is a multiscale problem, ranging from processes on a laboratory scale over miniplants up to worldscale production processes, that, again on a larger scale, are interconnected to form global supply chains. On each scale, not only the design itself is of interest, but also the model which it is built upon. Each scale has its specific design and objective spaces, and with those also specific demands on the decision support system. These different scales are summarized in Figure 2.

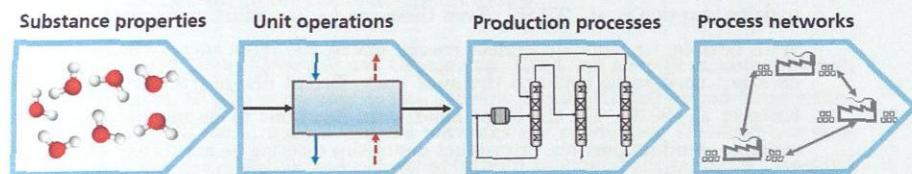


Figure 2: Scales of process design. On the left hand side, the context of the models is given; on the right-hand side, the scale of their industrial application.

In the following, the contributions of this work to the different scales in process design are summarized.

- **Substance properties:** The goal of substance property modelling is the prediction of macroscopic observables. Technically, this is achieved either by molecular models or by phenomenological models. Both model types depend on parameters that are chosen such that the values for the predicted macroscopic variables agree as closely as possible with the measured ones. Mathematically, this task constitutes a multiple output regression problem: A sum of weighted least squares containing the differences between different model predictions and the corresponding measurements has to be minimized subject to the model constraints. This model constraints make the regression problem multicriteria [Forte et al., 2017a],

which can lead to competing objectives given by the different contributions to the *weighted sum of least squares*. Thus, instead of dealing with one fixed model, it seems advantageous to describe substances by a model library, suited to predict different behaviours. Although this is not the main contribution of this work, it shows that the concept of Pareto-optimization is helpful also in this context. The characterization of substance properties is mostly done under laboratory conditions, with advanced measurement equipment.

- **Unit operations and production processes:** These are typically modelled within flowsheet simulators. The most common model for describing separation processes is the stationary equilibrium stage model, based on the MESH-equations encoding mass and enthalpy balances, phase equilibrium and closure conditions. Due to the phase equilibrium conditions, these equations form a nonlinear system. Each unit operation is modelled by a sequence of one or several equilibrium stages. The model of a complete production plant is then a network of unit operations. This set-up can be extended to different model approaches, like the inclusion of transport phenomena to describe non-equilibrium conditions, or time-dependent hold-ups to cast dynamic process modelling. On the one hand, cost functions to be minimized are typically OPEX and CAPEX, but also the ecological footprint or toxicity [Asprion et al., 2015b]. Even these can be in conflict amongst themselves: With flexible, i.e. time-dependent energy prices, the most energy-efficient design does not need to be equal to the most cost-efficient design [Nowak et al., 2015, Krieg et al., 2016]. On the other hand, gain functions to be maximized are, for example, product purities, or product quantities meeting as accurately as possible the demand [Burger et al., 2014]. These are in conflict with the cost functions, but also among themselves. For example, it will in general be difficult to assert the highest product qualities for different product quantities. Model-based optimization of unit operations and production processes is done either for existing production processes [von Kurnatowski et al., 2017] or for miniplants where the feasibility and the scale-up of processes is investigated.
- **Process networks:** Final products, e.g. for the consumer market, involve many special ingredients from different specialized companies, that must be processed according to a certain order under certain conditions. Scheduling the production of single sites and operating supply chains involving several production sites are multicriteria problems as well: Here, the cost functions include expenses for storage and delivery facilities, whereas the gain functions are a high adherence to delivery dates and a high availability of the products, irrespective of varying demand or availability of educts. Mathematical optimization techniques for this problem, which under certain conditions can be formulated as a linear optimization prob-

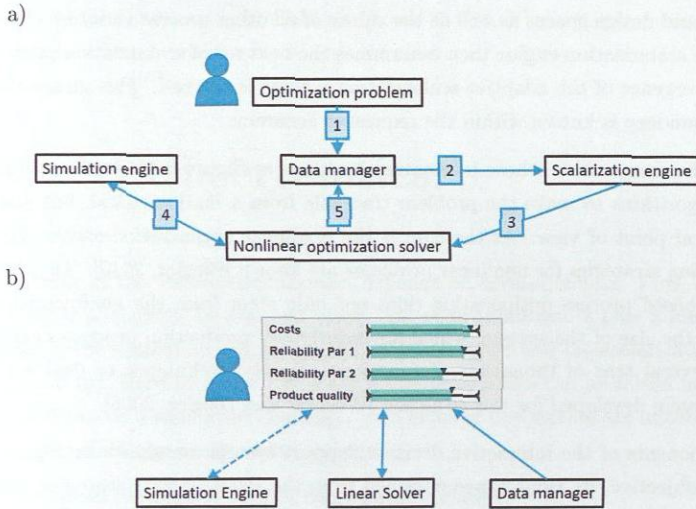


Figure 3: a) Sketch of software architecture of Pareto optimization and decision support tools. The numbers at the arrows are explained in the main text. b) Components of the decision support system.

lem, are well known [Birewar and Grossmann, 1989] and are still explored further, *for example, to take uncertainties into account* [Guillen-Gosalbez and Grossmann, 2009]. In this work, neither process networks nor production schedules are considered, but the scientific and industrial interest to extend the methods presented in this work to these questions as well is high.

The algorithmic implementation of the Pareto optimization and decision support tools was done according to the scheme visualized in Figure 3 a), cf. also [von Kurnatowski et al., 2017]. The optimization problem consisting of objectives, design variables and constraints is defined by the user, cf. arrow number 1 in Figure 3a). Additionally, the user defines the accuracy to which the Pareto boundary should be resolved. This accuracy measures the error made when linearly interpolating between Pareto points compared to moving on the true Pareto boundary. A data manager passes this problem to the scalarization engine (arrow number 2) which transforms the problem according to an adaptive scalarization scheme to a single criteria optimization problem with a set of scalarization parameters. A nonlinear optimization solver receives this optimization problem from the scalarization engine (arrow number 3) and then asks the simulation engine - in our case the flowsheet simulator - for function and gradient information until convergence is reached, cf. arrow number 4. The result is then given back to the data manager (arrow number 5) which stores the Pareto point - that is, the coordinates in

objective and design spaces as well as the values of all other process variables - in a data base. The scalarization engine then determines the next set of scalarization parameters, until convergence of the adaptive scalarization scheme is reached. This means that the Pareto boundary is known within the requested accuracy.

Each of the components whose interaction is shown in Figure 3 a) implements sophisticated algorithms to make the problem tractable from a mathematical, but also from a numerical point of view. At the core is the nonlinear optimization solver. Different optimization strategies for nonlinear problems are known [Biegler, 2010]. The challenge of model-based process optimization does not only stem from the nonlinearities, but also from the size of the system, which for industrially production processes can easily contain several tens of thousands of equations. Special techniques to deal with this situation were developed for this situation [Wächter and Biegler, 2006].

The components of the interactive decision support system are shown in Figure 3 b). For each objective, its value range obtained from the Pareto points stored in the data manager is made available. The user can then navigate on the Pareto boundary in objective space by dragging interactive user elements like sliders. This triggers the solution of a linear optimization problem, which updates the positions of the other sliders on the convex hull of the Pareto points. All other quantities like design and further process variables are updated during the navigation process as well in real time. Details are given in [Bortz et al., 2014].

A navigated solution is exact only within the approximation accuracy of the Pareto boundary. Thus it is also possible to trigger the run of a rigorous simulation for a given navigated solution, as indicated by the dashed arrow in Figure 3. This can be a single run, taking as design variables their navigated values, or also an optimization run, in which a Pareto-optimal solution close to the navigated solution is sought for.

3 Model Uncertainties

The reliability of the Pareto optimization depends on several factors: First of all, the model itself is a concern. In a second place, also algorithmic issues play a role, like the accuracies of the simulation engine, the optimization solver and the scalarization engine (cf. Figure 3 b)). Here we assume that the algorithmic issues can be solved in principle - which still can be a significant challenge. The focus of this section are uncertainties in the model itself. These can have two origins:

- The model parameters are not chosen appropriately.
- The model structure is inadequate or insufficient. This can be for example the case if the equilibrium stage model is used to describe a non-equilibrium situation like a narrow-boiling mixture.

In this work, uncertain model parameters are dealt with by scenario generation techniques. Different such techniques have been analysed and implemented to represent those uncertainties, among them deterministic and stochastic ones [Asprion et al., 2015a, Bortz et al., 2015b, Asprion et al., 2017a, Bortz et al., 2017]. In each step of the optimization solver, i.e. for fixed design variables, the objective functions for the different scenarios are calculated. A measure for their dispersion can then be obtained and can also be included into the Pareto optimization as one objective function. Alternatively, the worst case of all objectives among all scenarios can be taken as objective, which is robust in the sense that under fluctuations of the uncertain model parameters, no worse value in any objective will be obtained.

The analysis of the impact of different model structures has also been carried out [Asprion et al., 2017a]. This is done by Pareto patches, a concept that also provided useful when comparing different process designs according to different criteria [Burger et al., 2014]. This means that one could, for example, perform Pareto optimization for different models separately, where the objective space consists of distance measures between *measured and simulated quantities*, and the design space is spanned by the model parameters. It would then become transparent which model reproduces which measured data better. Furthermore, Pareto optimization of process designs can be done using different models, again resulting in different Pareto patches. The distance between the patches is then a measure for the uncertainty resulting from the model choice.

If the model uncertainties are too big, and one has the opportunity to record data from additional measurements, then these measurements should be made under such conditions that the information that they provide in order to reduce the model uncertainties is maximal. This is the well-known task of model-based design of experiments. Different information measures are known in the literature (see, for example, [Franceschini and Macchietto, 2008] and references therein), and maximizing them amounts to a nonlinear optimization problem. When it comes to models of chemical process designs, for example of miniplants or production processes, additional process-related criteria, like the product purity or product streams, are important as well. The key idea presented in [Bortz et al., 2015b, Forte et al., 2017b], [Bortz et al., 2016] is to use Pareto optimization maximize both selected sensitivities and to meet the process-related criteria as well. This Pareto optimization is done based on a single design for each Pareto point. Then a user-defined restriction using the decision support system shown in Figure 3 b) is possible resulting in lower and upper bounds for each design parameter. These bounds are then used to calculate a model-based experimental plan by maximizing a scalar measure of the Fisher matrix, now as a function of as many designs as experiments are to be carried out.

In [Bortz et al., 2018], the prediction errors in objective functions resulting from a previous model adjustment based on least squares estimators are used as the model-related objectives in the Pareto optimization. These prediction errors are well-suited in this context: They carry both the information about the previous experiments in them, as well as the design point at which the objective functions are actually calculated.

4 Industrial Applications

Adaptive Pareto optimization and interactive decision support as presented in this work was applied to the design of miniplants [Bortz et al., 2015b, Forte et al., 2017b] and worldscale production plants [Burger et al., 2014, von Kurnatowski et al., 2017] in chemical industry. For reasons of confidentiality, gains in energy efficiency and product quality due to the application of Pareto optimization and decision support cannot be disclosed in all cases. However, the article [von Kurnatowski et al., 2017] shows that energy savings above 10 % are possible even for existing chemical production processes by a redesign.

Considerable energy savings were achieved by adjusting the design and operation of public drinking water suppliers [Nowak et al., 2015, Krieg et al., 2016]. Here, the process consists of the delivery of drinking water, starting from the water reservoirs, to the waterworks and water treatment plants, up to the water storage tanks and the consumers. The objectives are to minimize CAPEX and OPEX, consisting of:

- i) The invest of buying and installing pumps.
- ii) The invest of installing water storage tanks and the operational cost to maintain them.
- iii) The cost to run the pumps, consisting of the price for electricity.
- iv) Life cycle cost for maintenance and servicing. This also includes to minimize the number of switching operations, for each switching operation contributes to the wear and tear of the pumps.
- v) Holding available reserves for droughts or for fire water.

These objectives are at least partially in conflict: For example, no storage tank would be needed if the pumps would be operated exactly according to the demand. However, this would generally need many switching operations, and could also compromise fire water reserves.

Contrary to the applications in chemical industry, a new model that was based on pump and water work characteristics was built. These characteristics describe the pressure-flow-dependence of the pumps and of the water networks. The design variables (number

and type of running pumps, speed of the pumps, filling level of the storage tanks) are discrete or were discretized in order to meet practical requirements for their realization. In this case, there are time-dependent model parameters (e.g. the water consumption), but also fixed ones (e.g. the topology of the water supply). For the optimization solver, a branch and bound algorithm was implemented. In a dialogue with waterworks, the user interface was adjusted such that all relevant information for the operator is available. The decision support system is now running in German waterworks. It lead to an exchange of pumps and a more energy efficient operation of water storage tanks. Compared to the situation before, energy savings above 20 % could be realized.

5 Modeling aspects

Pareto optimization needs many model evaluations. Therefore, it is important that the model suits the optimization solver. In this section, three aspects of this work are highlighted that contribute to a more reliable and faster solution of the Pareto optimization problem.

5.1 Reformulation of the MESH-equations

In the case of Pareto optimization of chemical process designs, the model builds upon the MESH-equations. Industrially relevant production processes are described by several hundred equilibrium stage units and can be operated with more than fifty substances. The nonlinear system thus resulting contains several ten thousand process variables, which however are not completely determined by the MESH-equations.

To obtain a solution, further equations, so-called specifications, must be provided by the user, until the number of equations equals the number of variables. The variables involved in these specifications are the design variables. In flowsheet simulators, the solution of this system is obtained by simultaneous or sequential-modular methods. In both cases, starting points are needed. The closer the starting point to the actual solution is chosen, the more reliable and faster the methods converge.

When it comes to optimization, the user relaxes some specifications from equalities to box constraints. These are the design variables that the optimization solver can act upon. However, as long as the coupling is as loose as sketched in Figure 3, each time the optimization solver calls the simulation engine to deliver some function or gradient information the system of equations is solved by the simulation engine alone. That is, the optimization solver never has the complete information on all model constraints.

For a high-performant optimization solver capable of efficiently processing sparse Jacobians and Hessians, it is possible to declare the full set of MESH-equations as equality constraints. However, such a solver is not always available in industrial applications, and, furthermore, many of the process variables are determined by the MESH-equations anyway.

It thus seems natural to look for a reformulation of the MESH equations that allows the optimization solver to act on the free design variables directly, without the need to define and afterwards relax specifications.

Such a reformulation was obtained in [Hoffmann et al., 2017] for distillation columns. Within the equilibrium stage model, distillation columns are described by sequences of equilibrium stages, each interacting with two neighbours, except the lowest and the highest stage. By reformulating the MESH-equations according to a fixed-point iteration scheme, all process variables between the lowest and highest stages are obtained with a mathematically proven convergence rate. The outer variables describing the feed and product streams are available as design variables for the optimization solver. Comparison of this approach to a flowsheet simulator based on the simultaneous solution of the MESH-system yielded promising results.

5.2 Asymptotic models

Having an approximate insight into the influence of important design variables on the objectives is extremely helpful to provide reasonable starting values and judge the results of the optimization solver.

One approximation scheme consists in simplifying the rigorous model when certain process variables tend to their limiting values. In the ∞/∞ -model, that is in the limit of infinite reflux and infinite number of equilibrium stages, the feasible range in the design space of distillation columns is known explicitly [Ryll et al., 2012] and can even be linearized, which makes it ideal for optimization studies.

For practical applications, the question how to deduce information about the variables missing in the ∞/∞ -model - namely reflux and number of equilibrium stages - but required in the rigorous MESH-model is crucial. In this work, this question was addressed by using an asymptotic expansion around the ∞/∞ -limit [Bortz et al., 2015a]. At infinite reflux, the number of equilibrium stages needed to asymptotically approach a stationary point in the vapor liquid equilibrium phase diagram was calculated. It was found that these numbers only depend on the mixture properties and can thus be deduced from them without any flowsheet topology.

5.3 Hybrid modeling

Having a complete flowsheet model based on the MESH-equations is, for industrially relevant production processes, still rather an exception than a rule. The reasons can be:

- Not all substances in the mixtures are known.
- Not all thermodynamic mixture properties are known.
- In reactive systems, not all reaction kinetics are known.
- Unit operations cannot be described with sufficient accuracy.

Often, additional experiments in the laboratory are too time-consuming or just impossible, because, for example, there is not enough knowledge about which secondary components are involved at all in a reaction network. Thus a model of an entire production process which is an essential prerequisite for Pareto optimization is missing.

Still, process data exist from different sensors (temperature, pressure, flowrates, compositions). In how far statistical methods to extract data-driven models can complement the existing, but patchy physical models is the question that is addressed by hybrid modelling.

There is no general answer that can be given to that question. Rather, the answer depends on the type of process considered, on how large the patches in the physical models are and on the amount, quality and diversity of the available process data.

Since no general answer is possible, a workflow was established and software tools developed to support hybrid modelling [Asprion et al., 2017b]. This workflow is flexible concerning to what extent process data are used. In one extreme, the complete process can be modelled in principle by statistical learning methods like regression or artificial neural networks. In the other extreme, only parameters of the otherwise known MESH-equations are adjusted in order to match simulation results and measurements.

One typical example considered in [Asprion et al., 2017b] is a Cumene production process involving a reaction taking place in a tubular reactor, followed by a distillative separation sequence. Insufficient information on the reactions is assumed, but reconciled process data allowed an artificial neural network to be trained in order to model the reactor. This leads to a model of the entire process, for which also Pareto optimization studies could be successfully performed.

It is a common mistake
to suppose that the
definition of a word

is a matter of mere
convention. It is not.
The definition of a word
is a matter of fact.
It is a matter of fact
that the word 'cat' refers
to a certain kind of animal.
It is a matter of fact
that the word 'dog' refers
to a certain kind of animal.
It is a matter of fact
that the word 'bird' refers
to a certain kind of animal.

- 1. The word 'cat' refers to a certain kind of animal.
- 2. The word 'dog' refers to a certain kind of animal.
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- 4. The word 'fish' refers to a certain kind of animal.
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6 Conclusion and Outlook

Adaptive Pareto optimization and interactive decision support proved to be versatile approaches for the improvement of process designs. Their assets are:

- Numerically efficient calculation of Pareto points as supporting points allowing a reliable, interactive exploration of the Pareto boundary in real time.
- Identification of regions with small trade-offs leading to quick wins, compared to those regions where the trade-offs are important.
- Transparent comparison between different design options, both within one flow-sheet, but, using Pareto patches, also between different flowsheets or different model approaches.
- Slim software interfaces to enable usage in different application contexts.

To maximize the benefit from these assets, it is advantageous to exploit the model hierarchy and model structure and to tailor the optimization algorithms accordingly.

It goes without saying that there is ample room for further directions of research. Three such directions are mentioned in the following.

The first direction aims at an even more intuitive assistance for exploring the Pareto boundary. Especially in high dimensions of the objective space, it becomes obvious only during the navigation process where significant and where negligible trade-offs are expected. These regions could be identified before and highlighted to the user.

The second direction focusses on the improvement of the optimization runs. In practise, this is often enough still a serious problem due to convergence issues. On the one hand, the reformulation of the MESH-equations of a distillation column as fixed-point iterations offers more possibilities than exploited so far: Performing the iterations alternately from bottom to top and vice versa, it might be possible to efficiently identify the feasible range of the design variables. On the other hand, machine-learning algorithms might contribute to gradually learn the dependence of objectives on the design variables. This statistically learnt knowledge could be helpful in order to guide the optimization solver and to avoid steps into infeasible ranges in design space, without getting stuck in local optima and to accelerate convergence to the global optima.

The third aspect addresses the availability of process models, especially for large production plants. Often enough, in industrial practise, not all unit operations can be described by physical models with the same accuracy. For example, missing knowledge about reaction kinetics can lead to an insufficient model of a chemical reactor, whereas at the same time, the thermodynamic parameters may be known sufficiently well to be used in an equilibrium stage model for a distillative separation. However, if process data are available, there are chances that the blind spots of the physical model can be filled by statistically learned model components. That is, if one thinks of a chemical production process as a network of unit operations connected by streams, some of these units could be described rather by data-driven approaches, whereas other units are modelled by physics like the MESH equations, for example. One possible realization is the incremental model identification [Bardow and Marquardt, 2004, Kahrs and Marquardt, 2007]. Its implementation and application to industrially relevant flowsheets has been demonstrated recently [Asprion et al., 2017b]. Still, this hybrid modelling scheme is a topic of intense research. Of special importance is the parameter identifiability, model discrimination and the predictive power of these models. All these questions are of high relevance to guarantee the reliability of multicriteria optimization studies.

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Appendix

Paper I: Multi-criteria Optimization in Chemical Process Design and Decision Support by Navigation on Pareto Sets [Bortz et al., 2014]



Multi-criteria optimization in chemical process design and decision support by navigation on Pareto sets



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ABSTRACT

Designing chemical processes is a multi-criteria optimization problem with conflicting objectives. It can efficiently be solved using Pareto sets. These sets contain all solutions for which an improvement in any objective can only be achieved by accepting a decline in at least one other objective. This work integrates a novel algorithm to determine Pareto sets in a state-of-the-art steady-state flow sheet simulator. An approximation of predefined accuracy of the Pareto set, which can be convex or non-convex, is calculated. The decision maker can then navigate interactively on the Pareto set and explore the different optimal solutions. His decision is, hence, embedded in the knowledge of the entire Pareto set. The application of the method is illustrated by an example in which a distillation process for the separation of an azeotropic mixture (acetone+chloroform) is designed. Two process variants are compared: a pressure-swing and an entrainer distillation.

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1. Introduction

Optimization in chemical process design is usually not focusing on just one economic objective. Rather, two levels of objective criteria are often considered: design criteria and final decision criteria. The first group contains, for example, product purities, column duties and reboil ratios. The second group consists of hard economic objectives like investment and operating costs, often more softer environmental issues as sustainability key figures and objectives regarding health and safety. Thus, almost every design decision in process engineering is a compromise between multiple conflicting objectives.

In practical process design, the engineer often tries to find an optimal solution in the multi-dimensional objective space by an empirical iterative change of the process parameters in the design space. Usually, this procedure is continued until either a solution is found which fulfills certain requirements, or some deadline is reached where a solution has to be delivered. This procedure may lead to good results, however, no guarantee on optimality can be given. Furthermore, the empirical optimization only covers restricted areas in both the design and objective space, so that only

limited information on the trade-offs between the different objectives is available and the decision cannot be based on an overview of the full solution space. This limitation may lead to overlooking interesting solutions.

It is by far not necessary to calculate all feasible solutions. In principle, only best compromises need to be studied. These are solutions where an improvement in any objective can only be achieved by accepting a worsening in at least one other objective. The respective solutions are called Pareto-optimal (Geoffrion, 1968) and the set comprising all these solutions is the Pareto set, often also called the Pareto frontier because the Pareto set lies on the border between feasible and infeasible solutions.

A common strategy to find single Pareto-optimal solutions is to weight the objectives and subsequently optimize the weighted sum. A drawback of this approach is that the weights have to be chosen beforehand. As the choice of the weights is ambiguous, many solutions will not be accepted without exploring alternative choices. Hence, this approach is, in practice, also empirical and iterative. Furthermore, it is difficult to extend this approach to "soft" objectives, describing safety, environmental, sustainable, or social issues. These are difficult to weight and compare directly to technical or economic objectives. Moreover, not every Pareto-optimal solution can be found by the weighted sum approach: namely if the Pareto set is not convex (Chankong & Haimes, 1983; Haimes, 1977).

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The chemical engineering literature describes many algorithms to determine Pareto-optimal solutions more systematically and efficiently than the weighting approach. They can be classified in deterministic and stochastic algorithms. Deterministic algorithms on the one hand, like for example derivative-based methods, are time-efficient and yield accurate results for the optima, however, they usually only find the local optimum related to the starting point. Examples of deterministic algorithms in process design are goal programming techniques (Chakraborty & Linninger, 2002), including the ϵ -constraint method (Hugo, Ciamei, Buxton, & Pistikopoulos, 2004), or weighting approaches with methodical variation of the weights (Lim, Floquet, Joulia, & Kim, 1999). On the other hand, stochastic algorithms try to find the global optimum by sampling large areas of the objective space, which also leads to time-consuming and less accurate procedures. For examples of stochastic algorithms in process design see Gutiérrez-Antonio and Briones-Ramírez (2009), Leyland (2002), or Micovic, Beierling, Lutze, Sadowski, and Górak (2013). Evolutionary approaches in particular are intensively used for stochastic algorithms as they can be applied straightforward to any process simulation, are robust and somewhat insensitive to local optima. For general reviews and classifications of algorithms to find Pareto-optimal solutions the reader is referred to Andersson (2000), Bhaskar, Gupta, and Ray (2000), or Rangaiah (2008).

There have also been efforts to create multi-purpose numerical tools which apply multi-criteria optimization techniques to arbitrary models in a black box. An example is the commercial tool modeFRONTIER¹ that has been successfully coupled to chemical process simulators (Altendorfner, 2008). To ensure robustness the software uses an evolutionary algorithm. Using this type of algorithm the user has to accept, however, a computationally expensive calculation, and gets only an approximation of the Pareto set. Additionally, the accuracy of this approximation is not known.

Hakanen, Hakala, and Manninen (2006) presented an interactive tool that couples a process simulator and a deterministic multi-criteria optimization algorithm. To avoid an expensive approximation of the complete Pareto set they use an interactive algorithm: individual Pareto optimal points are subsequently calculated until the user terminates the algorithm. Thereby, the user specifies the search direction by updating constraints on the objectives. The major drawback of this interactive method is that the user only explores parts of the Pareto set. Which parts of the Pareto set he explores is somewhat intuitive and dependent on the user's experience.

In this work we present a tool, which couples a commercial process simulator with multi-criteria techniques and overcomes the earlier mentioned drawbacks related to calculation speed, accuracy and Pareto set exploration. The work is inspired by the concepts for determining and visualizing the Pareto set reviewed by Küfer et al. (2009, chap. 5). The basic idea is to first, efficiently determine an approximation of the complete Pareto set of a given chemical process design problem. This allows the decision maker to focus his attention only on relevant solutions, so that the decision process is facilitated. We calculate the approximation of the Pareto set by using a combination of evolutionary and efficient derivative-based algorithms. During a short initial evolutionary phase, a variety of starting points close to the expected Pareto surface is generated. From these starting points, a sequential quadratic-programming algorithm is applied to find the Pareto points. We calculate only a minimum number of Pareto points to approximate the full Pareto set to an accuracy which is set by the user a priori. Unnecessary computationally expensive simulations are thus avoided. The

Pareto points are calculated using a method which combines a sandwiching and a hyperboxing algorithm. Therefore, also non-convex Pareto sets can be efficiently approximated.

The decision maker can then interactively explore the Pareto set by navigating with a graphical user interface (GUI). Graphical sliders are used for this purpose, each corresponding to one objective. By moving one slider, the other sliders are updated in real time, i.e., information on the trade-offs between the best compromises is directly visualized. Further, the GUI allows a simultaneous visualization of different Pareto sets which enables comparing different variants of the process based on different flow sheets. The areas that are explored can successively be restricted to those which are identified as the most promising. Thus, we postpone the restriction to a limited area of the decision space until the decision maker has got insight into the complete set of optimal solutions. This interactive multi-criteria optimization (IMCO) maintains full flexibility until the final choice of the design point. This choice is, hence, embedded in the knowledge of alternative designs. All choices are left to the decision maker, who is efficiently supported by the tool in all steps of the design.

The tool can in principle deal with an arbitrary number of objectives in calculation as well as in visualization. As it is integrated into a state-of-the-art process simulator, its applications range from optimization of single apparatuses up to the design of new plants. Rather than treating the simulator as a black box model, the algorithms are directly coupled with the flow sheet solver which leads to high speed and robustness. This could in principle be done with any state-of-the-art process simulator, provided that the source code is available. For reasons explained below in more detail, it cannot be expected to achieve a similar performance if the process simulator is only addressed as a black box.

In the following, we first describe the MCO methods used in the present work together with their implementation, and then illustrate their application in a case study in which two processes for separating chloroform from acetone are compared: an entrainer and a pressure-swing distillation.

2. Method for MCO in chemical process design by navigation on Pareto sets

2.1. Overview

The MCO chemical process design problem which is addressed in the present work is of general nature. In principle, any problem, for which a process simulation can be set up, can be addressed. The MCO methods described in the present work were implemented in CHEMASIM, a steady-state flow sheet simulator which was developed and is maintained by BASF SE (Hegner & Schoenmakers, 1985). The methods are generic in the sense that in principle any other flow sheet simulator could have been used. The main reason to choose CHEMASIM was that it is an equation-oriented simulator thus allowing for flexible and unified handling of all model parameters/variables and also providing fast convergence by suitable initial guesses. Furthermore, the source code was available for the present study and CHEMASIM developers were able to join the team. Other advantages of CHEMASIM are its efficiency and robustness² which make it a good choice for the endeavor.

Fig. 1 shows a scheme of process optimization based on process simulation and serves for defining the nomenclature used in the following. The process simulation has input variables, some of

² To solve the non-linear model equations, a set of process variables as a start point has to be given to the solver. Empirically we found that the CHEMASIM solver is more robust to perturbations in this start point and converges faster than other process simulators. Both properties are crucial during the optimization process.

¹ Product of ESTECO, Trieste, Italy.

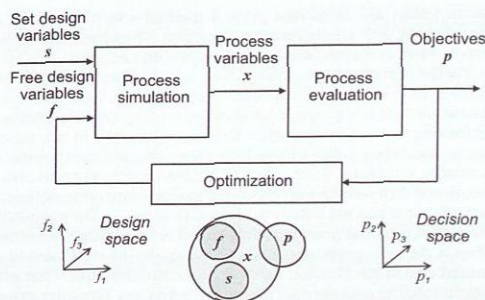


Fig. 1. Scheme illustrating the interaction between process simulation and optimization.

which are set a priori and remain unchanged in the optimization (set design variables s). The remaining design variables are free and subject to variation in the optimization (free design variables f). The sets of design variables s and f together determine the design. The free design variables span the design space. Other process variables are calculated in the process simulation. All variables of the process simulation (design and calculated) are called process variables x . The process variables are used for the evaluation of the process which yields the objectives p . The objectives may contain process variables like heat duties but also derived properties like capital expenditures (CAPEX) and operational expenditures (OPEX). These objectives are generally conflicting, and span the decision space. Process specifications are introduced either simply by assigning numbers for set design variables s of the process simulation or in the course of the optimization by imposing constraints on any process variable x . These constraints can be equalities or inequalities. Variables may be continuous or discrete.

For Pareto based MCO, both the design and the decision space need to be defined. In many applications, the dimension of the decision space will be lower than that of the design space. The Pareto set is a part of the decision space. Its determination is explained in more detail below and involves going through the cycle shown in Fig. 1 a number of times. The optimization then finally yields the Pareto set on which the decision maker selects a "design point". That point is firstly an element of the Pareto set in the decision space. But from the way the Pareto set is determined it follows that for any element of the Pareto set, a corresponding element in the design space is known. So after choosing a design point on the Pareto set in the decision space the corresponding point in the design space is known. Generally, there may be more than one element in the design space corresponding to a given element of the Pareto set. If such multiplicity occurs the alternatives must be subjected to a more detailed analysis to choose a final process design. As the Pareto set is only approximated in the course of the optimization, the chosen design point generally is not a Pareto point itself. Thus, a final process simulation is carried out and, optionally, a slight adjustment of the free design variables can be done so that the design point satisfies the Pareto conditions.

The MCO method for chemical process design developed in the present work consists of three successive steps:

- First, the MCO problem is set up: the process simulation model is supplied and both the design and the decision space are defined.
- In a second step, the Pareto set of the problem is determined, including non-convex regions, if present. The result is an approximation of the Pareto set within a predefined arbitrary accuracy.

- Third, the data are visualized in a GUI which allows the decision maker to explore the Pareto set and its trade-offs between the different objectives by using graphical controls. Based on this, the design point is selected and optionally reoptimized.

In the following, these three steps will be explained in more detail.

2.2. MCO problem set up

The set up of the simulation itself is standard and not discussed here. The main task in the first step is to suitably define the design and decision space. The definition of both the design and the decision space is ambiguous. For a given practical process design task, it may turn out to be useful to explore different choices for the design and decision variables. The number of design and decision variables should not only be limited for computational reasons but also in order to keep the dimensions of the according spaces so low that a reasonable navigation by the decision maker is possible. The definition of the design and decision space does not only include the choice of the variables but also the definition of their bounds. Setting bounds too narrow may exclude interesting solutions, setting them too wide is not favorable for the computational performance.

Typical examples of variables in the decision space are either process variables (like heat duties) or variables obtained as a function of process variables (like OPEX or CAPEX). The latter will often be determined by post-processing the process simulation results. Soft objectives, like safety, environmental, sustainability, or social issues can be included explicitly, e.g. by numeric index systems (Azapagic, Millington, & Collett, 2006; Othman, Repke, Wozny, & Huang, 2010). As no weights have to be assigned, it is not critical to mix such indices with objectives describing technical or economic properties, as the ones mentioned above.

Objectives that are not included in the decision space during the determination of the Pareto set (due to minor importance or for the sake of keeping numerical efforts small) can still be calculated and displayed during the navigation. They are welcome to guide the decision maker in his choice among the mathematically equivalent Pareto-optimal solutions.

2.3. Approximation of the Pareto set

In order to reduce computational expenses in the numerical approximation of Pareto sets, only the minimal number of points should be calculated which is necessary to approximate the Pareto set in the region of interest with a sufficient accuracy. Since the optimization problems considered here are generally non-convex, an algorithm was developed that efficiently samples both convex and non-convex regions of the Pareto set. That algorithm is outlined in the following, details are published in Hernández (2012). The two scalarizations used here, the weighted sum and Pascoletti–Serafini scalarizations, are explained in Appendix A.

Motivated by our practical experience we assume that significant non-convexities do not occur frequently, and that most regions of the Pareto sets are convex. The basic idea is to use a sandwich approximation method which is able to approximate the convex part of the Pareto set efficiently. Once a certain approximation quality is achieved there, candidate regions for non-convex behavior are identified and tested for non-convexity. Finally, the non-convex regions are sampled using a hyperboxing scheme.

The sandwich approximation method creates successively inner and outer approximations to the Pareto set by using a weighted sum scalarization to calculate Pareto points. The weight vectors are the normals to the supporting, tangential hyperplanes of the Pareto set at the calculated points. These hyperplanes represent the outer approximation. The inner approximation is found from

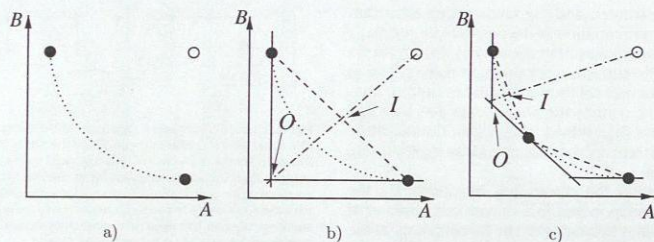


Fig. 2. Sketch of approximating the Pareto set by the sandwich method for two objectives A, B . Full circles denote Pareto points, the open circle is the Nadir point. The dotted line shows the (unknown) Pareto set, full (dashed) straight lines illustrate the outer (inner) approximations. The intersection points I and O are used to compute the sandwich quality, details are given in the main text.

the close-by facets of the convex hull of the Pareto points. New Pareto points are added as long as the difference between outer and inner approximation – the sandwich – is still beyond some arbitrary but fixed threshold, i.e. the desired approximation quality δ_5 . The basic idea of the algorithm is sketched in Fig. 2 and works as follows (Hernández, 2012; Klamroth, Tind, & Wiecek, 2002; Küfer et al., 2009, chap. 5; Solanki, Appino, & Cohon, 1993):

1. Find the extreme compromises and therefrom construct the Nadir point,³ which serves as the reference point for determining the approximation quality, cf. panel a) in Fig. 2.
2. Calculate the outer and inner approximations to the Pareto bound from the computed Pareto points, shown in panels b) and c) of Fig. 2.
3. Determine the quality of the current approximation. This is done as follows: for each facet, the distance between the inner and the outer approximations with respect to the reference point is calculated. This is schematically shown in Fig. 2: here, these are the distances between the reference point and points I (O) for the inner (outer) approximation, respectively. In each step, the maximum of the ratio between outer and inner distances is taken as the current approximation quality σ_5 .
4. If $\sigma_5 > \delta_5$, compute the Pareto point that corresponds to the weighted sum with weight vector perpendicular to that facet and go to 2, otherwise stop.

Naively, one would expect the number of Pareto points needed for a satisfactory approximation grows exponentially with the number of objectives. In practice, however, objectives are often correlated, because of the correlations between the different apparatuses in a flow sheet. A large number of case studies were conducted in collaboration with the industrial partner to gain practical experience with the method. Based on these studies, we found that the number of Pareto points needed for a sufficient approximation quality (usually δ_5 in the range of 1.02–1.10 is acceptable) increases often only about linearly with the number of objectives, which is welcome regarding the computational expenses.

Because of the weighted sum scalarization, the approximation quality is valid only for the convex regions of the Pareto set. To detect possible candidate regions which might show non-convex behavior, we take the Pareto points calculated so far and exclude the strictly dominated and non-dominated regions for every Pareto point and thus obtain hyperboxes with Pareto points on some corners (see for example the three boxes in panel b) of Fig. 3). If the width of such a hyperbox with respect to the Nadir point exceeds some threshold δ_H – here the same or a slightly higher value than δ_5

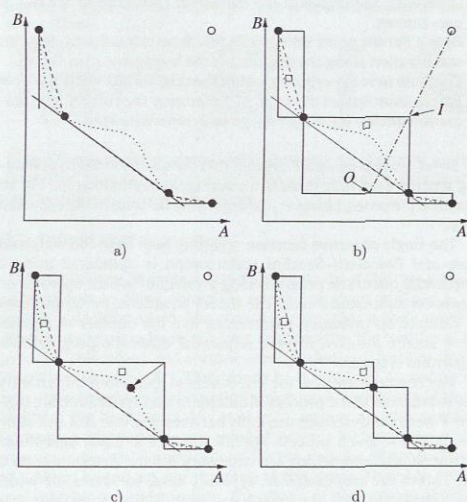


Fig. 3. Sketch of the hyperboxing scheme to approximate non-convex regions of the Pareto set for two objectives A, B . Additionally to the symbols explained in Fig. 2, the tests for convexity (open squares close to the Pareto set) and the hyperboxes for the Pascoletti–Serafini scalarization are shown. The points I and O are used to determine the current approximation quality, for details see the main text.

can be used – a candidate region for non-convex behavior is found. In that case, a Pareto point in the middle of the hyperbox is determined by using a Pascoletti–Serafini scalarization. If this Pareto point lies to the inner of the inner approximation from the sandwich procedure, the Pareto bound is indeed non-convex and hyperboxes are constructed using the newly calculated Pareto point. The algorithm then includes the following steps⁴ which are also illustrated in Fig. 3:

0. The method starts with a set of Pareto points resulting from the sandwich algorithm, approximating the convex regions of the Pareto set within a known accuracy, see panel a) in Fig. 3. The

⁴ These steps are essentially those which have been proposed recently (Hernández, 2012), with a different quality measure than we use it here. The reason for our modification is a better comparability with the scaling factor from the sandwich algorithm. The reader is referred to the original work for further details.

³ The coordinates of the Nadir point are the worst value for each objective.

true Pareto set is non-convex, and the sandwiching algorithm suggests inaccurate approximation in the non-convex region.

- Construct the initial hyperboxes from the already known Pareto points and compute the current approximation quality. This is done as follows: the distances of the outer and inner approximations to the Nadir point, namely the points O and I as sketched in panel b) in Fig. 3, are determined. The biggest ratio of these distances yields the current approximation quality σ_H . If $\sigma_H > \delta_H$, go to 2, otherwise stop.
- Test for convexity within the chosen box by calculating the objective functions corresponding to a convex combination of the set of design variables belonging to the Pareto points at the corners of the boxes (open squares close to the Pareto set in the panel b) in Fig. 3). If the point in the decision space is within the sandwich (for example in the upper box in the panel b) in Fig. 3), exclude that box from further considerations and go back to 1. Otherwise, the region of the Pareto set contained in the box is non-convex.
- Find a Pareto point within the box from a Pascoletti–Serafini scalarization along the diagonal of the box (panel c) in Fig. 3).
- Compute new hyperboxes within the original box using the new Pareto point (panel d) in Fig. 3). Determine the current approximation quality σ_H . If $\sigma_H > \delta_H$, go to 2, otherwise stop.

So far, there is no rigorous proof that the quality of the hyperboxing scheme used here leads to a convergent approximation. For all practical purposes, however, the algorithm behaves in the expected way.

The single objective function resulting both from the weighted sum and Pascoletti–Serafini scalarization is optimized using a sequential quadratic programming algorithm⁵ which operates on a process simulator solving the model equations. In the presence of discrete optimization parameters, like the number of equilibrium stages, a mixed integer sequential quadratic programming algorithm is used.

The requirements on the effectiveness and, more importantly, the robustness of the process simulator in that application are high. The Pareto set describes the limit between feasible and infeasible solutions for given process specifications. The input parameters of the simulations which are necessary for the determination of the Pareto set are, therefore, typically close to values for which the simulation will no longer converge. Thus, non-convergent runs must be expected and handled. The accuracy that can be achieved for the approximation of the Pareto set may be determined by the robustness of the algorithms used in the process simulation and not by the underlying process model. In the present work, both types of algorithms were integrated within CHEMASIM. Details are not discussed here as they are specific for the simulator.

2.4. Navigation on the Pareto set

The result of the automated calculations of the hybrid algorithm is a finite set of points which approximate the Pareto set within a certain accuracy. To support the decision maker, it is desirable to enable a real-time navigation on the continuous Pareto set via a GUI. In a first step, a linear interpolation between the points on the Pareto set is carried out. This interpolation is not only done in the objective space but also in the design space. A GUI was developed, with which the user can navigate the interpolated solutions by moving sliders corresponding to the objectives. In the

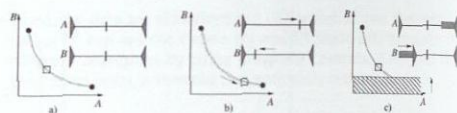


Fig. 4. Interaction of sliders operating on the Pareto set for two objectives A, B. The upper (lower) slider corresponds to the horizontal (vertical) axis. The dotted line represents the Pareto set, approximated by the full polygon line. The open square shows the navigated point corresponding to the slider position, full circles are the extreme compromises. In panel b), one of the sliders is changed, and the other adjusted accordingly. In panel c), a restriction to the accessible values for the vertical axis is introduced. This reduction entails a restriction on the accessible values for the horizontal axis as well (gray bars on the sliders).

following, first the exploration of the decision space is discussed, then we address the related exploration of the design space.

The way the objective sliders work is illustrated in Fig. 4 for the simple case of two objectives. During slider change on one objective, a linear problem is solved such that the remaining objectives are all changed in a definite manner according to a scheme described in Appendix B. In this way, the complete Pareto set is navigable for the decision maker, who can explore visually the trade-offs between the different objectives. This visual exploration can be done in a twofold manner: on the one hand moving one slider causes the displacement of the other sliders according to the shape of the Pareto set. This interaction between the values on the sliders shows nicely the best compromises between the conflicting objectives. On the other hand, the user can restrict the range of the sliders. For example, one may want to prescribe that the operating profit exceeds some lower threshold. Restricting the range of one of the objectives, will in general also affect the range of the other objectives. This restriction of the decision space is also visualized, yielding information on which alternatives remain feasible and which are now infeasible. Therefore, while setting up the MCO problem (cf. Section 2.2), it is advisable not to set constraints on objectives which also can be set during navigation. These constraints on objectives should not be confused with constraints on the free design variables f . Constraints on the free design variables are crucial in order to define the region in design space on which the optimization operates in order to find the Pareto points. Notice that at the moment the scheme in Appendix B can only be used to navigate on convex parts of the Pareto set. Although non-convex regions of the Pareto set are approximated correctly as described in the previous section, the navigation is done so far on the convex hull of the set, even if non-convexities are present. Schemes to navigate in similar manner on non-convex regions are highly interesting and subject of our present research.

In order to analyze which values of the objectives in the decision space correspond to the best compromises in the design space, the navigation tool also contains sliders for the free design variables. These sliders cannot be moved actively by the user, but are adapted according to the slider change of the objectives. Still, the ranges of the free design variables can be restricted actively and are adjusted upon restriction of other sliders: information here is important to judge whether and how far the envisaged solution in the design space is sensitive to a change of a certain parameter.

Keeping track of the points in design space which belong to the Pareto set in decision space is crucial for the final simulation run by the process simulator. Namely, once a certain navigated solution is favored, a final simulation and optimization can be done: a Pareto-optimal point which is close to the navigated solution on the approximation is calculated by running the process simulator once again, starting from the navigated solution in design space. In this case, the Pascoletti–Serafini scalarization (see Appendix A) is used. For this purpose, the current navigated point in decision space is used as reference point. The Pascoletti–Serafini direction

⁵ The MISQP solver, cf. homepage www.klaus-schittkowski.de, E-mail: klaus@schittkowski.de.

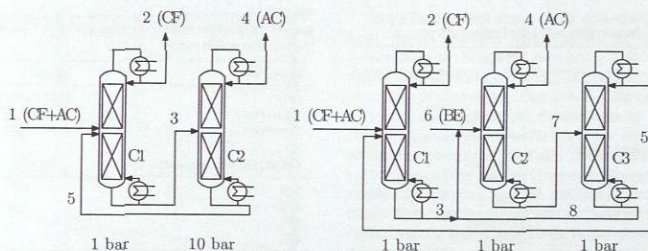


Fig. 5. Flow sheets of the pressure-swing (left) and entrainer (right) distillation processes for separating chloroform (CF) and acetone (AC). The entrainer is benzene (BE).

points towards the ideal point with coordinates which are the best value for each objective calculated from the extreme compromises.

In the remainder of this work, benefits of applying the MCO approach will be highlighted using an example.

3. Comparative study of pressure-swing and entrainer distillation

In this section, we apply the MCO approach described in Section 2 to compare two types of distillation processes for separating a binary mixture of chloroform and acetone into pure components. As these two substances form a maximum boiling azeotrope, a separation in a simple single distillation column is not possible. Two variants for separating the azeotropic mixture are considered: the first is a pressure-swing distillation which takes advantage of the pressure dependency of the azeotrope. In the second an entrainer (benzene) is used to influence the phase behavior in a way which makes a separation by distillation feasible. The flow sheets for these two variants are shown in Fig. 5. In the pressure swing distillation chloroform is obtained as top product of the first distillation column C1 which is operated at 1 bar. The bottom product of column C1 is a mixture of composition close to the azeotrope. That mixture is fed to the second column C2 operated at 10 bar. In column C2 acetone is obtained as top product, while the bottom product is recycled to the column C1.

In the entrainer distillation, the first column C1 is similar to the first column in the other variant. The top product of column C1 is chloroform. The bottom product of column C1 is fed to a second column C2. The feed is mixed with the benzene-rich stream 8. The benzene lowers the volatility of chloroform, so that acetone is obtained as top product of column C2 even though it is operated at the same pressure as column C1. The bottom product of column C2 is fed to a third column C3 to recover benzene in the bottom product. The top product of column C3 comprises a binary mixture of acetone and chloroform and is recycled to column C1. To compensate small losses through the product streams 2 and 4, benzene is supplied in stream 6.

We consider a scenario in which the apparatus and equipment of both process variants are already built and depreciated. Based on a MCO study we want to decide which of both variants is more economic to separate a given feed stream of acetone and chloroform. The operating costs are assumed to be dominated by the heat duties of the reboilers of the columns. All other costs are neglected.

3.1. Process models

The distillation columns are modeled with an equilibrium stage model. The vapor–liquid equilibrium is described with the extended Raoult's law using the NRTL activity coefficient model. For details of the property model see Appendix C. Note again, that

Table 1

Objectives used in the case studies of this work for both process variants. For definitions see text.

Objective	Short name	Unit	Goal
Total reboiler heat duty	qTot	kW	Minimize
Purity chloroform	MassFracCF	g/g	Maximize
Purity acetone	MassFracAC	g/g	Maximize

the MCO approach presented in the present work is generic and can be applied to any process model. There are no restrictions regarding unit operations or modeling depth.

3.2. Design and decision spaces

Our goal is to perform a comparative study of the two variants with respect to three objectives which are given in Table 1 and form the decision space. The objective qTot, that is the sum of all reboiler duties, is to be minimized. Additionally, the purities of the products chloroform and acetone are regarded as objectives (MassFracCF and MassFracAC). They are to be maximized. Including the latter two objectives in the optimization study provides additional insights: the decision maker is able to answer e.g. the question, how much additional heat is needed, when a higher purity of one product is desired. Specifications for the purities of product such as a lower bound are not required at this stage. They can still be applied after the optimization. The choice of the number of objectives (here three) is not due to restrictions of the method. Also in the navigation, an arbitrary number of objectives can be handled with the presented slider concept.

As the same three objectives are used, both process variants share the same decision space. The design spaces of both variants, however, are different as described in the following. As the process equipment already exists the number of process optimization parameters is reduced: the number of stages of the columns, feed stage positions, the amount and composition of the external feed (Stream 1, cf. Fig. 5) and the pressures in the columns are set. Numbers are given in Table 2 for the pressure swing distillation and Table 3 for the entrainer distillation. Even though the study is only an example so that the actual result is not practically important, the choices were made so that the numbers are technically reasonable: all columns are operated at 1 bar, except for the second column of the pressure swing distillation which is operated at 10 bar. The resulting reboiler and condenser temperatures are acceptable. The sum of the number of stages in all columns is about 60 for both variants, so that the separation capacity of the columns is quite high. The feed stages are chosen at reasonable, though not necessarily optimal positions. We want to stress that the fixed equipment variables of the considered scenario are not due to restrictions of the method. Any fixed process variable mentioned above could have been taken as free variable and included in the optimization. This

Table 2
Set and free design variables of the pressure-swing distillation variant.

Set design variables	Value
Pressure C1	1 bar
Pressure C2	10 bar
Feed mass flow	1250 kg/h
Chloroform fraction feed	0.86 g/g
Number of stages in columns (feed stage ^a) C1, C2	28 (14)
Free design variables	Bounds
SP1, SP2	[0.01; 0.99]
RR1, RR2	[0.5; 60]

^a Counted from bottom.

Table 3
Set and free design variables of the entrainer distillation variant.

Set design variables	Value
Pressures C1, C2, C3	1 bar
Feed mass flow	1250 kg/h
Chloroform fraction feed	0.86 g/g
Number of stages in columns (feed stage ^a) C1, C2, C3	20 (10)
Free design variables	Bounds
SP1, SP2, SP3	[0.01; 0.99]
RR1, RR2, RR3	[0.5; 60]
CB3	[0.01 mol/mol, 0.7 mol/mol]

^a Counted from bottom.

also holds for discrete parameters as stage numbers. Thus, it is also possible to design and optimize new equipment and plants with the presented method.

The remaining variables that need to be specified in order to run the process simulation are the reflux ratios RR and the molar distillate to feed ratios SP in the distillation columns, as well as, for the entrainer distillation, a variable which controls the entrainer cycle rate. The mole fraction of benzene in the bottom in stream 8 (cf. Fig. 5) was chosen for this purpose. It is called CB3 in the following. This results in 4 (respectively 7) free design variables for the pressure-swing variant (entrainer variant) which are used for the optimization. Their bounds are chosen very loose but within a technically feasible range (cf. Tables 2 and 3).

3.3. Calculation of Pareto boundaries

For the design and decision spaces as defined above the Pareto sets were calculated for both process variants using the methods described in Section 2. The parameters to steer the quality of the approximation were set to $\delta_S = 1.02$ and $\delta_H = 1.10$. The total number of points required to reach the desired accuracy for the convex parts of the Pareto sets is 10 (12) for the pressure-swing (entrainer) alternative respectively. However, significant parts of the Pareto sets are detected to be non-convex. To approximate those areas within the required accuracy, 46 (21) Pascoletti–Serafini runs are required for the pressure-swing (entrainer) distillation.

3.4. Results

The Pareto sets are two-dimensional surfaces in the three-dimensional decision space. Bounds were set only on free design variables (cf. Tables 2 and 3), but not on the objectives (cf. Table 1). Hence, only a part of the design space was admissible, but in principle the entire decision space. We would like to stress that in practice, the engineer often is interested only in a certain part of the decision space – here, for example, in purities larger than a certain

Table 4
Ranges for objectives and free design variables resulting from the MCO analysis for the pressure swing variant.

Objective	Range
qTot	[148.5 kW; 4396 kW]
MassFracAc	[0.1462 g/g; 0.9992 g/g]
MassFracCf	[0.8601 g/g; 0.9998 g/g]
Optimization parameter	Range
SP1	[0.01; 0.99]
SP2	[0.01291; 0.99]
RR1	[0.5; 41.74]
RR2	[0.5; 60]

Table 5
Ranges for objectives and free design variables resulting from the MCO analysis for the entrainer distillation variant.

Objective	Range
qTot	[150.1 kW; 7036 kW]
MassFracAc	[0.1402 g/g; 0.9962 g/g]
MassFracCf	[0.8602 g/g; 0.9996 g/g]
Optimization parameter	Range
SP1	[0.01; 0.99]
SP2	[0.01; 0.99]
SP3	[0.01; 0.5252]
RR1	[0.5; 23.55]
RR2	[0.5; 60]
RR3	[0.5; 30.8]
CB3	[0.01 mol/mol; 0.07514 mol/mol]

minimal value. For illustrative reasons, here, we did not introduce such bounds. These can be set in the navigation process.

Tables 4 and 5 give the ranges actually covered by the Pareto sets in decision space and their pictures in the design space. They are found only in a certain part of the overall admissible spaces. The ranges covered by the Pareto sets already give valuable information on the processes. In the decision space, it becomes evident, in which range feasible numbers for the objectives are found. The decision maker immediately sees what can be achieved and, consequently, also what cannot be achieved. Namely, it becomes evident that in terms of the maximally achievable purity of acetone, the pressure swing variant is superior to the entrainer distillation, whereas the performance in the chloroform purities is similar. We will confirm this finding in more detail below, when analyzing the whole Pareto sets.

In the design space, Pareto-optimal ranges for the free design variables become clear. Since no bounds were set in decision space, large parts of the admissible ranges defined in Tables 2 and 3 are covered during the optimization. While navigating on the Pareto set, one recognizes how the (physically motivated) bounds imposed on the free design variables restrict the accessible decision space. For example, the overall maximum in the acetone purity is limited by the upper bound on the reflux ratio of column C2 for the entrainer distillation.

As the same objectives are used for both variants, their Pareto sets can be compared in the common decision space. This will be done in the following. With our GUI, the user is able to navigate on the Pareto sets with the help of sliders as described above. Since this process is rather difficult to describe in a paper, we provide the reader with graphical representations of the Pareto sets. In Fig. 6 the Pareto sets of both variants are shown in a level curve plot. On the axes the product purities are given. The level curve parameter is the total reboiler heat duty. Fig. 7 shows a zoom into the upper right corner of the plot, in which the level curves are difficult to discern in Fig. 6. In order to create the plots for this paper a large number

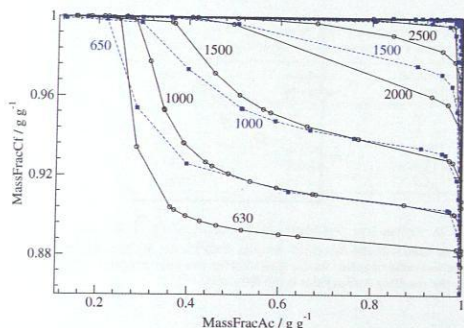


Fig. 6. Level curve plot of the Pareto sets of both variants in the decision space. On the axes the product purities are given. The level curve parameter is q_{Tot}/kW . Blue squares (black circles) denote Pareto points for the entrainer (pressure swing) variant. Fig. 7 shows a zoom into the upper right corner of the plot. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

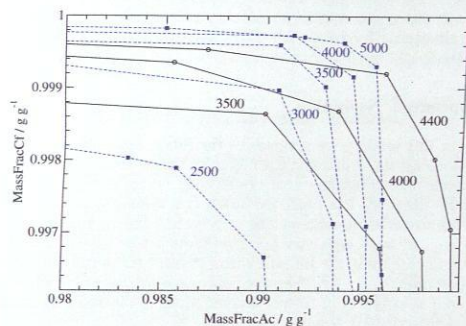


Fig. 7. Zoomed level curve plot of the Pareto sets of both variants in the decision space. On the axes the product purities are given. The level curve parameter is q_{Tot}/kW . Blue squares (black circles) denote Pareto points for the entrainer (pressure swing) variant. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

of Pareto-optimal points (about 120 per Pareto set) has been calculated by the ϵ -constraint (Andersson, 2000; Cohon, 1978) method in which the total reboiler heat duty could easily be discretized.

The Pareto-optimal points that were calculated earlier by our novel efficient hybrid method contain the same information within the specified approximation accuracy. They constitute the approximation of the Pareto sets and underlay the navigation with the sliders by interpolation. In principle, Figs. 6 and 7 could have been created through navigation with the sliders: to obtain a certain level curve the total reboiler heat duty is first restricted to that level (cf. panel a) in Fig. 4), afterward one of the product purity sliders is moved stepwise (cf. panel b) in Fig. 4). The other product purity slider follows automatically. Thus, the user can access the information displayed in the level curve plot in Fig. 6 by navigation with the sliders in the GUI. Further, the effects on other process variables, for example the design variables, can be viewed at the same time. The strongly reduced number of calculated Pareto-optimal points clearly demonstrates again the efficiency of our proposed hybrid method.

Both Pareto sets show clear non-convexities for total reboiler heat duties smaller than 2000 kW; even though the non-convexities of the Pareto sets occur only for small, technically not interesting acetone purities, the example clearly demonstrates the necessity of algorithms that can handle non-convexities.

Fig. 7 shows that the Pareto sets of both variants are intersecting: curves of the same level are intersections, e.g. for a total reboiler heat duty of 3500 kW. Thus, there is no clear better variant in the sense of the chosen three objectives. If acetone purities below about 0.99 g/g are accepted, the entrainer variant requires less heat than the pressure-swing variant and is, hence, the better choice regarding the given objectives. If, however, higher acetone purities are desired, the pressure-swing variant becomes competitive or even better, as it operates at lower heat duties.

The higher heat duty for high acetone purities in the entrainer alternative can be explained by an increased separation effort in column C2 (cf. Fig. 5). The task of this column is to separate acetone from benzene. For high acetone purities this task becomes difficult, particularly as the benzene level in the process needs to be high to enable the separation of the azeotropic mixture chloroform/acetone. This results in a higher reflux ratio and a higher heat duty in column C2.

This process example demonstrates the essential benefits of the MCO approach and the restriction to Pareto points: a comparison between different alternatives can be performed in much more detail as would be the case when the focus would be on a single objective only, and tradeoffs between the objectives can be grasped immediately.

4. Conclusion

The generation of Pareto sets for multi-criteria optimization problems in chemical process design is a powerful concept. In this work, a novel and effective algorithm to calculate Pareto sets was integrated in a state-of-the-art process simulator. For any process for which a simulation can be set up, Pareto sets can be generated after defining a suitable design and objective space. The decision maker then navigates on the Pareto sets to find a process design of his choice. That choice is embedded in the knowledge of the entire set of Pareto-optimal solutions. The navigation is an interactive process, so that the process design method introduced in the present work can be characterized as interactive multi-criteria optimization (IMCO).

A minimal set of Pareto points that approximates the Pareto set with sufficient accuracy is calculated. The user can specify the quality of the approximation. The approach is a hybrid of sandwiching combined with hyperboxing and can handle non-convexities of the Pareto set. The Pareto optimal points calculated by the algorithm are stored in a database which includes a convergent flow sheet simulation for every point. The user can then navigate the database. The stored parameters and results for the Pareto optimal points are interpolated to enable continuous navigation on the whole Pareto set. The user can explore the trade-offs between objectives, compare different alternatives with respect to different objectives and finally arrive at a well-founded decision. As only optimal compromises are included in the Pareto set a guarantee for optimality can be given.

The Pareto-optimal solutions necessarily lie on the border between feasible and infeasible process designs. As a consequence, the design found with the method presented here has to be relaxed for detailed engineering to account for uncertainties and operability, just like in any process design. To calculate the Pareto-optimal solutions, robust and efficient algorithms are needed and the coupling of the process simulation with the algorithms for determining the Pareto set is strong. In the present case, the programming was

If the limits in the constraints are also uncertain then their enumeration can be used to investigate the impact of these limits on the results of the multi-criteria optimization.

Among the implemented methods to take the constraints for the different scenarios in stochastic optimization into account there is also a method to define a probability that constraints are fulfilled – so-called chance-constraint approach [14] – which is not considered here.

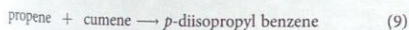
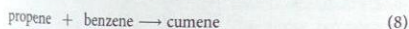
3.2 Stochastic Optimization

In stochastic optimization the objectives of the different scenarios should be weighted according to their probability to determine the expected value $E[\dots]$. Since normally the probability distribution is not known quite often equal weighting (uniform distribution) or normal distribution of the different scenarios are chosen which results in the mean value for the objective. One possibility is to replace an objective by its mean over all uncertainty scenarios. In some cases it might be interesting to reduce the variance (square of the standard deviation) of the distribution. Therefore, in the setup of the stochastic optimization it is alternatively possible to replace the objective by its standard deviation.

If inequality constraints are present in the stochastic optimization problem there are different possibilities to take them into account. Using also an expected value for the constraints will lead to solutions in which the active constraints are only fulfilled for 50 % of the scenarios in case of a normal distribution. This normally is not acceptable. In chance-constraint optimization (cf. [14]) it is possible to define a probability to which extent the constraints should be fulfilled. Here a version in which the constraints have to be fulfilled simultaneously for all scenarios similar to the proceeding for the robust optimization was used.

4 Cumene Process Example

A scheme of the cumene process is shown in Fig. 4. Benzene and propene containing 5 mol % of propane are used as feedstocks. The feeds are mixed with recycled, mainly unconverted benzene and fed into an evaporator. The mixture is then heated in a feed-effluent heat exchanger and subsequently heated up to temperatures above 330 °C. The reactor is a shell-and-tube reactor. The tubes are filled with catalyst and there the following reactions take place:



The model for the reaction rate is:

$$r_1 = k_1 c_{\text{propene}} c_{\text{benzene}} \quad (10)$$

$$r_2 = k_2 c_{\text{propene}} c_{\text{cumene}} \quad (11)$$

The kinetics are expressed by the Arrhenius ansatz:

$$k_i = k_{0,i} \exp\left(\frac{E_{A,i}}{RT}\right) \quad (12)$$

with:

$$k_{0,1} = 2.8 \cdot 10^7 \text{ L mol}^{-1}, E_{A,1} = 104\,251 \text{ J mol}^{-1} \quad (13)$$

$$k_{0,2} = 2.32 \cdot 10^9 \text{ L mol}^{-1}, E_{A,2} = 146\,873 \text{ J mol}^{-1} \quad (14)$$

The reaction heat is used to produce 40 bar(g) steam. The reactor outlet is cooled and flashed. Propane is removed with the overheads of the flash. In the first column of the process unconverted benzene is removed and recycled to the feed section of the reactor. The remaining bottoms are fed in a second column where cumene is the top product with a desired purity of 99.9 mol %. The design capacity target is 98 kt per year. The bottom product of the column contains the undesired side product *p*-diisopropyl benzene (*p*-diipb).

Details about the cumene process have been described by Luyben [18]. The fluid properties in the system are modelled with the Soave-Redlich-Kwong (SRK) equation of state with Peneloux volume correction [19]. Parameters of this model are given in Tab. 2. Based on a total cost (for 10 a with discounted operational expenditures, discount rate 11 %) minimization the design of the process shown in Fig. 4 has been determined, the gray parameters reflect the numbers which have been adjusted, the black ones were fixed during optimization.

Table 2. Parameters of the Soave-Redlich-Kwong equation of state for the binary system cumene + *p*-diisopropylbenzene. The binary interaction parameter is $k_{ij} = 0$.

	p_C [bar]	T_C [K]	ω [-]
cumene	32.00	638.35	0.3444
<i>p</i> -diisopropylbenzene	24.50	684.00	0.3587

The following assumptions are made for the basis of this design. The heat exchanger, pumps, and columns are designed for 120 % load, the reactor design is dimensioned for 105 % load, and the reactor tubes length and diameter are built as described by Luyben [18]). The heat exchanger are assumed with heat transfer coefficients (U -values) for gas of $60 \text{ W m}^{-2} \text{ K}^{-1}$ and for all others of $1 \text{ kW m}^{-2} \text{ K}^{-1}$, column height (2 stages per m + 5 m) and diameter ($F_{\text{max}} = 2 \text{ Pa}^{0.5}$), and costs for catalyst 9.2 € kg^{-1} , benzene 957 € m^{-3} , propene 192 € t^{-1} , steam 7.3 € t^{-1} , cooling water 1.8 ct m^{-3} , electricity 7.3 € MWh^{-1} , fuel gas 20 € MWh^{-1} , and boiler feed water 0.275 € m^{-3} . The catalyst life time is assumed as of 2 a: initial fill is included in investment, refill is part of operational expenditure, and credit for heating value (cf. [18]) of stream 7 and 9 has been taken into account.

Tab. 3 shows the results for the sizes of the heat exchangers. A stream table for this design is given in Tab. 4. Concerning the design there exist some uncertainty about the

done in the frame of the CHEMASIM source code, taking advantage of the equation-oriented CHEMASIM approach. Nevertheless, the approach is generic and can be implemented in principle in any process simulator. There are no limitations regarding modeling depth, used equipment, or cost functions.

The approach is illustrated by an example, the design of a separation of an azeotropic mixture (acetone + chloroform) by distillation. Two variants are compared: a pressure-swing and an entrainer distillation. Even though the example is academic, the studied optimization problem is challenging enough to prove the feasibility and advantages of the presented MCO approach and its software implementation. By comparing not single optimal points but complete Pareto sets, the decision maker gains insight into the conditions for which a certain variant is better. This would be very difficult, if not impossible, when process parameters would be varied empirically.

We expect that with the new method for many existing plants, a substantial improvement in the performance can be obtained, and that the design of new processes will gain in quality and speed.

Acknowledgments

We are grateful for valuable discussions about the approximation algorithms with Ivan Serna Hernández and Phil Süß.

Appendix A. Scalarizations

In order to calculate Pareto-optimal points, we perform a scalarization of the objectives to arrive at a single objective function to be minimized. In the following, we shortly sketch the weighted sum (Ehrgott, 2005) and Pascoletti–Serafini (Pascoletti & Serafini, 1984) scalarizations.

A.1. Weighted sum scalarization

Let $\mathbf{f}$ be the n -component vector of objective functions, and $\mathbf{w}$ be a n -component vector of scalar weights. We define the scalarized objective function $F := \mathbf{w}^T \mathbf{f}$. We choose the signs of the weights such that Pareto-optimal points are calculated by minimizing F subject to the frontier conditions. We denote such a solution by $\mathbf{f}^*$, corresponding to a vector $\mathbf{f}^*$ in the objective space. The weight vector is normal to the tangent hyperplane which touches the Pareto set in $\mathbf{f}^*$. Fig. 8 illustrates this situation.

A.2. Pascoletti–Serafini scalarization

Whereas in the weighted sum approach, the hyperplane normal to the weight vector is shifted until it touches the Pareto set, the Pascoletti–Serafini scalarization (Pascoletti & Serafini, 1984) consists in choosing a direction along which the Pareto set shall be

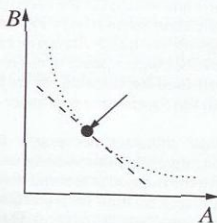


Fig. 8. Sketch of the weighted sum scalarization for two objectives A, B. The weight vector (arrow) is perpendicular to the hyperplane (dashed) tangent to the Pareto set (dotted). The corresponding Pareto point is the full circle.

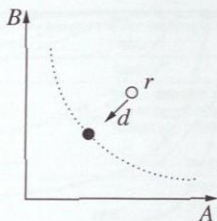


Fig. 9. Sketch of the Pascoletti–Serafini scalarization for two objectives A, B. The direction vector $\mathbf{d}$ points from a feasible reference point $\mathbf{r}$ (open circle) to the Pareto set; the resulting Pareto point is the full circle.

encountered. Let $\mathbf{f}$ be the n -component vector of objective functions, $\mathbf{d}$ be a n -component direction vector and $\mathbf{r}$ a feasible reference point in the objective space. Then the task is as follows:

$$\begin{aligned} \max \quad & \lambda \\ \text{s.t.} \quad & \mathbf{r} + \lambda \mathbf{d} = \mathbf{f}, \end{aligned}$$

where any further constraints are contained implicitly. The solution of this single-objective problem yields a Pareto-optimal point, parameterized by $\mathbf{d}$. A sketch of this scalarization scheme is shown in Fig. 9.

Appendix B. Navigation

In this section, we summarize the linear problem underlying the navigation process in the objective space. This formulation is closely related to Küfer et al. (2009, chap. 5). Let us first introduce some notation. The objective space is n -dimensional, all objectives are to be minimized. The m precalculated Pareto points are $\mathbf{p}^1, \dots, \mathbf{p}^m \in \mathbb{R}^n$, which we put together to a matrix $\mathbf{P} = (\mathbf{p}^1, \dots, \mathbf{p}^m)$. We denote by $\mathbf{e}_j$ the j th unit vector, $\mathbf{1} \in \mathbb{R}^m$ is the column vector of all ones $(1, \dots, 1)^T$. Then the approximated Pareto set, which is given by polyeder of convex combinations of the initial solutions, is defined by $\{\mathbf{P}\lambda : \lambda \geq 0, \mathbf{1}^T \lambda = 1\}$.

Assume we start navigation at a start point $\mathbf{p}^S \in \mathbb{R}^n$ and move slider j to some value $\mu \in \mathbb{R}$. Then we project the reference point $\mathbf{p}^R$, defined by $\mathbf{p}^R := \mathbf{p}^S + (\mu - \mathbf{p}_j^S) \mathbf{e}_j$, along the direction $\mathbf{r} := \mathbf{1} - \mathbf{e}_j$ onto the approximated Pareto set. This is sketched in Fig. 10. The direction $\mathbf{r}$ is chosen such that the projection is done in the plane with $p_j = \mu$, and that the remaining quantities are changed equally. We furthermore want the convex combination to satisfy some active

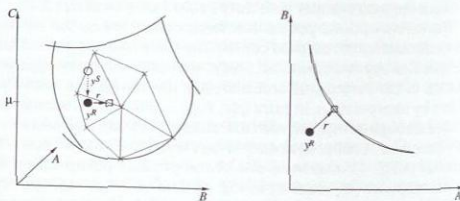


Fig. 10. Sketch of the projection done while navigating on a surface spanned by three objectives A, B, C. Here we assume that the slider corresponding to C is moved to a value μ . The start point $\mathbf{p}^S$ (open circle), reference point $\mathbf{p}^R$ (full circle) and projected point (open square) are shown together with the Pareto set. Crosses mark the calculated Pareto points, straight lines the corners of the convex hull which constitutes our approximation to the Pareto set. In the right panel, the $y_C = \mu$ -plane together with the projection direction are given.

Table 6

NRTL model (Renon & Prausnitz, 1968) parameters for the description of the vapor–liquid equilibrium in the ternary system (acetone + chloroform + benzene).

Component <i>i</i> Component <i>j</i>	Acetone Chloroform	Acetone Benzene	Benzene Chloroform
a_{ij}	0	0	0
b_{ij}/K	0	0	0
b_{ji}/K	−61.82	−40.14	−46.13
c_{ij}	−173.50	187.65	−10.71
c_{ji}	0.3	0.3	0.3

bounds lb and ub. Putting everything together, we arrive at the linear problem

$$\begin{aligned} \min \quad & z \\ \text{s.t.} \quad & p^R + zr \geq P\lambda \\ & (P\lambda)_j = \mu \\ & lb \leq (P\lambda)_j \leq ub \\ & 1^T \lambda = 1 \\ & \lambda \geq 0, \end{aligned}$$

which is solved during the navigation process. As a result, one obtains the convex coefficients λ which yield, according to $p_{\text{nav}} = P\lambda$, the new navigated point p_{nav} in objective space. To calculate the corresponding point in design space, we consider the design variables f^j corresponding to a Pareto point p^j and construct the matrix $F = (f^1, \dots, f^m) \in \mathbb{R}^L$. Then the convex combination of free design variables $f_{\text{nav}} = F\lambda$ is the navigated point in design space which corresponds to p_{nav} .

Appendix C. Physical property data of the example system

The pure component properties required for the simulation are: vapor pressure, enthalpy of vaporization, heat capacity of constant pressure of the ideal gas. The models for these properties are taken from the DIPPR Database (Dippr Project 801, 2009) for the substances acetone, chloroform and benzene.

Despite the high pressure in the pressure column of the pressure–swing distillation the vapor phase is assumed to be ideal. For the exemplary study of this work, this simplification is considered sufficient. More sophisticated approaches could be used without further problems within the described optimization method. For the non-ideality of the liquid phase the NRTL model (Renon & Prausnitz, 1968) is used. The parameters are given in Table 6.

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6 Remarks and Improvements

The investigations considered in this example relied on a conventional design based on a total cost minimization for the nominal (un-perturbed) values of the uncertain parameters. Since usually a design should work for all possible uncertainties also a robust design could be used. One problem in this case is that the design rules for sizing the equipment, which form the basis for the cost estimation, are normally already conservative to cover all uncertainties. So for the use of a robust-design optimization new design rules would be required.

Furthermore robust optimization often leads to a costly, overconservative design. The requirements of a robust design of a plant are closely related to the possibility to adjust operating parameters for a chosen design to account for the uncertainty. Here, it is possible to extend the robust optimization in future to a two-stage stochastic programming with recourse formulation, e.g., Steinmel and Engell [21]: "[...] process synthesis and design problems with uncertain parameters naturally lead to two-stage stochastic problems as the design parameters have to be fixed while the operating parameters can be adapted to the realization of the uncertain parameters. The core idea behind two-stage stochastic programming is to optimize the first stage decisions (here, the design parameters) for a suitable cost function that is computed for an optimal choice of the second stage variables for each scenario. Thus, the option to counteract the uncertainties is anticipated in the decision, making the result much less conservative than, e.g., a worst-case design. The design must be feasible for all realizations of the uncertainty, however, only after adaptation of the second stage variables (operational parameters)." But here also new design rules would be necessary.

Further helpful improvements of the setup and execution of the multi-criteria optimization under uncertainty are:

- Inclusion of feasibility runs which ensure that each initial run during the optimization is based on a feasible parameter set.
- In some cases problems with the solver might arise which are probably to be caused by the linear dependence of the gradients of the constraints. This can be improved by the use of entropic smoothening (cf. [22, 23])

7 Conclusions and Outlook

The possibilities to analyze the impact of uncertainty on simulation and optimization are useful in many contexts.

- (1) To investigate the impact of uncertainty on simulation:
 - show variability of simulation results,
 - identify parameters which have to be determined with lower uncertainty
 - identify significant parameters for model adjustment or optimization,

- investigate different control concepts for process fluctuations (Oldenburg et al. [9]),
- Sensor placement (Oldenburg et al. [9]).
- (2) To be used within optimization:
 - show variability of optimization results,
 - stochastic and/or robust optimization,
 - optimal design of experiments.

The use of the different options in sensitivity analysis and multi-criteria optimization produce a lot of different simulations which are of great value for decision support of the engineer. Only by comparing different solutions and options the engineer reaches a good understanding of the situation and can make a sound decision.

We are grateful for valuable contributions in the project by Oliver Hirth, Achim Wechsung (BASF) and Volker Maag, Karl-Heinz Küfer (Fraunhofer ITWM) and Hans Hasse (Univ. of Kaiserslautern).

Symbols used

c	[mol L ⁻¹]	molarity (moles per volume)
E_A	[J mol ⁻¹]	activation energy
D	[m]	Diameter
f	[-]	objective
F	[Pa ^{0.5}]	F factor
k	[L mol ⁻¹]	kinetic constant
k_{ij}	[-]	binary interaction parameter
N	[-]	Number of feed stage, total stages or tubes
p	[-]	parameter
p	[bar]	pressure
r	[mol h ⁻¹ L ⁻¹]	reaction rate per volume
R	[J mol ⁻¹ K ⁻¹]	universal gas constant
RR	[-]	reflux rate
s	[-]	scenario
T	[K]	temperature
U	[W m ⁻² K ⁻¹]	heat transfer coefficient
w	[-]	weights

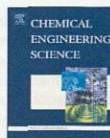
Greek symbols

θ_s	[-]	vector of uncertain parameters for scenario s
ω	[-]	acentric factor

Subscripts

C	at the critical point
feed	feed stage
max	maximal
p	parameter
*	worst case

Paper II: On the Effort of Approaching Pure Components and Azeotropes in Distillation [Bortz et al., 2015a]



On the effort of approaching pure components and azeotropes in distillation

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AUTHOR HIGHLIGHTS

- We quantify efforts to approach singular points in distillation.
- We propose novel augmented residue curve maps or distillation line maps.
- Empirical findings on the separation effort to remove impurities are confirmed.

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ABSTRACT

In most distillation problems, the desired products are located at the singular points of the vapor–liquid equilibrium, i.e. pure components or azeotropes. The effort to approach these points depends on the specified purity of the product and tends to infinity as the composition approaches that of a pure component or azeotrope. In the present work, a method to quantify this effort in terms of equilibrium stages is given. It is shown that there is a constant lower bound on the number of stages required to decrease the impurity δ of the product by a certain factor b . Further, it is shown that this lower bound is proportional to the logarithm of c . The results of the method are valid for ideal and non-ideal systems of any number of components. The information is obtained from the eigenvalues and eigenvectors of the singular points, no process simulations are needed. We propose adding key figures derived from the eigenvalues to distillation line/residue curve diagrams to immediately grasp the effort upon approaching the singular points.

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1. Introduction

In conceptual separation process design, two questions have to be answered: First, whether a certain flow sheet is thermodynamically feasible, irrespective of technical limitations. Second, if such a feasible flow sheet is found, whether the technical requirements can be met with an acceptable effort, for which estimates are needed. This contribution focuses on the second task and addresses the number of equilibrium stages needed for separations by distillation.

Diagrams of distillation lines (discrete, also called c-lines) and residue curves (continuous) are widely used in conceptual process design. For a definition, their construction and a survey on the use in conceptual design the reader is referred to the comprehensive review of Kiva et al. (2003). Both distillation lines and residue curves originate

and end in singular points of the vapor–liquid equilibrium (VLE) diagram, either unstable or stable nodes. Further, there may be saddle points which are singular points passed by distillation lines and residue curves (Gurikov, 1958). Singular points, and hence possible nodes or saddles, of the VLE are all pure components and azeotropes of the system (Haase, 1949). The type of a singular point (stable/unstable node or saddle) depends on the signs of the eigenvalues of a matrix derived from the differential equations that describe the residue curves. This was already shown by Russian researchers around Zharov and Serafimov in the late 1960s (Kiva et al., 2003).

The VLE and the topology of the dynamical system described by the residue curve equations determine the location and type of the singular points which are the basis of conceptual process design. A large number of methods which use distillation line and residue curve maps are available to determine the feasibility of a distillation column or the minimum reflux ratio of a column. They are usually based on the limiting cases of an infinite number of equilibrium stages (simply “stages” in the following) and/or total reflux. The minimum reflux ratio, and thus minimum energy demand, is obtained for an

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infinite number of stages (Underwood, 1948; Widagdo and Seider, 1996). Thereby, pinches play a crucial role. Composition pinches are found at column cross-sections where vapor and liquid are in equilibrium, so that a concentration driving force is absent and the column composition profile is unchanging from stage to stage. Studies of the properties of pinches and their loci (pinch curves) in ternary diagrams led to a number of methods to determine minimum reflux ratios for given product specifications, e.g. the boundary value method (Levy et al., 1985), an eigenvector method (Poellmann et al., 1994), the rectification body method (Bausa et al., 1998) or the method of the shortest stripping line (Lucia et al., 2006, 2008). Two ideas among these approaches are of direct relevance to this work. Firstly, Poellmann et al. (1994) linearized the VLE around the pinch point and used eigenvalue theory to calculate volumes inside which the column profiles have to approach the pinch points. As their motivation was different, they did not give measures of how fast the profiles approach the pinch points. This work will finally provide these measures. Secondly, Lucia et al. (2006, 2008) found that the length of the stripping section's profile (defined using the 2-norm in the concentration space) correlates with the energy demand of the column. For the minimum length of this profile, the energy demand (and hence the reflux ratio) of the column is minimized. When approaching the singular points of the VLE, the length of the profile does however not change significantly. Thus, this is an insensitive measure to quantify the separation effort to approach the singular points. This work provides the required measure in terms of the number of stages.

In continuous distillation, the minimum number of stages to meet given product specifications is obtained at total reflux (Stichlmair and Herguicela, 1992; Widagdo and Seider, 1996). In this case, the profile of the column in the ternary diagram equals a segment of the distillation line connecting both column products (Kiva et al., 2003). The number of vertices of the segment, usually determined by tray-to-tray calculations, equals the number of stages (Stichlmair and Fair, 1998). Thus, the distillation lines provide a direct measure for the difficulty of the separation: the larger the distance (measured by the 2-norm) from stage to stage in the concentration space, the easier the separation (Stichlmair, 1988).

Of particular practical interest are column products in close vicinity of pure components or azeotropic points, thus in vicinity of the singular points of the VLE. In real columns, the singular points cannot be obtained as column products since an infinite number of stages would be required (even with total reflux provided). While the remainder of the introduction concerns the separation effort for approaching a node singular point, the proposed method is also applicable for separations in which the profile at total reflux and infinite number of stages passes through a saddle. This case is discussed in more detail in the main text.

Consider a distillation column in which one desired product is a pure component which is a node of the VLE diagram and the total amount of impurities δ is specified. Upon decreasing δ the effort for the separation (expressed in terms of number of stages at total reflux) will increase, with the number of stages approaching infinity as δ tends to 0. In the present work, a method to assess that effort without having to carry out process simulations is described. As the analysis underlying the method is based on distillation line/residue curve diagrams, the case of total reflux is considered, and the separation effort is expressed in terms of the required number of stages. Any number of stages given in the present work is therefore a lower bound to the number of stages which would be required for a corresponding separation at finite reflux ratio, i.e. a separation in a real distillation column.

Assume that two design options for the above column with different specifications on δ are given, e.g. $\delta_{\text{spec},1} = 0.01$ mol/mol and $\delta_{\text{spec},2} = 0.001$ mol/mol. Clearly, additional stages are required to achieve the lower impurity specification $\delta_{\text{spec},2}$. We are interested

in quantifying that increase in the number of stages and therefore only consider the transition from points with $\delta = \delta_{\text{spec},1}$ to those with $\delta = \delta_{\text{spec},2}$ which lie on the same distillation line or residue curve. The number of stages required for such a transition in the vicinity of a singular point can be obtained from an analysis of the eigenvectors and eigenvalues of the singular point. It is shown that a logarithmic relation exists between the ratio $\delta_{\text{spec},1}/\delta_{\text{spec},2}$ of the impurities and the number of stages N required to achieve the desired step in purity, which is of the type $\ln(\delta_{\text{spec},1}/\delta_{\text{spec},2}) = cN$. In the literature, this logarithmic dependency was analytically derived for the special cases of systems of constant relative volatilities (Fenske, 1932; Cao et al., 2012) but, to the best of our knowledge, not in a general way. Further, such a logarithmic dependency was found empirically through simulations and experiments for non-ideal systems (Burger and Hasse, 2013; Eduljee, 1975). This work analytically derives the logarithmic dependency for the general case of non-ideal systems. The factor c depends on the eigenvalues of the singular point which is approached and the direction from which it is approached. The eigenvalues and eigenvectors of the singular points, as well as the value of c can be readily calculated from the thermodynamic VLE model without tray-to-tray calculations.

The paper is organized as follows. The next section is devoted to the mathematical derivation of a lower bound on the number of stages required to change the impurities of column products. In Section 3 the practical use of the calculated information is demonstrated. In Section 4 an augmented diagram of distillation lines is suggested which contains information about separation complexity.

2. Methodology

2.1. Basic definitions

The prescription to calculate distillation lines is as follows (Kiva et al., 2003):

$$\mathbf{x}^{(n+1)} = \mathbf{y}(\mathbf{x}^{(n)}) \quad (1)$$

starting from any point $\mathbf{x}^{(0)}$ in the composition space. The vector $\mathbf{x} \in \mathbb{R}^{N_C}$ denotes the liquid phase composition (mole fractions) in a system of N_C components. The vector function

$$\mathbf{y} = \mathbf{y}(\mathbf{x}), \quad \mathbf{y} \in \mathbb{R}^{N_C} \quad (2)$$

maps $\mathbf{x}$ to the composition $\mathbf{y}$ of the vapor phase in equilibrium with $\mathbf{x}$.

Whereas the stage index n in Eq. (1) is discrete, residue curves are described by in terms of a continuous parameter τ (Van Dongen and Doherty, 1985):

$$\frac{dx_i}{d\tau} = y_i - x_i, \quad i = 1, \dots, (N_C - 1), \quad (3)$$

where in this context, one can think of τ as a measure of the normalized column height. The solutions of these differential equations are called residue curves. In this work, we assume total reflux of the column. In this case the pinch points of the column, denoted $\mathbf{x}_P$, are equal to the stationary or singular points of Eq. (1). They are the common singular points of (1) and (3) given by

$$\mathbf{x}_P = \mathbf{y}(\mathbf{x}_P). \quad (4)$$

A singular point is either a pure component or an azeotrope, and is either an unstable node, a stable node or a saddle. Its type is defined by the eigenvalues of the matrix $\mathbf{A}$ on the right side of (3) at the singular point P which involves the Jacobi matrix with negative sign as follows:

$$A_{ij} = -\left| y_j - \frac{\partial y_j}{\partial x_i} \right|, \quad i, j = 1, \dots, (N_C - 1). \quad (5)$$

Therein, $\mathbb{1}$ is the unit matrix with entries $\mathbb{1}_{ij} = 1$ for $i = j$ and 0 otherwise. For ternary systems ($N_C = 3$) for instance, matrix $\mathbf{A}$ is given by

$$\mathbf{A} = \begin{pmatrix} \left(1 - \frac{\partial y_1}{\partial x_1}\right)_p & -\frac{\partial y_1}{\partial x_2}\bigg|_p \\ -\frac{\partial y_2}{\partial x_1}\bigg|_p & \left(1 - \frac{\partial y_2}{\partial x_2}\right)_p \end{pmatrix}. \quad (6)$$

If the eigenvalues of $\mathbf{A}$, denoted with λ_i^A , are all negative (all positive), then the singular point is stable (unstable respectively). If there are positive and negative eigenvalues, then the singular point is a saddle. The $(N_C - 1)$ eigenvectors of $\mathbf{A}$, denoted $\mathbf{v}_i$, evaluated at a pure component, are collinear with the $(N_C - 1)$ binary edges of the concentration simplex meeting in the pure component. For a ternary system visualized in a ternary diagram the two eigenvectors of $\mathbf{A}$ at a pure component vertex point along the two adjacent binary edges.

In Appendix B, the dependence of matrix $\mathbf{A}$ on the activity coefficients in infinite dilution is derived, for the common case in which the VLE is modeled by the extended Raoult's law. This derivation also shows the sensitivity of $\mathbf{A}$ and its eigenvalues on errors in property data.

Our question now is as follows: How many stages do we need at least to reduce the impurity close to a singular point by a certain factor?

2.2. Distillation lines

The deviation $\delta^{(n)}$ from the singular point is defined such that the liquid composition on stage n is split into the contribution from the singular point, $\mathbf{x}_p$, and $\delta^{(n)}$:

$$\mathbf{x}^{(n)} = \mathbf{x}_p + \delta^{(n)}. \quad (7)$$

Inserting into Eq. (1), and after a Taylor expansion of the VLE function $\mathbf{y}$ around $\mathbf{x}_p$, we obtain

$$\delta^{(n+1)} = \frac{\partial \mathbf{y}}{\partial \mathbf{x}} \bigg|_p \delta^{(n)} + \mathcal{O}\left(\left(\delta^{(n)}\right)^2\right), \quad (8)$$

where the $\mathcal{O}$ -notation on the right-hand side is defined as follows: $f(x) = \mathcal{O}(g(x)) \Leftrightarrow \lim_{x \rightarrow 0} f(x)/g(x) = c$ with an unknown constant c . In Eq. (8), we only keep the linear term which is justified if the deviation from the singular point is sufficiently small (i.e. the terms of second order and higher of the Taylor expansion are discarded). We will show below that numerically, this is already the case for moderately small deviations.

Starting from $\delta^{(0)}$, the corrections can be updated from stage to stage. By iterating only the leading term in Eq. (8), one arrives at

$$\delta^{(n)} = \left(\frac{\partial \mathbf{y}}{\partial \mathbf{x}} \bigg|_p\right)^n \delta^{(0)} = (\mathbf{1} - \mathbf{A})^n \delta^{(0)}, \quad (9)$$

where we have inserted the definition of matrix $\mathbf{A}$ from Eq. (5).

Let us, for now, assume that

$$\delta = \delta_i^v \mathbf{v}_i \quad (10)$$

for some single $i \in \{1, \dots, (N_C - 1)\}$, the respective eigenvector $\mathbf{v}_i$ and a constant δ_i^v , i.e. δ is parallel to an eigenvector of $\mathbf{A}$. In this case, Eq. (9) simplifies to

$$\delta_i^{(n),v} = (1 - \lambda_i^A)^n \delta_i^{(0),v} \quad (11)$$

where λ_i^A is the eigenvalue corresponding to $\mathbf{v}_i$. Furthermore, we define $\delta_{\text{spec},1} := \delta_i^{(0),v}$ and $\delta_{\text{spec},2} := \delta_i^{(N_i),v}$ which are now interpreted as specifications on the impurity. Then, with $n = N_i$, one can reformulate Eq. (11) as

$$N_i = \left[\ln(1 - \lambda_i^A) \right]^{-1} (\ln \delta_{\text{spec},2} - \ln \delta_{\text{spec},1}). \quad (12)$$

Eq. (12) yields the answer to our initial question, namely the minimum number of stages N_i needed to reduce the impurity with respect to the singular point to a certain amount. In Appendix C it is shown that evaluation of Eq. (12) for systems with constant relative volatilities results in the well-known Fenske (1932) equation. This is not surprising as the Fenske equation is derived using an analogous stage to stage mapping.

In the more general case that δ is not parallel to an eigenvector of $\mathbf{A}$, it can be written as linear combination of the eigenvectors $\mathbf{v}_i$ of $\mathbf{A}$:

$$\delta = \sum_{i=1}^{N_C-1} \delta_i^v \mathbf{v}_i, \quad (13)$$

where δ_i^v are again constant pre-factors. The scalar specification δ_{spec} on the impurity is defined by

$$\delta_{\text{spec}} := \sum_{i=1}^{N_C-1} \delta_i^v. \quad (14)$$

Insertion of Eq. (13) into Eq. (9) yields

$$\sum_{i=1}^{N_C-1} \delta_i^{(n),v} \mathbf{v}_i = \sum_{i=1}^{N_C-1} (1 - \lambda_i^A)^n \delta_i^{(0),v} \mathbf{v}_i. \quad (15)$$

A further simplification is possible by noting that in the sum of powers on the right hand side, asymptotically for $n \gg 1$, the term with the smallest λ_i^A dominates, leading to a maximal value in $(1 - \lambda_i^A)$. The index i of this eigenvalue is denoted by $i = \min$. Then

$$\delta_{\min}^{(n),v} \left(\mathbf{v}_{\min} + \sum_{i \neq \min}^{N_C-1} \frac{\delta_i^{(n),v}}{\delta_{\min}^{(n),v}} \mathbf{v}_i \right) = \left(1 - \lambda_{\min}^A \right)^n \delta_{\min}^{(0),v} \mathbf{v}_{\min} + \sum_{i \neq \min}^{N_C-1} \left(\frac{1 - \lambda_i^A}{1 - \lambda_{\min}^A} \right)^n \frac{\delta_i^{(0),v}}{\delta_{\min}^{(0),v}} \mathbf{v}_i. \quad (16)$$

Asymptotically for large n , each term in the sum on the right-hand side becomes arbitrarily small due to the exponent n , and so do the corresponding terms on the left-hand side. Thus for large stage numbers,

$$\delta_{\min}^{(n),v} = (1 - \lambda_{\min}^A)^n \delta_{\min}^{(0),v}, \quad (17)$$

and all other terms $\delta_i^{(n),v}$ are negligible. This result permits an explicit solution for n . One defines the specifications $\delta_{\text{spec},1} := \delta_{\min}^{(0),v}$ and $\delta_{\text{spec},2} := \delta_{\min}^{(N_i),v}$. All other contribution to δ_{spec} in Eq. (14) can be assumed to be exponentially small as argued above. Then from Eq. (17) with $n = N_i$, the number N_i of additional stages to reach $\delta_{\text{spec},2}$ instead of $\delta_{\text{spec},1}$ is

$$N = c (\ln \delta_{\text{spec},2} - \ln \delta_{\text{spec},1}), \quad c = \left[\ln(1 - \lambda_{\min}^A) \right]^{-1}. \quad (18)$$

This result is remarkable in so far as only one eigenvalue dominates the separation effort close to the singular points (except for the case that the singular point is approached exactly along one of the other eigenvectors). Not only is the separation effort dominated by that eigenvalue, but also the direction in which any distillation line approaches the singular point. Asymptotically, all distillation lines approach the singular point along the eigenvector corresponding to $\lambda_{\min}$. Thus one is back to Eq. (12), with the index i replaced by the index $\min$, denoting the smallest eigenvalue. This asymptotic approximation improves for larger differences between the smallest eigenvalue and eigenvalues other than the smallest.

If all eigenvalues are of similar size, then in Eq. (15) one can approximately factor out the eigenvalue-terms, leading then to a relation equivalent to Eq. (12), which then would be independent of the eigenvector index i . Summarizing, the case where the singular point is approached from any direction is given by expressions equivalent to Eq. (12), which we will refer to in the following.

2.3. Residue curves

As shown in Appendix A, one can treat the residue curves described by Eq. (3) in a similar way. We start with

$$\mathbf{x}(\tau) = \mathbf{x}^p + \delta(\tau), \quad (19)$$

and instead of Eq. (12), we arrive at

$$N_i = \left[-\lambda_i^A \right]^{-1} (\ln \delta_{\text{spec},2} - \ln \delta_{\text{spec},1}), \quad (20)$$

where N_i now denotes the normalized height of the column. Similar to Eq. (18), one finds for the case when the singular point is approached from a general direction not along the eigenvectors:

$$N = c (\ln \delta_{\text{spec},2} - \ln \delta_{\text{spec},1}), \quad c = \left[-\lambda_{\min}^A \right]^{-1}, \quad (21)$$

Eq. (20) is obtained from Eq. (12) by expanding the logarithm to linear order and neglecting the higher order terms. This approximation gets better with a decreasing absolute value of λ_i^A . In other words, the difference between residue curves and distillation lines with identical starting points increases with increasing values of λ_i^A . To the best of our knowledge, this quantitative relation between residue curves and distillation lines has not been discussed before.

3. Application to column design

Eqs. (12) and (20) have a practical meaning. First note that apart from the number of stages, they only depend on the distances to a pinch along the corresponding eigenvectors and on the eigenvalues of the matrix $\mathbf{A}$. It is straightforward to compute the number of stages N_i (or the packing height) needed to reduce the impurity concentration close to a pinch along an eigenvector by a factor $b > 1$: simply put $\delta_{\text{spec},2} = b^{-1} \delta_{\text{spec},1}$. For example, to reduce the impurity by one order of magnitude, one would choose $b=10$. With b arbitrary, one arrives at our final result:

$$N_i^b = \begin{cases} \left(\left(-\log_b (1 - \lambda_i^A) \right) \right)^{-1} & \text{equilibrium stages} \\ \left(\lambda_i^A \right)^{-1} \ln b & \text{normalized height.} \end{cases} \quad (22)$$

In the first line, the notation $[x]$ denotes the smallest integer which is equal to or larger than x . These quantities are universal in the sense that they only depend on the substance properties.

In the derivation of Eqs. (22), we have implicitly assumed that the singular point is unstable, by requiring that the distance decreases when applying Eq. (1), or, alternatively, Eq. (3). For stable nodes or saddles, the derivation works in complete analogy by starting with

$$\mathbf{y}^{(n+1)} = \mathbf{x}(\mathbf{y}^{(n)}) \quad (23)$$

or, alternatively, with the continuous version:

$$\frac{dy_i}{d\tau} = x_i - y_i. \quad (24)$$

Let us now define the matrix $\mathbf{B}$ as

$$B_{ij} = \frac{\partial x_i}{\partial y_j} \bigg|_p, \quad i, j = 1, \dots, (N_C - 1). \quad (25)$$

By following the same steps that lead to Eqs. (22), we obtain e.g. for the discrete case

$$N_i = \left[\ln (1 - \lambda_i^B) \right]^{-1} (\ln \delta_{\text{spec},2} - \ln \delta_{\text{spec},1}), \quad (26)$$

Here, λ_i^B stands for the i th eigenvalue of the matrix $\mathbf{B}$, which is the counterpart of Eq. (12). Eventually, this leads to

$$N_i^b = \begin{cases} \left(\left(-\log_b (1 - \lambda_i^B) \right) \right)^{-1} & \text{equilibrium stages} \\ \left(\lambda_i^B \right)^{-1} \ln b & \text{normalized height.} \end{cases} \quad (27)$$

This completes our derivation of lower bounds on the stage number or normalized height.

4. Verification and augmented residue curve map

Eqs. (12) and (26) give a quantitative functional relationship for the number of stages required at total reflux to obtain a product of high purity close to a singular point. In order to demonstrate the validity of these equations, we calculated stage-to-stage profiles according to Eq. (1) close to the singular points along their eigenvectors for a separation in the ternary system acetone, benzene and chloroform. Thereby, we assumed total reflux and used the stage-to-stage equations presented in Lucia et al. (2008). A ternary residue curve map of this system is shown in Fig. 1 along with the eigenvectors of all singular points. Both eigenvectors pointing towards (away from) a singular point represent a stable (unstable) node; one eigenvector pointing toward and the other away from the singular point represent a saddle. For the pure components, the eigenvectors follow the binary edges of the triangular diagram. Additionally, a binary azeotrope (Az) exists in the binary acetone–chloroform subsystem. The VLE is modeled by a NRTL model as given in Bortz et al. (2014).

Distillation lines were calculated in both directions with the following starting points:

- equimolar mixture of acetone and benzene,
- equimolar mixture of chloroform and benzene,
- two points in the binary mixture acetone, chloroform on both sides of the azeotrope,
- one point on the distillation boundary (0.279 mol/mol acetone, 0.0825 mol/mol benzene).

By choosing the starting points on the edges of the diagram and on the distillation boundary, the distillation lines approach the singular point along the eigenvectors. The number of stages N_i counted from the starting point is plotted over the logarithmic distance from the singular point with index i , i.e. the purity specification δ_{spec} for all

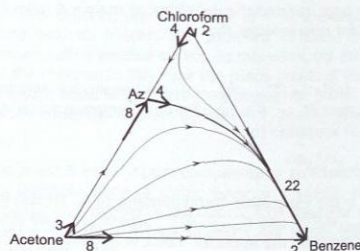


Fig. 1. Augmented residue curve map of the system acetone, benzene and chloroform at 1 bar. At the singular points, the eigenvectors are shown. Their lengths are proportional to the indicated numbers which are the separation efforts N_{10} .

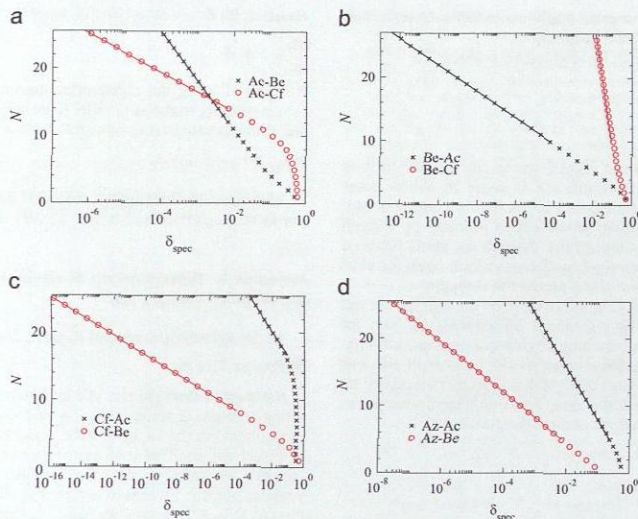


Fig. 2. Stage number vs specification on the impurity for column profiles approaching the four singular points in the ternary mixture acetone, benzene, chloroform. Top left: acetone (Ac), top right: benzene (Be), bottom left: chloroform (CF), bottom right: azeotrope (Az). The symbols denote values obtained from the stage-to-stage profiles at total reflux. Straight lines show the result of the linearization, Eq. (12).

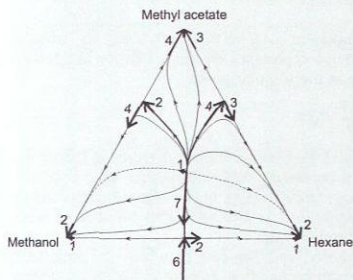


Fig. 3. Augmented residue curve map of the system methanol, methyl acetate, n-hexane at 1 bar. Property modeling adopted from Ryll et al. (2012). At the singular points, the eigenvectors are shown. Their lengths are proportional to the indicated numbers which are the separation efforts N_{10} .

eigenvectors in Fig. 2. In order to facilitate the comparison to Eqs. (12) and (26), only the dependency of N_i on one specification is considered:

$$N_i = c_i \ln \delta_{\text{spec}} + \text{const}_i, \quad (28)$$

where $\delta_{\text{spec},2}$ was renamed to δ_{spec} and the other specification is contained in the constant term; the slope c_i is given in Eqs. (12) and (26). Eq. (28) is a prediction for the stage number N_i as a function of the impurity specification δ_{spec} , which holds asymptotically for small δ_{spec} . Since it is not known a priori how small the impurity specification value has to be in order to yield accurate results, the constant term in Eq. (28) is taken as a fit-parameter that is adjusted such that numerical results of stage-to-stage calculations with very small values for δ_{spec} are met.

In all cases, the prediction of Eq. (28) becomes exact for very small δ_{spec} . Even for impurities in the percentage range the agreement is excellent. For moderate impurities in the order of 0.1 mol/mol, in

many cases, the difference is still as small as one stage number, see, for example, the Be–Ac system in Fig. 2b. In other cases, such as the system Ac–Be, the deviation is substantial for moderate impurities. This is due to higher-order effects in the asymptotic expansion that have not been taken into account here. It would be an interesting challenge for future work to obtain an improvement here that also permits quantitative predictions for the stage number in this moderate-impurity range.

Generally, the different slopes of the lines show the differences in the separation efforts depending on the eigenvalues of the matrices **A** and **B** which are given by the substance properties only. Note that due to the logarithm scale, the slopes of the straight lines in Fig. 2 represent the number of stages required to decrease the impurity by a factor of $b=10$.

We propose to generally augment ternary maps as in Fig. 1. It shows not only the distillation boundary and residue curves, but also contains the values of Eqs. (22) and (27) for the factor $b=10$, which are associated with the appropriate eigenvectors. These are the absolute values of the slopes from Fig. 2 divided by $\ln 10 \approx 2.3$ in order to obtain the logarithm to base ten. These are lower bounds for the number of stages (or normalized height) needed close to the singular point in order to reduce the impurities along the eigenvectors by one order of magnitude. We denote these numbers by the “separation effort N_{10} ”. In Fig. 1, the lengths of the eigenvectors are proportional to the indicated values of N_{10} . The values of N_{10} also have a clear influence on the curvature of the residue curves near the singular points. The singular point is approached by the residue curves rather in the direction of the eigenvector with the greater N_{10} .

For further illustration, Fig. 3 shows the augmented residue curve map for the ternary system methanol, methyl acetate, n-hexane which exhibits a ternary azeotrope. Note that the distillation boundaries (thick lines) and the residue curves approach the ternary azeotrope exclusively in direction of the eigenvector respective to $N_{10}=7$ (parallel or antiparallel), except for a single pair, marked dashed in Fig. 3. The corresponding eigenvector with $N_{10}=1$ shows that approaching the

azeotrope along its direction costs much less in terms of separation effort than along the distillation boundary.

Distillation line maps can be augmented analogously.

5. Conclusions

In this work, we linearized residue curves and distillation lines around the singular points of the VLE in order to obtain lower bounds for the number of equilibrium stages and the packing height, needed to reduce the impurity of distillation products by a given factor. It was shown that a logarithmic dependency exists between this ratio and the minimum number of stages which holds for ideal as well as non-ideal systems of any number of components.

It was further shown how the information on the eigenvalues and eigenvectors of the singular points can immediately be used for assessing the effort upon approaching singular points. These information depend only on the physical properties of the system and it is suggested to add them to maps of distillation lines/residue curves. By this, the designer can immediately grasp how much effort is needed to increase the purity specifications of distillation products.

Nomenclature

A	characteristic matrix of the vapor–liquid equilibrium
b	factor by which the product's purity is increased
B	bottom product of the distillation column
B	reverse characteristic matrix of the vapor–liquid equilibrium
c	proportionality factor
D	distillate
ij	counter for components and eigenvectors
K_i	vapor–liquid distribution coefficient of component i
min	minimal
n	counter for stages
N, N_i	number of stages
N_{10}	minimum number of stages required to increase purity by factor 10
N_C	number of components
p	pressure of the system
p_i^s	vapor pressure of component i
P	singular point
T	temperature
v	eigenvector
x_i	mole fraction of component i in the liquid phase
x	composition vector of the liquid phase based on mole fractions
y_i	mole fraction of component i in the vapor phase
y	vector function resulting in the vapor phase in equilibrium with x
α_{ij}	relative volatility of components i and j
γ_i	activity coefficient of component i
γ_i^∞	activity coefficient of component i at infinite dilution
δ_{spec}	impurity specification of a distillation product
δ	deviation from the singular point
λ	eigenvalue
τ	normalized column height

Appendix A. Asymptotic expansion based on residue curves

In this section, Eq. (20) is derived starting with Eq. (3). One inserts Eq. (19) into Eq. (3) and finds the following differential

equation for δ :

$$\frac{d\delta}{d\tau} = -A \cdot \delta. \quad (\text{A.1})$$

It is solved using the eigenvector decomposition for δ from Eq. (13). Assuming that δ is parallel to the eigenvector i as in Eq. (10), one finds by integrating Eqs. (A.1) from $\tau = 0$ to $\tau = n$:

$$\delta_i^{n,v} = \delta_i^{0,v} \exp(-\lambda_i^n n). \quad (\text{A.2})$$

This equation is analogous to (9) for distillation lines. Following the same steps that lead to Eq. (12) one arrives at Eq. (20).

Appendix B. Determination of eigenvalues of singular points for extended Raoult's law

In the following, extended Raoult's law

$$p_i^s(T)x_i\gamma_i(x, T) = py_i \quad (\text{B.1})$$

is assumed to describe the VLE in which p is the pressure, p_i^s the vapor pressure of component i , y_i and x_i are the molar fraction of component i in the vapor and the liquid phase, respectively, and γ_i is the activity coefficient of component i in the liquid phase. Let us consider a pure component k as singular point of the VLE, i.e. the singular point is located in a vertex of the concentration simplex. First, matrix A according to Eq. (5) is calculated:

$$y_i = \frac{p_i^s(T)\gamma_i(x, T)}{p}x_i \quad (\text{B.2})$$

$$\frac{\partial y_i}{\partial x_i} = \frac{1}{p} \left(p_i^s(T)\gamma_i(x, T) + \frac{\partial(p_i^s(T)\gamma_i(x, T))}{\partial x_i} x_i \right) \quad (\text{B.3})$$

For a component $i \neq k$, x_i equals 0. With γ_{ik}^∞ being the activity coefficient of component i at infinite dilution in k , it follows for the derivative at the singular point:

$$\left. \frac{\partial y_i}{\partial x_i} \right|_P = \frac{p_i^s(T)}{p} \gamma_{ik}^\infty(T). \quad (\text{B.4})$$

Hence, the elements on the main diagonal of matrix A are directly dependent on the γ_{ik}^∞ . This means that large uncertainties in γ_{ik}^∞ lead to large uncertainties in the eigenvalues of matrix A and to large uncertainties in the estimated number of stages and the estimated reflux ratio.

In a similar way, the case in which the singular point is an azeotrope can be handled. For the matrix A we have to calculate the change of y induced by some small shift of x_P . For definiteness, we take this shift to be along an eigenvector v . Thus we are interested in $\partial y(x_P + \lambda v) / \partial \lambda|_{\lambda=0}$. One can show that this quantity is obtained as

$$\left. \frac{\partial y_i}{\partial \lambda} \right|_{\lambda=0} = 1 + x_{i,P} \frac{p_i^{(v)}(T)\gamma_i(x_P + \lambda v)}{p_0} \frac{\partial \lambda}{\partial \lambda} \Big|_{\lambda=0}. \quad (\text{B.5})$$

Thus in this case, it is the slope of γ_i along the direction of the eigenvectors which affects the estimate.

Appendix C. Constant relative volatilities

In the special case of constant relative volatilities, Eq. (12) is equal to the well-known Fenske (1932) equation. This is illustrated for the ternary case and an unstable singular point located at the pure component 1. The relative volatilities are defined as follows:

$$\alpha_{21} = K_2/K_1 = (y_2x_1)/(x_2y_1) = \text{const.} \quad (\text{C.1})$$

$$\alpha_{31} = K_3/K_1 = (y_3x_1)/(x_3y_1) = \text{const.} \quad (\text{C.2})$$

Using that the component fractions sum up to unity,

$$x_1 + x_2 + x_3 = 1 \quad (\text{C.3})$$

$$y_1 + y_2 + y_3 = 1 \quad (\text{C.4})$$

it follows that

$$y_1 = x_1 / (\alpha_{31} + (1 - \alpha_{31})x_1 + (\alpha_{21} - \alpha_{31})x_2) \quad (\text{C.5})$$

$$y_2 = \alpha_{21}x_2 / (\alpha_{31} + (1 - \alpha_{31})x_1 + (\alpha_{21} - \alpha_{31})x_2). \quad (\text{C.6})$$

The derivatives of these expression with respect to x_1 and x_2 are evaluated at the singular point $P = (1; 0; 0)$:

$$\left. \frac{\partial y_1}{\partial x_1} \right|_P = \alpha_{31} \quad (\text{C.7})$$

$$\left. \frac{\partial y_1}{\partial x_2} \right|_P = \alpha_{31} - \alpha_{21} \quad (\text{C.8})$$

$$\left. \frac{\partial y_2}{\partial x_1} \right|_P = 0 \quad (\text{C.9})$$

$$\left. \frac{\partial y_2}{\partial x_2} \right|_P = \alpha_{21} \quad (\text{C.10})$$

Matrix A is given by

$$A = \begin{pmatrix} (1 - \alpha_{31}) & (\alpha_{21} - \alpha_{31}) \\ 0 & (1 - \alpha_{21}) \end{pmatrix}. \quad (\text{C.11})$$

The eigenvalues of A are $\lambda_1^A = 1 - \alpha_{21}$ and $\lambda_2^A = 1 - \alpha_{31}$. Considering the binary subsystem 1–2, the required number of stages to reduce the impurity of component 2 from $\delta_{\text{spec},1}$ to $\delta_{\text{spec},2}$ is given by Eq. (12):

$$N_1 = (\ln \delta_{\text{spec},2} - \ln \delta_{\text{spec},1}) / \ln \alpha_{21} \quad (\text{C.12})$$

The Fenske (1932) equation gives the number of stages to obtain the mole fractions x_1^D and x_1^B in the distillate and bottom products of a distillation column:

$$N = \frac{1}{\ln \alpha_{21}} \ln \frac{x_2^D}{x_2^B} \cdot \frac{x_1^B}{x_1^D}. \quad (\text{C.13})$$

Thus, the required number of stages to reduce the impurity of component 2 in the distillate from $\delta_{\text{spec},1}$ to $\delta_{\text{spec},2}$ is

$$N_1 = \frac{1}{\ln \alpha_{21}} \left[\ln \left(\frac{\delta_{\text{spec},2}}{1 - \delta_{\text{spec},2}} \right) - \ln \left(\frac{\delta_{\text{spec},1}}{1 - \delta_{\text{spec},1}} \right) \right]. \quad (\text{C.14})$$

In the vicinity of the singular point of component 1, i.e. $\delta_{\text{spec},1}$, $\delta_{\text{spec},2} \ll 1$, Eq. (C.14) approximates Eq. (C.12).

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Paper III: Efficient Approach for Calculating Pareto Boundaries under Uncertainties in Chemical Process Design [Bortz et al., 2017]

Efficient Approach for Calculating Pareto Boundaries under Uncertainties in Chemical Process Design

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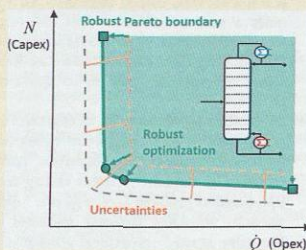
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Supporting Information

ABSTRACT: Taking account of uncertain model parameters in simulation-based flowsheet optimization is crucial in order to quantify the reliability of the optimization results. Since chemical process design is a multicriteria optimization (MCO) task, methods to deal with uncertain Pareto boundaries are needed. The simplest of such methods consists of a sensitivity analysis of the Pareto boundary. In this work, it is shown how going beyond sensitivity analysis can yield favorable process designs not seen by sensitivity analysis alone. This is achieved by taking uncertainties into account by worst and best case Pareto boundaries or by considering the robustness of the Pareto boundary with respect to uncertain model parameters as additional objectives. In order to increase computational efficiency, for the first time, an adaptive scalarization approach is used to deal with uncertainties in MCO. The methods are illustrated by the calculation of a NQ curve of a distillation column.



INTRODUCTION

During flowsheet simulation and evaluation, values of different quantities have to be assigned. These quantities may be categorized with respect to their origin/definition:

- Physical model parameters, e.g., reaction constants or interaction parameters of thermodynamic phase equilibrium models
- Design parameters describing unit operations, like the number of theoretical stages of a distillation column and feed stage or the separation efficiency of a theoretical stage
- Operating parameters, like a feed or product composition, boil-up and reflux ratio, split ratios, flow rates
- Evaluation parameters, e.g., cost parameters or parameters of sustainability metrics

Here, all parameters are allocated to one of the groups that are shown in Figure 1: parameters that are fixed and considered certain in the sense that their uncertainty is neglected, parameters that are fixed but uncertain, and parameters that are used as optimization variables. For example, physical model parameters are typically not available as design parameters. Depending on how accurately they are known, they will be considered as either fixed, certain parameters, or uncertain parameters.

Depending on the problem formulation, several cases are common. In classical optimization, the optimization variables are varied to obtain some optimal value(s) for the objective(s).

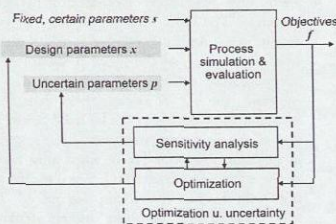


Figure 1. Scheme illustrating the simulation-related quantities when dealing with optimization under uncertainties.

If some optimum is found, the optimization variables can be fixed, and the influence of the uncertainties represented by the uncertain parameters can be analyzed using sensitivity analysis that varies the uncertain parameters systematically. When optimization and the systematic variation of the uncertain parameters are combined, one speaks of optimization under uncertainty. The difference of these two approaches is described below along with the literature.

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Different strategies for such an integration of sensitivity analysis and optimization have been established; an overview and references for the various approaches can be found, e.g., in ref 1.

For optimization under uncertainty, there are two main concepts which can be used depending on what information about the uncertainties/uncertain parameters is available:

- Robust optimization: If, e.g., a constraint function g depends on some uncertain parameter vector $\mathbf{p} \in P$, where P is the set of permissible parameter vector values, and no distribution information about its values is available, the most cautious and common way to deal with this constraint is to use its worst case reformulation

$$g(\mathbf{x}, \mathbf{p}) \leq 0 \quad \forall \mathbf{p} \in P \quad (1)$$

where $\mathbf{x}$ denotes the vector of design parameters or optimization variables. If P is finite, eq 1 represents finitely many, possibly more complicated, ordinary constraints. If P is a set with infinite cardinality, eq 1 constitutes formally a semi-infinite constraint (see, e.g., ref 2 for an introduction into semi-infinite optimization). General references in robust optimization are found in refs 3–5. Other concepts in robust optimization can be found in ref 6.

- Stochastic optimization: If, in addition to the knowledge of the possible parameter vector values, distribution information is available, the uncertain parameters can be modeled as random variables ending up in a stochastic optimization problem (see, e.g., refs 7 and 8 for an introduction) involving different measures of uncertainties like value at risk,⁸ conditional value at risk,⁹ and a nested conditional value at risk metric.¹⁰ For proceeding in this way, two concepts have been established:
 - Two- and multistage stochastic programs with recourse: The basic idea of recourse (or compensation) relies on the possibility to adjust constraints after observation of the random variables by later compensating actions. Accordingly in a two-stage program, the set of optimization variables splits into first stage decisions (to be fixed before realization of the uncertain parameters) and second stage or recourse decisions (to be fixed after realization of the uncertain parameters). For a recent application with further references, see ref 11. Bardow and co-workers¹² compare robust optimization with a two-stage optimization approach to quantify trade-offs in the costs to ensure robustness applied to energy supply systems.
 - Stochastic programs with chance/probabilistic constraints: If the emphasis is on the reliability of a system, it can be claimed that the (system) constraints are not fulfilled for every value of the uncertain parameters but with a high predefined probability (see, e.g., ref 13 for details and its application in process engineering). Recently, sigma-points have been used to calculate the probabilities needed in this approach.¹⁴
- Multicriteria mean-variance optimization: Another way to handle uncertainties in an optimization problem is to add uncertainty measures as further objectives to the problem and treat the problem as a multicriteria one. The simplest, not even obvious, multicriteria approach is

to add the variability (e.g., variance or standard deviation) of the uncertain parameters multiplied by a weight to the expected value of the objective function, which is nothing more than the scalarization of the (two) objective functions by means of a weighted sum. In the optimization of portfolios of financial assets, this approach is well known and widely used as mean-variance (portfolio) optimization.¹⁵ Alternatively, nonscalarizing methods are known in the context of stochastic optimization, which will however not be our focus here.

Any of these strategies can be used as a basis to address uncertainties in a multicriteria optimization framework. Concepts of dominance in the presence of uncertainties are reviewed in ref 16. In ref 17, a method to obtain a robust (or worst case) Pareto boundary using the weighted sum scalarization was presented. Ideas from mean-variance optimization have been integrated into a multicriteria setting¹⁸ where appropriate standard deviations were taken as additional objectives.

Tackling process design tasks as multicriteria optimization problems has proven very fruitful; for brevity, the reader is referred to refs 19–22 for an overview. Its integration into an interactive decision support framework by navigating on the Pareto boundary reveals favorable solutions which are difficult to obtain with single-objective techniques.^{20,23} This framework allows the user to filter and select interactively those regions of the Pareto boundary which are most interesting. These studies are typically built on fixed values of the design and the model parameters. The aim of this work is to include the uncertainties of those parameters. The simplest method consists of a sensitivity analysis, where the impact of uncertainties in set design and model parameters on the objective functions, i.e., the Pareto boundary, is calculated. However, more favorable solutions can be found by integrating uncertainties into the optimization directly.

In the chemical engineering literature, Plazoglu and Arkun²⁴ were among the first authors who coupled considerations of robustness with a multicriteria optimization (MCO) problem formulation. They introduced the two-stage approach, in which the MCO problem is formulated as a discrete number of structurally fixed single-objective problems through scalarization techniques (they used the ϵ -constraint scalarization), and the uncertainty is considered in each single-objective optimization independently. Dantus and High²⁵ solved the MCO problem of costs competing with environmental objectives by a stochastic optimization approach (simulated annealing). For each set of optimization variables selected by the algorithm, several Monte Carlo runs of process evaluations are performed to sample the uncertainties. A generalized scheme of the two-stage approach is presented by Fu et al.²⁶: The master MCO algorithm formulates a series of single-objective problems into which the uncertainty is included via sampling schemes (Fu et al.²⁶ proposed to use Hammersley sequence sampling²⁷). A similar generalization of the two-stage approach coupled with specialized (genetic) algorithms was presented by Kheawhom et al.^{28,29} Kim and Diwekar³⁰ applied the general scheme of Fu et al.²⁶ to a solvent design problem with discrete optimization variables describing the solvent's structure. They found that the shape of the probability distribution of the uncertain parameters influenced their results. Not following the two-stage approach, Chakraborty et al.^{31,32} applied MCO under uncertainties to plant-wide optimization using superstructures. They defined a

flexibility index which characterizes the robustness against uncertainties of a design. The flexibility index was used to assess the Pareto set obtained as result of optimization costs against global warming potential in a MCO problem. Similarly, Hoffmann et al.³³ calculated a Pareto set first assuming certain parameters. Afterward the Pareto-optimal solutions are assessed by sampling of the uncertain parameters. The resulting deviations of the objectives were visualized in the objective space. Hugo and Pistikopoulos³⁴ introduced parametric MCO, which consists of defining a discrete number of scenarios for which the MCO problem is solved. Afterward, the Pareto sets are compared. A more probabilistic method has been demonstrated by Tock and Maréchal,³⁵ who used Monte Carlo simulation to quantify the probability of each Pareto set.

Madetoja and Tarvainen⁴⁶ studied a papermaking process and reformulated the MCO problem with uncertainties as a deterministic MCO problem which is then solved instead. The objectives are the mean values of the original objective and one additional objective to reflect the influence of the uncertainties. To solve the MCO problem, an interactive approach was chosen in which the decision maker updates his/her priorities while solutions are generated.

Achenie and co-workers^{37,38} discuss how uncertainty considerations can be included in two types of scalarization schemes (weighted-sum and ϵ -constraint). Their approach is computationally expensive but leads to a less conservative Pareto set compared to the two-stage approach used in refs 24 or 26.

Very recently, Bardow and co-workers³⁹ used robust optimization in a multicriteria setting to determine robust Pareto boundaries in the context of distributed energy supply systems, based on a mixed-integer linear simulation model.

All these works have in common that points on the Pareto boundary are calculated uniformly, without exploiting the shape of the boundary. Since the number of function calls increases significantly with an increasing number of objectives and uncertain model parameters, this can lead to unnecessarily long computation times. To increase computational efficiency, especially for practical applications, in this work, adaptive scalarization schemes²⁰ are applied for the first time to MCO under uncertainties.

A further novelty consists of the implementation of these methods into a flowsheet simulator—the BASF in-house flowsheet simulator CHEMASIM. To make the implementation robust in practical applications, additional effort is required, which is described in this work.

The benefit of such methods is a support of the process designer in discerning robust parts of the Pareto boundary from more sensitive ones and to obtain a consistent estimate of the impact of uncertainties in the different parameters on the objectives. Therefore, some of the above-mentioned methods are suitably combined.

The remainder of this paper is organized as follows. In the next section, a detailed description of the workflow is given. Afterward, the workflow is applied to the calculation of an NQ curve for a simple distillation process.

■ QUANTIFYING UNCERTAINTIES OF PARETO BOUNDARIES

The setup of an MCO task consists of the choice of free design parameters with their intervals of objective functions and of additional constraints. The resulting Pareto boundary with the model parameters fixed to their nominal values will henceforth be called the “nominal Pareto boundary”. Additionally,

uncertainties in the Pareto boundary are assumed to be induced by uncertainties in the model parameters and set design parameters. The uncertainties are encoded here in a finite set of scenarios, which can also bring additional boundary conditions into the optimization problem.

The workflow described in this work to quantify uncertainties in the Pareto boundary is as follows:

- (i) Calculation of the nominal Pareto boundary is needed.
- (ii) Application of screening methods from sensitivity analysis to identify the impact of uncertainties in different parameters and of design variables to be manipulated in order to compensate for the uncertainties is needed.
- (iii) For the scenarios from the sensitivity step (ii), the worst and best case Pareto boundaries are calculated by integrating the sampling of scenarios into the optimization solver.
- (iv) A further option to model robustness is to include an additional objective function which measures the sensitivity of the original objectives.

These four steps are explained in the following.

Nominal Pareto Boundary. The Pareto boundary is determined according to the scheme presented in ref 20, while keeping the uncertain parameters fixed at their nominal values. In that scheme, Pareto points are calculated successively until a certain quality for the linear interpolation between the Pareto points compared to the true unknown Pareto boundary is reached. Pareto points are placed where they are needed most, namely, in regions of strong curvature of the Pareto boundary. Furthermore, both convex and nonconvex parts of the Pareto boundary can be sampled efficiently.

This sampling starts with the calculation of the extreme compromises by finding the individual optimum of each objective function, including a reoptimization step which becomes necessary in the multicriteria context (Supporting Information). After that, weights for a weighted sum scalarization or directions for a Pascoletti–Serafini scalarization are chosen adaptively. The corresponding scalarized optimization problems are solved using a mixed integer sequential quadratic programming (MISQP) algorithm.^{40,41} Further details²⁰ and application examples²³ are given elsewhere.

Sensitivity Screening. Once the nominal Pareto boundary is determined as described in the previous section, the impact of uncertain parameters is calculated by a sensitivity analysis. Methods to perform such an analysis have been described extensively.⁴² Furthermore, the decision support approach by interactive navigation as presented in ref 20 is modified and applied to the results of the sensitivity analysis.

The goal of the sensitivity analysis is to obtain results for the uncertainties in the objectives induced by uncertainties in the model parameters with a small number of sample points in the uncertain model parameter space, cf. Figure 1. To quantify the impact of the uncertain parameters, screening methods like reduced factorial designs or one-at-a-time samplings are known, where the number of sample points N_{scen} scales linearly with the number of uncertain parameters N_{unc} . Here, we favor factorial designs because they allow us to calculate the main effects more reliably than one-at-a-time samplings.⁴² These methods allow us to distinguish between more robust and more sensitive Pareto points. This helps to save computation time. The more advanced methods of robust or mean-variance optimization, presented in the next paragraphs, should be applied only to the rather sensitive points.

The sensitivity analysis consists of the following three steps:

- (I) Given are N_{Pareto} nominal Pareto points $\mathbf{F}^{(\alpha=1, \dots, N_{\text{Pareto}})} = \{f_1^{\alpha}, \dots, f_{N_{\text{obj}}}^{\alpha}\}$, each containing the values of the N_{obj} objectives. Each objective depends on the N_{var} optimization variables and N_{unc} uncertain parameters, i.e., $\mathbf{F}^{(\alpha)} = (f_1(\mathbf{x}^{(\alpha)}, \mathbf{p}^{(\beta)}), f_2(\mathbf{x}^{(\alpha)}, \mathbf{p}^{(\beta)}), \dots, f_{N_{\text{obj}}}(\mathbf{x}^{(\alpha)}, \mathbf{p}^{(\beta)}))^T$, where $\mathbf{x}^{(\alpha)} = (x_1^{(\alpha)}, \dots, x_{N_{\text{var}}}^{(\alpha)})$ is the efficient solution and $\mathbf{p}^0 = (p_1^0, \dots, p_{N_{\text{unc}}}^0)$ are the nominal values of the uncertain parameters.
- (II) For each nominal Pareto point, N_{scen} sample points in the uncertain parameter space are calculated, leading to N_{scen} many function evaluations $\mathbf{F}^{(\alpha, \beta)} = (f_1(\mathbf{x}^{(\alpha)}, \mathbf{p}^{(\beta)}), \dots, f_{N_{\text{obj}}}(\mathbf{x}^{(\alpha)}, \mathbf{p}^{(\beta)}))^T$ with $\beta = 1, \dots, N_{\text{scen}}$. The sampling is done with different points in the uncertain parameter space, $\mathbf{p}^{(\beta)} := (p_1^{(\beta)}, p_2^{(\beta)}, \dots, p_{N_{\text{unc}}}^{(\beta)})^T$. Here, a reduced factorial design sampling is used, where the number of sample points scales linearly with the number of uncertain parameters, $N_{\text{scen}} \sim N_{\text{unc}}$. But of course, the method is not restricted to this kind of sampling. During the sampling, the values of the optimization variables $\mathbf{x}^{(\alpha)}$ are fixed.
- (III) Using $\mathbf{F}^{(\alpha)}$ and $\mathbf{F}^{(\alpha, \beta)}$, sensitivities $S_{j,k}^{(\alpha)}$ are calculated with $\alpha = 1, \dots, N_{\text{Pareto}}$, $j = 1, \dots, N_{\text{obj}}$ and $k = 1, \dots, N_{\text{unc}}$ as described in the Supporting Information.

Thus, $S_{j,k}^{(\alpha)}$ measures the uncertainties caused by the k th uncertain parameter at the Pareto point α in the j th objective. Furthermore, the variance of the j th objective due to the sample points is used here as a sensitivity measure which does not distinguish between the influences of the different uncertainties. Other sensitivity measures are conceivable.⁴³ Like different sampling schemes, also different sensitivity measures have a numerical impact on the final results. These are additional valid options during the interactive decision support workflow for process design under uncertainties established in this paper. An in-depth study of these effects is, however, beyond the scope of this work.

This general concept is demonstrated in the Supporting Information for the one-at-a-time and factorial design samplings.

In Figure 2, an interactive decision support scheme to visualize these results of the sensitivity analysis is sketched. The nominal Pareto points, as well as the results of the sensitivity sampling, are shown in a 2D-projection in the objective space. The uncertainties $S_{j,k}^{(\alpha)}$ are given on additional axes, the bounds of which can be adjusted interactively in the algorithmic implementation similar to the ones used in refs 20 and 23.

Worst and Best Case Pareto Boundaries. *Extreme Compromises under Uncertainty.* When uncertainty is taken into account in single objective optimization by a discrete number of scenarios N_{scen} finding the worst case optimum is achieved simply by comparing the optima of all scenarios. Calculating the extreme compromises in multicriteria problems is more complex because they have to be placed into the multicriteria context although being single objective optimization problems. This is illustrated in the Supporting Information.

Worst and Best Case Scalarizations. We now proceed with the application of the methods described in ref 20 to adaptively sample the worst and best case Pareto boundaries. Therefore, the weighted sum and Pascoletti–Serafini scalarizations have to be formulated to calculate worst and best case Pareto points.

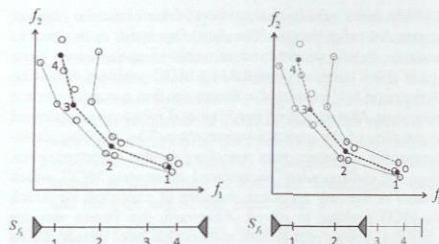


Figure 2. Exploration of uncertainties in a set of Pareto points. The full circles denote the Pareto points calculated for the nominal set of parameters. The open circles are obtained from four scenarios for each Pareto point. On the axis below, the standard deviation in f_1 for each Pareto point, obtained from the four corresponding scenarios, is represented. On the right, the most sensitive Pareto points have been deselected by moving the restrictor on the standard deviation axis.

For the worst case weighted sum scalarization, this results in¹⁷

$$\min_{\mathbf{x} \in \mathbb{R}^{N_{\text{var}}}} \max_{\beta=1, \dots, N_{\text{scen}}} \sum_{i=1}^{N_{\text{obj}}} w_i f_i(\mathbf{x}, \mathbf{p}^{(\beta)}) \quad (2)$$

$$\text{s.t. } g(\mathbf{x}, \mathbf{p}^{(\beta)}) \geq 0 \quad \forall \beta = 1, \dots, N_{\text{scen}} \quad (3)$$

where inequality constraints that may also depend on the scenarios, $g(\mathbf{x}, \mathbf{p}^{(\beta)})$ have been included. It has been shown recently⁴⁴ that multiexpert multiobjective decision making leads to similar min–max formulations.

The objective function in eq 2 is nondifferentiable and thus hard to handle for gradient-based optimization solvers. Therefore, the optimization problem should be implemented in the following equivalent way (epigraph reformulation; see, e.g., ref 45 for details):

$$\min_{(\mathbf{x}, t) \in \mathbb{R}^{N_{\text{var}}+1}} t \quad (4)$$

$$\text{s.t. } \sum_{i=1}^{N_{\text{obj}}} w_i f_i(\mathbf{x}, \mathbf{p}^{(\beta)}) \leq t \quad \forall \beta = 1, \dots, N_{\text{scen}} \quad (5)$$

$$g(\mathbf{x}, \mathbf{p}^{(\beta)}) \geq 0 \quad \forall \beta = 1, \dots, N_{\text{scen}} \quad (6)$$

with additional N_{scen} -many inequality constraints. In the following, the min–max formulation will be used for brevity, but the equivalent epigraph formulation should be always kept in mind for the practical implementation.

The weights w_i are determined by the sandwiching technique,²⁰ which is an adaptive scalarization scheme for convex regions of the Pareto boundary, placing Pareto points there where the curvature of the Pareto boundary is large. The weighted sum scalarization is able to detect only convex regions of the Pareto boundary. For nonconvex areas, the Pascoletti–Serafini scalarization is used which can be deduced from the objective-wise worst case approach in ref 17. Then, the worst case reformulation is done as follows:

$$\max_{(\mathbf{x}, t) \in \mathbb{R}^{N_{\text{var}}+1}} t \quad (7)$$

$$\text{s.t. } f(\mathbf{x}, \mathbf{p}^{(\beta)}) - r - t d \leq 0 \quad \forall \beta = 1, \dots, N_{\text{scen}} \quad (8)$$

$$g(\mathbf{x}, \mathbf{p}^{(\beta)}) \geq 0 \quad \forall \beta = 1, \dots, N_{\text{scen}} \quad (9)$$

Here, the direction vector $\mathbf{d}$ pointing toward the Pareto boundary is chosen by the hyperboxing algorithm, and the reference vector $\mathbf{r}$ is set at the beginning within the feasible region.²⁰

In the worst case formulations, the inequality constraints in eqs 2–9 have to be fulfilled for all scenarios simultaneously. This guarantees feasibility of the worst case solution irrespective of the scenario. Therefore, these solutions are generally different from the ones one would obtain when calculating the Pareto sets for all scenarios separately each with its own inequality constraints and then taking the worst/best case. For an illustrative example, see ref 46.

The best case is treated analogously. Instead of eqs 2 and 3, the optimization problem for the weighted sum scalarization now reads:

$$\min_{\mathbf{x}} \min_{\beta=1, \dots, N_{\text{scen}}} \sum_{i=1}^{N_{\text{obj}}} w_i f_i(\mathbf{x}, \mathbf{p}^{(\beta)}) \quad (10)$$

$$\text{s.t. } \mathbf{g}(\mathbf{x}, \mathbf{p}^{(\beta)}) \geq 0 \quad \forall \beta = 1, \dots, N_{\text{scen}} \quad (11)$$

where the best case is defined such that the restrictions are fulfilled for each scenario. At this point, one might object that it is not clear in how far a solution that fulfills the constraints with all scenarios as in eq 11 exists at all. We assume here that the nominal case exists, and if the uncertain scenarios do not deviate too much from the nominal scenario, one can expect that the inequality constraints (eq 11) can be fulfilled. For a more mathematical background in the case of linear constraints, the reader is referred to ref 47, where best-case set efficiency has recently been explored.

At this point, it should be mentioned that in the general case of nonlinear dependencies on the model parameters the generation of fixed scenarios does not guarantee that the true best or worst case has been found. This limitation is not due to the factorial design used here to generate the scenarios but holds generally as long as one seeks for the worst or best case on a finite, predefined set of scenarios. One way to cope with this issue is to use semi-infinite programming.⁴⁸ That is, for a given design $\mathbf{x}$, the worst case parameter set $\mathbf{p}$ is sought. This would increase the algorithmic and computational complexity significantly and therefore requires sophisticated methods for the scenario identification, which is outside the scope of our work. Our implicit assumption is that the hyperbox from which the scenarios are taken is chosen sufficiently small so the dependency on the model parameters is sufficiently linear. In that case, the factorial design schemes represent an optimal scenario generation to capture the main effects.

While dealing with this situation, a formulation slightly different to eq 11 is conceivable: Only the constraints that belong to the actual best case are taken into account. The authors made first progress in this direction; however, this discussion goes beyond the scope of this work and is reserved for future work.

Mean-Variance optimization. The previous paragraphs contain methods that enable the determination of the best and worst case Pareto boundaries in the presence of a finite set of samples N_{scen} among the N_{unc} uncertain parameters. In the present paragraph, mean-variance optimization is described as a further option to deal with MCO under uncertainties. As pointed out in ref 8, this is a computationally simple form of stochastic optimization; a more sophisticated uncertainty measure relying on a stochastic generation of scenarios is, for example, the conditional value at risk.^{8,9} The key idea consists

of replacing the original objectives by their mean values with respect to the scenarios and to deal with their standard deviations as additional objectives to be minimized. Thus, it is possible to quantify the trade-off between robustness (in terms of minimizing the standard deviation) and the other objectives.

Therefore, we define the mean of an objective f_k for a Pareto point as

$$E_{\beta}[f_k(\mathbf{x}^{(\alpha)}, \mathbf{p}^{(\beta)})] := \frac{1}{N_{\text{scen}}} \sum_{\beta=1}^{N_{\text{scen}}} f_k(\mathbf{x}^{(\alpha)}, \mathbf{p}^{(\beta)}) \quad (12)$$

The variance

$$\sigma^2[f_k(\mathbf{x}^{(\alpha)}, \mathbf{p}^{(\beta)})] := \frac{1}{N_{\text{scen}} - 1} \sum_{\beta=1}^{N_{\text{scen}}} (f_k(\mathbf{x}^{(\alpha)}, \mathbf{p}^{(\beta)}) - E_{\beta}[f_k(\mathbf{x}^{(\alpha)}, \mathbf{p}^{(\beta)})])^2 \quad (13)$$

is calculated for each Pareto point, so that it can be included as additional objective. This shows the trade-off between an optimal mean value for f_k and the minimization of its standard deviation.

APPLICATION

As an example for an application, the separation of the binary mixture methyl formate–methanol (MF–MeOH) in a distillation column is studied. Methyl formate is the light component, enriched in the top of the column, and methanol is the heavy component in the bottom of the column. The vapor–liquid equilibrium of the components is described by the NRTL G^E -model. The interaction parameters are fitted to experimental data.⁴⁹ The comparison of experimental data and model for 1 bar is shown in Figure 3. There is no azeotrope, but the system is highly nonideal.

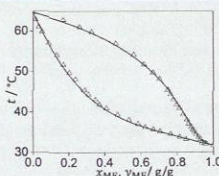


Figure 3. Nominal vapor–liquid equilibrium data of the system MF–MeOH at 1.013 bar. x_{MF} and y_{MF} are mole fractions of methyl formate. Δ : exp. data; —: model.

The distillation column with specifications for the feed and the products is shown in Figure 4. The pressure is 1 bar, and the feed is at liquid boiling state. The column is modeled with the equilibrium stage model. In the example, the very common MCO problem of the NQ curve is studied, i.e., design compromises between column height expressed in theoretical stages N_{th} and the reboiler duty $\dot{Q}_{\text{R}}$.⁵⁰ Optimization variables are the number of theoretical stages $N_{\text{th}} \in [5, 80]$ and the height of the feed stage $N_{\text{f}} \in [3, 80]$ (counted from the bottom). Due to the nonlinearities induced by the thermodynamics, this is a mixed-integer nonlinear problem.

In the example, $N_{\text{unc}} = 3$ uncertain parameters are considered: The mass flow rate of the feed, the mass fraction of methyl formate in the feed, and the activity coefficient of methanol at infinite dilution. Table 1 summarizes the assumed

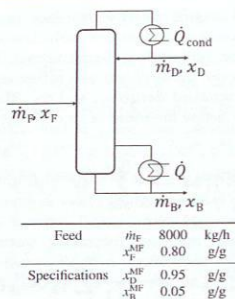


Figure 4. Process flow sheet and specification of the inlet and outlet streams of the distillation column for the separation of MF-MeOH.

Table 1. Uncertainties in Mass Flow Rate of Feed $\dot{m}_F$, Mass Fraction of Methyl Formate in Feed x_F^{MF} , and Limiting Activity Coefficient of Methanol γ_{MeOH}^∞

Parameter	Unit	Value	Relative uncertainty (%)
$\dot{m}_F$	kg/h	8000 ± 40	0.5
x_F^{MF}	g/g	0.8 ± 0.02	2.5
γ_{MeOH}^∞		1.342 ± 0.1342	10

uncertainty ranges in these parameters. The uncertainty in the activity coefficient represents uncertain property data. Although Figure 3 suggests good agreement between the experimental data and thermodynamic model, only slight uncertainties in the VLE model at the methyl formate-rich concentrations may cause considerable uncertainties in the design since the mixture is very close-boiling there. Here, a relative uncertainty in the activity coefficient γ_i^∞ of 10% is assumed, cf. refs 43, 46, and 51 for a motivation of this number. How to realize uncertainties in the activity coefficient by manipulating directly its limiting value at infinite dilution (γ_i^∞) in process simulation has been shown recently.^{51,52}

To quantify the impact of these uncertainties on the nominal NQ curve, a factorial design is used as sampling scheme. The three sources of uncertainties are cast into eight scenarios which can be visualized as the corners of a cube (Figure 5). The center of this cube represents the settings of the uncertain parameters for the nominal case. All scenarios are described by eight three-dimensional vectors which are given in the Supporting Information.

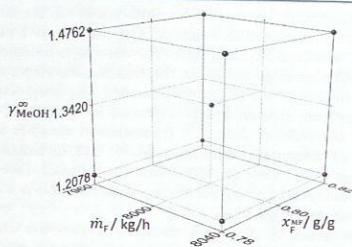


Figure 5. Factorial design of the analyzed uncertainties (corner points) in the MF-MeOH example.

In the following, the four steps of the workflow described in the previous section are realized. The results presented in the following were obtained using the BASF in-house flowsheet simulator CHEMASIM. The tools used here are not specific to the example discussed here but rather applicable to any process design problem.

Nominal NQ Curve. The nominal NQ curve has been calculated as a Pareto boundary using the adaptive sampling schemes for Pareto boundaries. The result is shown in Figure 6a.

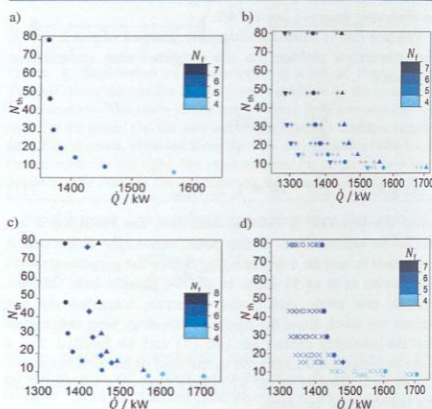


Figure 6. NQ curves for the separation of MF-MeOH. (a) Nominal NQ curve without uncertainties (circles). (b) Sensitivity analysis with uncertainties applied to the nominal NQ curve using a factorial design yielding eight sample points (plus sign) for each nominal Pareto point. The rightmost points are the worst cases (right-side up triangles) with the uncertain parameter combination of $\dot{m}_F = 8040$ kg/h, $x_F^{MF} = 0.82$ g/g, $\gamma_{MeOH}^\infty = 1.1$ $\gamma_{MeOH,nominal}^\infty$. The leftmost points are the best cases (upside-down triangles) of the sensitivity analysis with the uncertain parameter combination of $\dot{m}_F = 7960$ kg/h, $x_F^{MF} = 0.78$ g/g, $\gamma_{MeOH}^\infty = 0.9$ $\gamma_{MeOH,nominal}^\infty$. (c) Comparison of the robustly optimized NQ curve (tilted squares) with the nominal NQ curve (circles) and the worst case of the sensitivity analysis (right-side up triangles). The coloring indicates the feed inlet stage number (N_i). (d) Sensitivity analysis of the new design variables (N_B and N_D) for the robustly optimized NQ curve (tilted squares) resulting in sample points for each scenario (x). Here, the nominal case is characterized as a circle (O).

In this calculation, no uncertainties are considered yet. In the MISQP algorithm used for solving the scalarized optimization problems, an accuracy of 10^{-6} is used in all what follows as termination criterion for the relative change of the objective function between two solver iterates. Computational times are not an issue: The Pareto points are calculated within a few minutes at most on a standard PC (Intel processor 2.6 GHz).

Sensitivity Analysis of the NQ Curve. First, the impact of the scenarios on the nominal Pareto points with fixed design variables (N_B and N_D) is calculated. Thereby, the worst case of all scenarios can be determined. The result is shown in Figure 6b. For all eight scenarios (Figure 5), heat duties were calculated, producing eight sample points for each nominal Pareto point. The rightmost points are the worst case scenarios, in which the uncertainties shift the NQ curve to the highest heat duties. Here, the special case is encountered that all worst

case points stem from the same scenario. This will often be the case but is not necessarily true. Note that in Figure 6b, only $\bar{Q}$ is varied among the different scenarios, while N_{th} is constant. This is because N_{th} is also one of the optimization parameter which are fixed during the sensitivity analysis.

Robust Optimization of the NQ Curve. Worst Case.

In this section, robust NQ curves for the worst case of the uncertain parameters (Table 1) are calculated. The goal is to push the worst case points to lower heat duties. Thereby, new Pareto points are calculated (Figure 6c) with changed design variables N_{th} and N_f . These are now chosen such that the worst case is optimal. Figure 6c shows nominal NQ curve, the robust NQ curve, and the worst case from the sensitivity analysis (from left to right).

The worst case NQ curve detected by a sensitivity analysis is pushed in the direction of the nominal case at lower heat duties using robust optimization. Since no constraints were included here in the optimization problem, the Pareto boundary of the worst case optimization is identical to the worst case of a parametric optimization, where Pareto boundaries for each scenario would have been calculated separately.

The robust design is achieved by shifting the column's feed stage to slightly lower positions. This leads to higher nominal values of the reboiler duty but smaller values of reboiler duties in the worst case scenario.

To illustrate the robustness of the curve, a sensitivity analysis with factorial design is performed with the new calculated design variables of N_{th} and N_f (Figure 6d). It shows that now, in contrast to Figure 6b, all scenarios are on the left-hand side of the Pareto boundary.

The advantage of using the robust optimization scheme is 2-fold: On the one hand, the worst case scenario is detected automatically, and it may also change during the optimization run for a Pareto point. On the other hand, this scheme guarantees optimality: For example, it is not possible to obtain better robust NQ curves ensuring the product specifications. It is pointed out that the use of discrete scenarios also enables a probabilistic interpretation.¹⁴ From that point of view, the above sketched robust optimization acts as an optimization of a certain quantile of a probability distribution. The 50% quantile is equivalent to the mean of the objective; larger or smaller quantiles are captured in the discrete scenarios. A more rigorous description which also accounts for nonlinearities is a task of future research.

Best Case. After the worst case optimization, optimal design parameters N_{th} and N_f are determined for the best case optimization (Figure 6b). Therefore, the design variables are adjusted while at the same time the scenarios are free, so that the overall best Pareto boundary is obtained.

In the absence of boundary conditions in the optimization problem, the Pareto boundaries for the best and the worst cases enclose the nominal Pareto boundary and give lower and upper bounds for optimality achievable under uncertainties (Figure 7).

Alternative to Robust Optimization. Before practically applicable methods to perform MCO with uncertain model parameters were available in flowsheet simulators, NQ curves with tighter impurity specifications in the product streams were calculated in order to account for uncertainties.⁵⁰

This procedure is compared to the presented robust optimization approach in Figure 8. Sharper purity specifications in the distillate stream shift the NQ curve to a location that is close and parallel to the robust NQ curve. Namely, increasing the purity of the methyl formate product from 0.05 to 0.044 g/g methanol is enough to cover the uncertainties. Determining

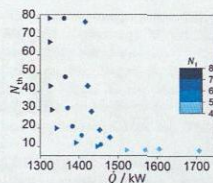


Figure 7. Pareto curves for the nominal (circles), best case (right-pointing triangles) and worst case scenario (tilted squares) of the uncertain parameters, enclosing the nominal Pareto points. The coloring indicates the feed inlet stage number (N_f).

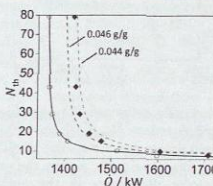


Figure 8. Comparison of NQ curves resulting from the nominal scenario (— and O), from robust optimization (tilted squares), and from sharper purity specifications (—).

this number needs however a lot more experience and works more or less by trial and error, which becomes hard to handle for larger flowsheets.

Mean-Variance Optimization. The mean-variance optimization approach realized here consists of replacing the original objectives by their means with respect to the sensitivity samples. Additionally, variances as in eq 13 can be added as additional objectives to be minimized. Here, the standard deviation $\sigma[\bar{Q}]$ is included; the choice of design variables are kept as before, cf. Table 2.

Table 2. Objectives and Optimization Variables Used in Stochastic and Robust Optimization in Present Work

Objectives minimized		
Stochastic optimization	Robust optimization	Optimization variables
N_{th}	N_{th}	N_{th} : 8–80
$E[\bar{Q}]$	$\bar{Q}$	N_f : 3–80
$\sigma[\bar{Q}]$		

The resulting Pareto points are presented in Figure 9a. This illustrates clearly how minimizing $\sigma[\bar{Q}]$ competes with minimizing the mean $E[\bar{Q}]$ defined in eq 12. In Figure 9a, a 2D Pareto boundary in the 3D objective space is visualized by showing some selected points. Two objectives are shown on the axes, the third one in the color code. The better the objectives N_{th} and $E[\bar{Q}]$ are, the worse is $\sigma[\bar{Q}]$ and vice versa. Furthermore, it shows how a smaller spread of the uncertainty scenarios results in a smaller variance, which comes with a trade-off in the mean value of the heat duty.

In Figure 9b, the same Pareto points as in Figure 9a are shown, but with the coloring indicating the feed height.

For designs with a small $\sigma[\bar{Q}]$, rather low feed positions are found. The trend observed earlier is confirmed: lowering the feed position leads to larger mean values and larger nominal

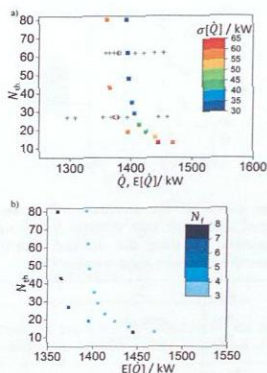


Figure 9. (a) Stochastically optimized NQ curve (squares) calculated with three minimized objectives: N_{dv} , $E[Q]$, and $\sigma[Q]$. The continuous coloring of the Pareto points shows the value of $\sigma[Q]$ in each Pareto point. Additionally, for two Pareto points, the scenarios (+) are given to illustrate the differences in the standard deviations. (b) Stochastically optimized NQ curve as shown in panel (a). Here, the continuous coloring indicates the feed inlet stage number.

values of the reboiler duty but at the same time to smaller standard deviations and higher robustness.

Figure 10 shows the nominal NQ curve together with results of the mean-variance optimization and the robust optimization.

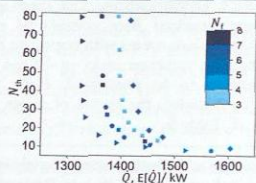


Figure 10. Comparison of the results using robust and mean-variance optimization. Nominal NQ curve (circles), robustly optimized NQ curve (tilted squares), best case optimized NQ curve (right-pointing triangles), stochastically optimized NQ curve (squares). The continuous coloring of the Pareto points shows the value of N_{dv} .

The robust curve is most conservative, whereas the nominal Pareto curve is nearly reproduced by the points with high standard deviation of the stochastically optimized Pareto points (with the heat duty replaced by its mean). This is not surprising as in both cases there is no (or only small) weight given to the $\sigma[Q]$ objective. Further, the scenarios are somewhat equally distributed around the nominal parameter values. In this example, the number of design and uncertain parameters is rather small, the design parameters are integer, and method is completely general and has been applied to complex problems with a larger number of both integer and continuous parameters.

CONCLUSIONS

In the present work, different approaches to model uncertainties in multicriteria optimization are discussed. The Pareto boundaries are calculated by adaptive scalarization schemes that

guarantee an accurate sampling while at the same time keeping the number of Pareto points small. This makes the scheme attractive also for a higher amount of objectives.

Uncertainties are considered as resulting from uncertain parameters. They are quantified by a finite set of scenarios. Robust, i.e., min–max optimization and mean-variance optimization, are employed and show the trade-off between robustness and the other objectives.

The different steps in the workflow described in this work do not rely on how the scenarios are generated nor on the uncertainty metric used. To be definite, reduced factorial designs were used here to generate the scenarios and the variance taken as uncertainty metric. Many other scenario generation methods are known in the literature, either deterministic or stochastic, and also other uncertainty metrics, as cited in the text. Generally speaking, as the results for the uncertainty metric become more reliable, the higher the invest in computational time is. One should consider the problem of exploring and quantifying uncertainties as an iterative procedure, where depending on the requirements in practice more or less accurate metrics and scenario generation techniques are employed. The resulting Pareto boundaries can then be compared and explored in the different criteria and design variables.

All methods presented here are implemented in the BASF in-house flowsheet simulator CHEMASIM and are thus applicable and relevant in industrial practice. This is illustrated using a simple example from distillation process design. It shows the benefits of taking uncertainties explicitly into account in process design and the suitability of the methods presented here for doing this. Furthermore, it shows that there is no single best way how to incorporate uncertainties in process design. Each of the methods presented here has its own strengths so that they should be used complementary. It would be desirable to integrate such methods also in other process simulation tools.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.7b02539.

Reoptimization of extreme compromises, reoptimization under uncertainties, one-at-a-time and factorial design sensitivity samplings, thermo-physical properties and sensitivity settings. (ZIP)

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Notes

The authors declare no competing financial interest.

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Paper IV: INES – An Interface Between Experiments and Simulation to Support the Development of Robust Process Designs [Asprion et al., 2015a]

INES – An Interface Between Experiments and Simulation to Support the Development of Robust Process Designs

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The development of chemical processes is based on both experiments and process simulations. Data evaluation and reconciliation, model development and validation, and design of experiments are essential steps in this procedure. The different tools and approaches available are usually not supported in an integrated way in the process developer's workflow. Therefore, a framework for process design was created and integrated in a tool box which supports process design comprehensively. It contains methods for data selection and reconciliation, sensitivity analysis, model validation and model adjustment.

Keywords: Data selection, Experimental design, Modeling, Robust planning, Sensitivity

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1 Introduction

Often models are used to represent a known good operation point to investigate the impact of different parameters and to optimize the process within the vicinity of this operating point in the process simulator. Since new methods and computational speed allow a more rigorous exploration of the complete design space, there is the necessity for reliable models applicable in this broader range. The modeling process is a decisive factor for the reliability of simulation and optimization results. A scheme of the process, which starts with experimental data and ends up in a robust and optimized plant design, is visualized in Fig. 1. The modeling, simulation and optimization loop might be passed several times in the iteration of process development. The aim of this work is to support this work flow.

Although the necessary steps for creating good models are known [1], there is, to our knowledge, no commercial tool available supporting the modeling process in all steps. Either existing tools (e.g., Vali from Belsim, Minitab from

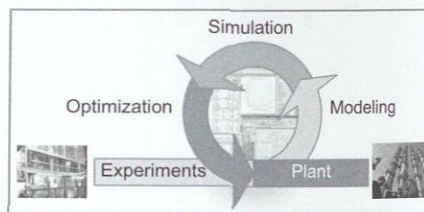


Figure 1. Modelling, simulation and optimization iteration loop starting from plant experiments and striving for a robust and optimized plant design.

Additive or ASPEN Plus) cover the aspects only partly or methods are available only in an academic environment sometimes not adjusted to industrial practice. Therefore the modeling is often complicated, error-prone and undefined. Furthermore, since the selection and processing of experimental data is also time-consuming frequently only a small fraction of the available experimental data is used for model development.

The goal of the project "INES – Interface between Experiments and Simulation" is to implement successful and tuned methods into a user-friendly, interactive interface which supports the process designer in his workflow. The ease-of-use and an obvious benefit for the user applying these tools are important guidelines to achieve high user acceptance for this development. Moreover, this also serves as verifiable documentation of process scale-up and optimization. Lastly, it also facilitates active know-how transfer and quality management.

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The project INES supports the process design based on both steady-state flowsheet models and plant data (from mini-, pilot or production plants). There is the chance to reduce both costly experimental efforts during model development and risks in the process design due to insufficient model quality. This can decrease time-to-market and make resources available for other process development projects.

It is assumed that a first simulation model already exists as a starting point for supporting the modeling process. This is reasonable since the planning of plants is usually based on such simulation results. INES supports the process developer in the following tasks as shown in Fig. 2:

- 1) Data selection: Removal of outliers and identification of different relevant steady-state operating points.
- 2) Data reconciliation: Reconciling flow and composition data from, e.g., analytics by using mass and/or component mass balances only. This task helps to detect gross errors in case that those balances cannot be closed within a reasonable range around the measurements.
- 3) Model validation: Comparing the model predictions with the experimental data at the selected operating points.
- 4) Model sensitivity analysis: Identifying the impact of variations in model parameters on selected objectives to either investigate the impact of parameter uncertainty or to identify the best model parameters when adjusting the model.
- 5) Model adjustment: Besides comparing different submodels like thermodynamic models or reaction models (e.g., different kinetic models) INES focusses on improving the agreement between model and experimental data by offering the possibility to estimate model parameters.
- 6) Optimal design of experiments (oDoE): Identifying operating regimes with multi-criteria optimization which provide a good trade-off between sensitivity and other operation-related objectives. Here, sensitivity measures will be maximized to obtain operating points where, e.g., parameters can be determined with high accuracy.

- 7) Robust planning: Identifying operating regimes, similar to oDoE with multi-criteria optimization which provide a good trade-off between sensitivity and other operation-related objectives. While in oDoE the sensitivity measure will be maximized, here it will be minimized to reduce the impact of uncertainties on the design.

The development is based on the BASF in-house simulation tool CHEMASIM. Integration of the workflow is easy because the source code is accessible and it is possible to further integrate the developed tools into BASF's processnet tool box for most efficient support of the process design workflow at BASF. However, the experience gained in this project is fundamentally generic and independent of the choice of the process simulator or the company's environment. The paper demonstrates the new ideas and prototype of the tools supporting the workflow.

2 Data Selection and Reconciliation

Large amounts of experimental data from plants (mini-plant, pilot or production plants) are typically available in industrial practice and can be used to develop and validate process models. However, identifying good data still is a tedious manual task. As a consequence, typically only a limited amount of data is used in model development and is selected very often by intuition and experience alone. Facilitating the data selection process supports the process developer in this modeling step.

Plant information management systems (PIMS) like Info-Plus.21 (ASPEN) or PI (OSIsoft) provide access to operating data needed for model validation and improvement. These systems are often used within BASF and therefore interfaces to these systems are provided.

Operating data from lab or mini plant-scale experiments is often stored and processed in MS Excel. Similarly, e.g., analytical data are in some cases provided in Excel files. Hence, an interface to Excel is also implemented and can be used simultaneously.

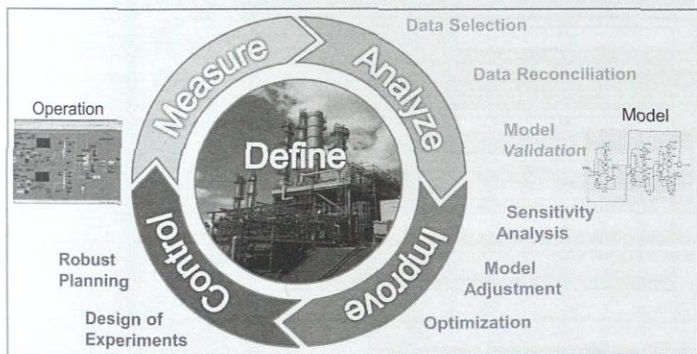


Figure 2. Steps in the workflow in process design and scope of the project INES.

2.1 Time Series and Steady-State Time Periods

Data selection in INES starts with analyzing time series data for a selected time period as shown in Fig. 3. In this screenshot of the visualization within the tool the following information is shown. In the first column ("Name") the name of the measurement tag is shown. The second column ("Contained") gives the percentage of the data visible compared to all available data. The selected time period can be reduced with the triangular sliders. When outliers are removed, for example, the percentage is lower than 100 % (Fig. 4). The third column ("Bounds") shows the maximum and minimum value of the available data in the full time period. Some statistical information is given on the right side ("Average, StdDev, Median, MAD"), which will be discussed below. Some of these statistics are also included in the time series plot of the data as straight lines and shaded intervals.

While PIMS typically can also generate time series and statistical data, each system is different and uses a different syntax. The main advantage of this tool is its independence from the chosen PIMS. Since there is only one interface to the different systems, the usability is facilitated and the risk of errors is reduced. Sometimes the user is also interested in derived quantities, e.g., feed ratios or reaction yields, in addition to plots of the measured quantities with respect to time in order to identify interesting operating conditions. It is possible to display quantities obtained by combining different measurement tags in user-specified nonlinear functions. These properties are visualized analogously in the time series analyzer. This makes it possible to identify time periods where different feed ratios are present or where dif-

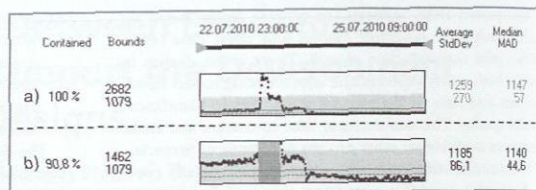


Figure 4. Use of the smart scaling method to remove outliers; a) before smart scaling: $a = \text{infinity}$, b) with smart scaling: $a = 2.8$.

ferent yields have been achieved. These time periods can then be analyzed in more detail as described below.

For more involved processes, it is cumbersome to check each tag and to identify a time period where all tags show steady-state behavior. Therefore, a limited number of tags are used to select steady-state time periods. Of course, the steady-state quality of the remaining tags must also be ensured. Outlier detection as, for example, described in [2,3] is one essential step in this pre-selection task. The method used in our framework to detect outliers is described next.

Often the arithmetic mean $\bar{x}$ is used to estimate the expected value of a distribution of data points. A measure for the variation of the data from the arithmetic mean is the standard deviation σ . In Fig. 4 the arithmetic mean $\bar{x}$ is shown as a solid line and an interval of $\pm 2\sigma$ about the arithmetic mean is indicated by a colored band (here only visible in gray). This interval includes more than 95 % of the data points in the case of normally distributed data.

The arithmetic mean is a non-robust estimator of the expected value since outliers directly influence the arithmetic mean. A more robust estimator is the median $MED(x)$.

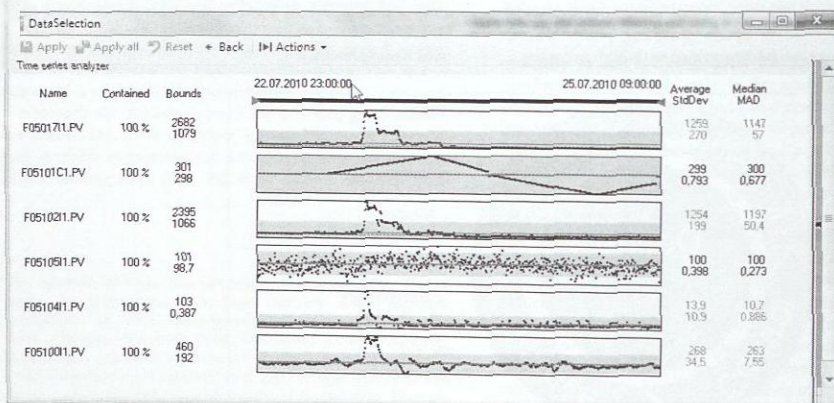


Figure 3. Time series analyzer to identify and select steady-state operating points.

The median is also shown in the trend as a dashed line. If no outliers are present, the agreement between mean and median is usually very good. This observation can be used to remove outliers here called smart scaling. The method uses a robust measure of the variation (also called measure of scale), the median absolute deviation

$$MAD(x) = MED(|x - MED(x)|) \quad (1)$$

The smart scaling method shrinks the selection of data points to the following interval around the median

$$[MED(x) - aMAD(x); MED(x) + aMAD(x)] \quad (2)$$

Herein, a is an adjustable factor. It can be changed interactively by moving a slider. The method is demonstrated using the first tag in Fig. 3 and is shown in Fig. 4. At the start, the data is not scaled (Fig. 4a, $a = \text{"infinity"}$). In the lower part of the figure a larger period with a peak has been removed by manually moving the slider to lower a values (Fig. 4b, $a = 2.8$). After the removal of the peak, the agreement between mean and median is quite good, but the visualization shows that there are two subsets of the data with different levels. Furthermore, the excluded part with the peak is too big to still consider the whole period as one data set, which is indicated by the broad gray vertical area. In the next step the time period can be reduced to represent, e.g., only the part either to the right or left of the removed peak.

In the literature [3] other robust measures of scale with a higher statistical efficiency¹⁾ have been proposed, but their determination is computationally more costly, which would forbid an interactive outlier removal as realized with the cri-

terion above. Apart from that, the numerical value of the measure of scale is not decisive for the interactive smart scaling method.

Although there is a mathematical definition for steady-state, i.e., first derivative with respect to time is equal to 0, there is no good practical definition. In the literature, methods for segmentation [4] to generate a pre-selection of different time segments are available. These methods usually have tuning parameters which greatly influence the obtained results for this segmentation. For such segmentation a stationarity test can be performed and the segments will be colored in green, yellow or red, depending on the result of the test. Here, an adapted version of Fukuda's method is realized: In the original work [4], averages between neighboring intervals are compared. A breakpoint is set if this difference exceeds a certain threshold. However, the value of the average depends significantly on outliers. The modification of Fukuda's method consists in taking a breakpoint found by this method as a starting point, removing outliers in the two intervals divided by that point, and then applying Fukuda's method again. The outlier detection is done using Eq. (2), with the fine tuning parameter $a = 5$. This outlier removal is only applied during segmentation and is not permanent. The previously performed outlier removal of the user will be maintained.

Furthermore, the KPSS (Kwiatkowski-Phillips-Schmidt-Shin) method for the stationarity test is implemented [5]. These automated options for segmentation and stationarity tests are available, but an interactive selection of the steady-state time periods is often easier and faster to use. Thus, the smart-scaling method is combined with the selection of the time period as shown in Fig. 5. Here, the period between the

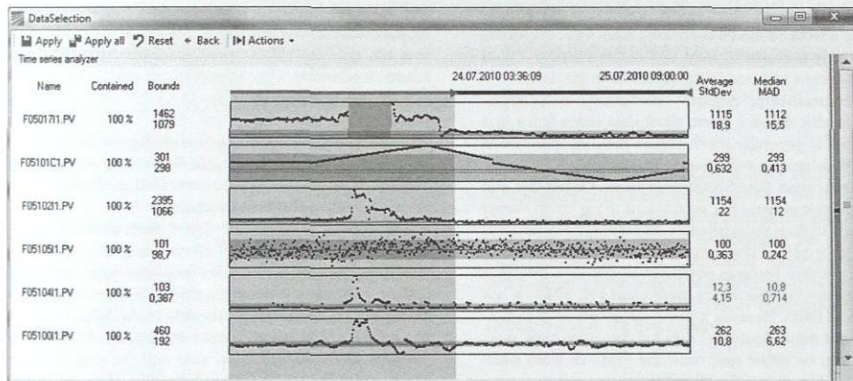


Figure 5. Selection of a steady state time period by moving the time sliders. The data between the two time sliders (24.07.2010, 03:36:09 and 25.07.2010, 09:00:00) is selected as a steady-state operating point. Data in the gray area is not taken into account.

1) The statistical efficiency refers to the variance of an estimated parameter: The less data points are needed in order to achieve a certain variance for an estimated parameter, the higher the efficiency.

triangular time sliders is used, the data not used is shaded in gray. It enables the user to interactively select the regions that are in agreement with his expectations without iterating any optimal parameters of an automatic selection method.

For the selected steady-state periods, averaged data together with standard deviations are stored for the following steps: data reconciliation, model validation, sensitivity analysis and model adjustment.

2.2 Mapping of Tags and Data Reconciliation

For subsequent design tasks a link between measurement tags and the flowsheet model is needed. The first step is a mapping from measurement tags to state variables of streams and unit operations in the simulation. This mapping is done interactively using the process flow diagram from the simulation, which is a MS Visio drawing in our case.

The selected data sets can be further used in the data reconciliation step.

In this step, a least-squares sum is used where the single terms are the squared differences between measured and simulated streams and concentrations, and where each term is weighted by the inverse variance of the measurement [6]. The minimization of the least squares sum is done under the restriction that the mass- and component balances are fulfilled. For a reactive system the reaction stoichiometry must be provided in the latter case [7, 8]. Additionally, the user has the possibility to define further restrictions, e.g., purity specifications on product streams. The complete optimization problem is set up from the topology of the process flowsheet. In other words, within the full process simulator a reduced model containing mass and component balances only is available. Here, this reduced model is used to obtain insight into possible gross errors in the data.

Data reconciliation requires redundancy in measurements. Usually, this is a given, albeit data redundancy in a mini-plants is generally much higher than for production plants. To determine redundancy, an analysis of the topology of the process flowsheet is performed. Observable and non-observable streams are determined using graph theory for the case of total mass balances according to Narasimhan and Jordache [6]. If also component balances are considered, the problem becomes nonlinear. In this case, detection of redundancy requires much more effort [9], which is not the focus of INES. Here, an a-priori classification of redundancy is not done. Analytical data for the component mass balances can be either read from the PIMS or from additional Excel files as mentioned before.

The control volumes for data reconciliation are defined directly in the process flow diagram of the simulation. Unit operations can be grouped to construct control volumes. A first indication of the deviation of the mass balances helps to identify unsteady states or measurement errors in tags or whole data sets.

The data reconciliation in this step is solely based on experimental data (except for using the mass balances as a basic assumption). For this reason, it can evaluate the quality of the data and identify gross errors. In the subsequent steps either reconciled or raw data can be used.

Data reconciliation can be done simultaneously with the model validation or model adjustment step [6]. But this introduces additional complexity without great benefits as will be discussed in these steps and in the examples.

Data reconciliation based on energy balances requires a lot of information based on physical property models and can be done simultaneously in the model validation or model adjustment step (similar to data reconciliation based on mass balances). Since models are needed for a data reconciliation based on energy balances, it is not included in this preceding data analysis step.

3 Model Analysis and Improvement

Before starting with model adjustment, a model validation step can show how well the existing model agrees with the measured operating data. So the data selection is an important step before model validation. Sensitivity analysis helps to identify which parameters to adjust in case of disagreement between model and operating data.

In model validation our interest is to compare a larger data set with the model predictions without requiring as many simulation files as data points. For this reason and also for the subsequent task of model improvement different loops have been implemented which provide much flexibility to run these tasks automatically. Tab. 1 outlines the tasks and how the different loops are used in the different contexts.

3.1 Model Validation

The goal of model validation is to determine the capability of the model to describe several different operating points. Here, only one master simulation is used as a basis for comparing operating data and simulation.

The selected experimental data including several operating points is stored in a CSV-file and is used in the validation step. The use of the inner loop within the simulation software (Tab. 1) enables the user to maintain only one simulation. In the loop some of the data of the different operating points will be used as input for this simulation. Comparisons of the experimental data and the simulated data are possible in stream tables and within the process flow diagram of the simulation.

Besides model validation, the inner loop structure might also be used for representing special scenarios of a simulation such as summer/winter cases, start-of-run/end-of-run conditions to account for, e.g., catalyst deactivation or different load scenarios.

Table 1. Implemented loops in the simulation software to fulfill different tasks in the project INES.

	Model Validation	Model Adjustment	Sensitivity Analysis	oDoE / Robust Planning
Inner Loop	Iterate operating points	Iterate operating points	Iterate uncertain parameters	Iterate uncertain parameters
Outer Loop	–	Optimize parameters (single-objective)	Iterate operating points	Optimize parameters (single-objective)
External Loop	–	Multi-objective optimization (Pareto)	–	Multi-objective optimization (Pareto)
Additional details	Only one simulation	No weighting of operating points	Interactive sensitivity analysis	Sensitivity as additional objective

In principle, it is possible to perform data reconciliation simultaneously with the model validation step, but in our experience, it will not change the results (i.e., the deviations of the simulated from the experimental values) significantly as will be discussed in the examples. If the model is unable to predict the operating points, then simultaneous data reconciliation will not improve the situation significantly if the data was previously carefully selected. If the model agrees with the data, then also simultaneous data reconciliation will not greatly change the resulting parameter values nor will it improve agreement between model and data.

Typically, the available measured data of an operating point i can be divided into two subsets: one vector $\mathbf{x}_i^{\text{exp}}$ reflecting data which can be used as an input for the simulation model, e.g., flows of raw materials into the process considered, and another vector $\mathbf{y}_i^{\text{exp}}$ reflecting data which can be compared with the output of the process simulation. For a model validation without data reconciliation, some or all of the measured data $\mathbf{x}_i^{\text{exp}}$ will be taken as input for the simulation. If this set is not sufficient, an additional set $\mathbf{x}_i^{\text{inp}}$ of input data for the remaining necessary inputs of the simulation has to be provided by a reasonable choice of the user and/or might also be estimated in a subsequent model adjustment step. Some or all of the measurements $\mathbf{y}_i^{\text{exp}}$ can be compared with the result of the simulation $\mathbf{y}_i^{\text{sim}} = \mathbf{y}_i^{\text{sim}}(\mathbf{x}_i^{\text{exp}}, \mathbf{x}_i^{\text{inp}})$. The model parameters $\mathbf{p}$ are assumed to be fixed and are therefore not included in the list of inputs for the simulation.

In case of simultaneous data reconciliation and model validation the input variables of the simulation $\mathbf{x}_i^{\text{sim}}$ are not fixed to the measured values $\mathbf{x}_i^{\text{exp}}$, but have now to be varied to minimize the deviations of the simulation results from the selected measurements. Here, for example, a least squares minimization can be used, where the squares are weighted with weighting factors $\mathbf{w}^x$ and $\mathbf{w}^y$

$$\min_{\mathbf{x}_i^{\text{sim}}} \left\{ (\mathbf{w}^y \cdot (\mathbf{y}_i^{\text{sim}}(\mathbf{x}_i^{\text{sim}}, \mathbf{x}_i^{\text{inp}}) - \mathbf{y}_i^{\text{exp}}))^2 + (\mathbf{w}^x \cdot (\mathbf{x}_i^{\text{sim}} - \mathbf{x}_i^{\text{exp}}))^2 \right\} \quad (3)$$

Here, multiplication $\cdot$ is component wise with a vector as a result and not a scalar product. The square $(\cdot)^2$ is denoting a scalar product of a vector with itself. The weights can be defined by the user. For example, they can be chosen all

equal to 1 or according to the variances or to expected measurement accuracies.

Since the experimental values $\mathbf{x}_i^{\text{exp}}$ are good starting values for the $\mathbf{x}_i^{\text{sim}}$ for the minimization it is possible to set $\mathbf{x}_i^{\text{sim}} = \mathbf{d}_i \mathbf{x}_i^{\text{exp}}$. The factors $\mathbf{d}_i$ represent a fractional deviation from the measured value $\mathbf{x}_i^{\text{exp}}$ (starting values $\mathbf{d}_i \approx 1$). The minimization problem formulation changes to

$$\min_{\mathbf{d}_i} \left\{ (\mathbf{w}^y \cdot (\mathbf{y}_i^{\text{sim}}(\mathbf{d}_i \cdot \mathbf{x}_i^{\text{exp}}, \mathbf{x}_i^{\text{inp}}) - \mathbf{y}_i^{\text{exp}}))^2 + (\mathbf{w}^x \cdot (\mathbf{d}_i - 1) \cdot \mathbf{x}_i^{\text{exp}})^2 \right\} \quad (4)$$

and has the advantage that all parameters $\mathbf{d}_i$ to be varied in the minimization are in the same order of magnitude.

This minimization has to be done in principal for each operating point i individually. For example, if you have only one input stream with 10 components to be set, already 10 parameters have to be adjusted to estimate the flow and the composition for each point. A possibility to reduce the computational effort is to use only one set of factors $\mathbf{d}$ equal for all operating points and to fit these factors simultaneously for all operating points, i.e.,

$$\min_{\mathbf{d}} \left\{ (\mathbf{w}^y \cdot (\mathbf{y}_i^{\text{sim}}(\mathbf{d} \cdot \mathbf{x}_i^{\text{exp}}, \mathbf{x}_i^{\text{inp}}) - \mathbf{y}_i^{\text{exp}}))^2 + (\mathbf{w}^x \cdot (\mathbf{d} - 1) \cdot \mathbf{x}_i^{\text{exp}})^2 \right\} \quad (5)$$

The bounds on the factors can then be chosen to reflect the variances or the expected accuracies. This allows identifying more systematic deviations than purely statistical variations. Of course it reduces the flexibility, but also reduces the computational effort significantly. Only one optimization must be solved instead of N optimizations in case of N operating points. The differences of these options will be demonstrated in the first example.

3.2 Sensitivity Analysis

Sensitivity analysis is important in model development, validation and optimization [10]. Several different parameters influence a simulation model as shown in Fig. 6. Process parameters include design parameters like the number of theoretical stages of a column and operating parameters like

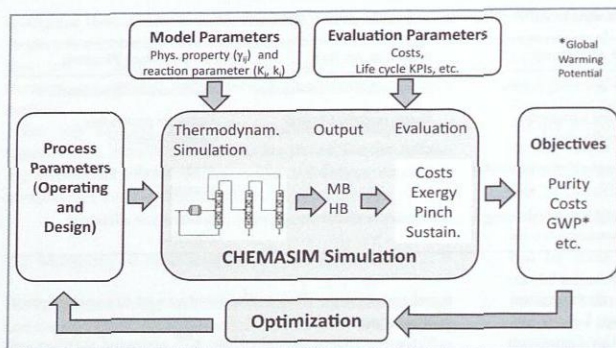


Figure 6. Parameters influencing simulation and optimization objectives.

pressures. These process parameters specify the necessary input of the simulation, when a certain model for physico-chemical properties (including thermodynamics, physical properties and reaction models) is chosen. These physico-chemical property models also contain model parameters for pure components, e.g., the vapor pressure correlations or for binary mixtures the interaction parameters of the Gibbs excess enthalpy models or equations of state and reaction parameters like kinetic constants or equilibrium constants. Additionally, parameters are needed to evaluate, e.g., investment cost estimates or raw material costs.

Within the project we increased the number of properties accessible for variation by introducing new interfaces. Now the following list of parameters can be chosen within a sensitivity analysis:

- Process parameters:
 - Operating parameters ($T, p, m, x, \dots$)
 - Design parameter (number of theoretical stages of a column, ...)
- Model parameters:
 - Physical properties (activity coefficients, vapor pressures, enthalpies, ...)
 - Reaction parameters (equilibrium and kinetic constants)
 - Mass transfer coefficients and enhancement factors
- Evaluation parameters
 - Costs
 - Pinch temperature difference
 - Life cycle indicators, etc.

A sensitivity analysis can be used in different contexts; hence, different methods of analysis are required. Those methods implemented in INES are summarized in Tab. 2. Generally, each method is applied to a user-defined range in the space of model parameters. A small range corresponds to a local sensitivity analysis, where the different methods yield equivalent results, since the sensitivity analysis only probes the linear behavior of the model in that small region. On the contrary, for a

relatively large range, i.e., for global sensitivity analysis, the results from the different methods can differ due to non-linearities. The study of these differences can reveal important information about the nature of those non-linearities.

For the investigation of uncertainties local sensitivity measures can be used. Here, uncertainties of process parameters or of model parameters will be investigated. The use of model parameter uncertainty (e.g., as reflected by confidence intervals) can be abstract in some cases. For example, the uncertainty of a binary interaction parameter of the NRTL model is hard to quantify. Therefore, we implemented methods which rather use uncertainties in directly measurable or

derived experimental data. For example, instead of binary interaction parameters, the activity coefficients at infinite dilution include uncertainty measures to investigate model sensitivities as described in Mathias [11].

Another application for sensitivity analysis is investigating the impact of parameters prior to estimation. Here, global sensitivity measures should be applied since the parameter ranges might be large. Sensitivity analysis in this context helps to focus on the most sensitive parameters for the estimation, to avoid over-fitting and to reduce the effort of parameter estimation.

Sensitivity analysis might also be used prior to solving an optimization problem (single or multi-objective) with the simulation model. It might be used either to identify the sensitive optimization parameters or to investigate the impact of parameter uncertainties on the result of the optimization.

Many different sampling techniques for uncertain parameters are available, e.g., elementary effect analysis and factorial design (see [10, 12] for an overview). We implemented different options within our framework (Tab. 2). All these methods define different sampling points for the parameters and will be simulated and the results are stored in a data base. Depending on the method chosen (Tab. 2), either finite differences or variances will be computed automatically. Further method-dependent options for the users are, e.g., to choose the difference to be used for the calculation of finite differences relative to the uncertainty interval or to decide how many sample point should be evaluated.

Table 2. Implemented sampling techniques for the sensitivity analysis (see Saltelli et al. 2008 [10] for a description of the techniques).

Type	Averaged Difference Quotients	Variances
Deterministic	- One at a time - Factorial Design: Full or fractional	Quadrature
(Quasi-)Random	Elementary Effect Method	Sobol Sequences

The choice of method determines the effort and the accuracy. A sensitivity analysis might be computationally more costly than an optimization run since in the sensitivity analysis the full parameter space has to be investigated. So if the application is to investigate which parameters have a big impact on the chosen objectives then either the method "one at a time" or the fractional factorial design might be a relative cheap method to obtain this information.

One of the new key concepts is the interactive sensitivity analysis, which offers an interactive visual representation of the sensitivities not only of a single, but also of a large set of operating points. A screenshot of this tool is given in the first example in Fig. 7. When a model validation with different operating points is combined with a sensitivity analysis, then it is possible to navigate the operating points and visualize in real time the corresponding sensitivities of the objectives of interest. Especially, the navigating environment allows setting and changing restrictions on the output functions, their sensitivities and the operating parameters. If, e.g., one is interested only in solutions whose sensitivity in a certain output function smaller than a given value, only those solutions are highlighted. Furthermore, different sensitivity runs can be compared. This enables the user to compare the outcomes of different sensitivity measures, but also to study in detail how sensitivities change depending when different uncertainties or uncertainty ranges are chosen.

3.3 Model Adjustment

Model adjustment generally includes two steps: On the one hand, comparing the output of different models or sub-models (like, e.g., thermodynamic models or reaction models) to measured data and favoring those alternatives which improve the agreement between experimental data (operating points) and simulation. On the other hand, adjusting unknown parameters or parameters estimated only roughly (like, e.g., number of theoretical stages of a distillation column) by solving an optimization problem which minimizes the difference between model output and measured values. Before estimating these parameters, a sensitivity analysis will give an idea about the data variances in the operating points (Fig. 7). While the evaluation of the impact of exchanging submodels can be easily investigated with the model validation, the project INES also supports the parameter estimation.

The classical approach for parameter estimation is to minimize the sum of the least squares between experimental and simulated data by varying the parameters to be estimated. If $\mathbf{p}$ represent the vector of parameters to be estimated and the fixed parameters are neglected in the input list of the simulation results, then the problem can be formulated as follows

$$\min_{\mathbf{p}} \sum_i \left\{ \left(\mathbf{y}_i^{\text{sim}}(\mathbf{p}, \mathbf{x}_i^{\text{exp}}, \mathbf{x}_i^{\text{inp}}) - \mathbf{y}_i^{\text{exp}} \right)^2 \right\} \quad (6)$$

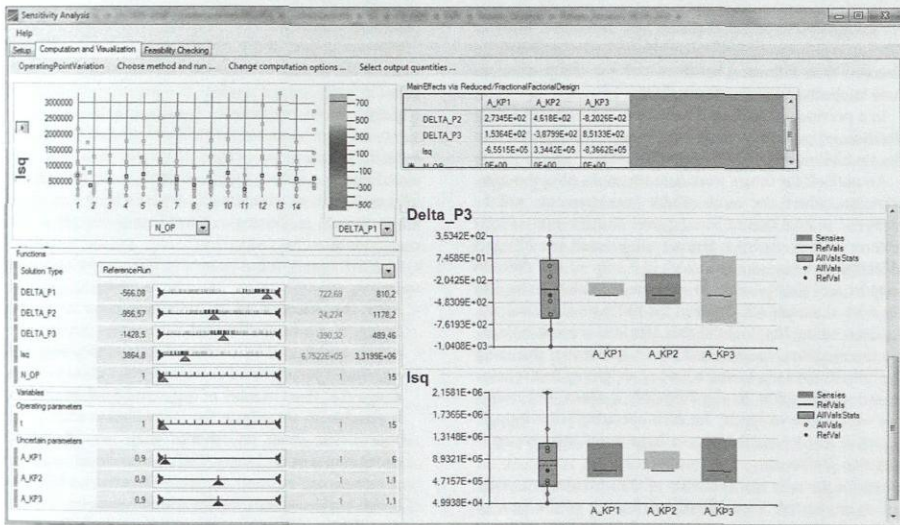


Figure 7. Schematic view of interactive sensitivity analysis support tool. The objectives together with sensitivity measures Δ are given as well as the corresponding process parameters and the uncertain parameters entering the simulation. By navigating on the objectives or process parameters the corresponding sensitivities are updated online.

Here, again multiplication $\cdot$ is component wise with a vector as a result and not a scalar product. The square $\langle \cdot \rangle^2$ is denoting a scalar product of a vector with itself. It is possible to combine this parameter estimation with a simultaneous data reconciliation step. But as discussed before (see model validation), the amount of factors increases linearly with the number of operating points considered and would lead to large problems. Therefore, here only a data reconciliation using the same factors for all operating points is given, since this reduces complexity of the problem to be solved. In this case, the following problem has to be solved

$$\min_{\mathbf{p}, \mathbf{d}} \sum_i \left\{ \langle \mathbf{w}^y \cdot (\mathbf{y}_i^{\text{sim}}(\mathbf{p}, \mathbf{d} \cdot \mathbf{x}_i^{\text{exp}}, \mathbf{x}_i^{\text{inp}}) - \mathbf{y}_i^{\text{exp}}) \rangle^2 + \langle \mathbf{w}^x \cdot (\mathbf{d} - 1) \cdot \mathbf{x}_i^{\text{exp}} \rangle^2 \right\} \quad (7)$$

If also a vector $\mathbf{d}'$ of factors for the relative deviation from a parameter value is introduced, then the classical approach reads

$$\min_{\mathbf{d}'} \sum_i \left\{ \langle \mathbf{w}^y \cdot (\mathbf{y}_i^{\text{sim}}(\mathbf{d}' \cdot \mathbf{p}, \mathbf{x}_i^{\text{exp}}, \mathbf{x}_i^{\text{inp}}) - \mathbf{y}_i^{\text{exp}}) \rangle^2 \right\} \quad (8)$$

and for the parameter estimation with simultaneous data conciliation follows

$$\min_{\mathbf{d}', \mathbf{d}} \sum_i \left\{ \langle \mathbf{w}^y \cdot (\mathbf{y}_i^{\text{sim}}(\mathbf{d}' \cdot \mathbf{p}, \mathbf{d} \cdot \mathbf{x}_i^{\text{exp}}, \mathbf{x}_i^{\text{inp}}) - \mathbf{y}_i^{\text{exp}}) \rangle^2 + \langle \mathbf{w}^x \cdot (\mathbf{d} - 1) \cdot \mathbf{x}_i^{\text{exp}} \rangle^2 \right\} \quad (9)$$

The classical approach is usually very sensitive to outliers. Decreasing the weight of uncertain data sets may help to decrease their influence, but there is always the question on how to choose weighting factors [13].

In a previous project, multi-objective optimization with a decision support system was developed and integrated into the simulation tool CHEMASIM [14–16].

An outlook for future work is to use multi-objective optimization, where the most reliable measurements will be clustered in one sum of least squares and the sum of least squares of each doubtful data set will be used as additional objective to be minimized. With the help of the decision support tool it is possible to navigate the solutions and to see what the trade-offs between the different objectives are, i.e., how taking the doubtful data sets into account influences the model parameters and the fit. Of course, clustering the reliable data sets is also a kind of weighting, but it helps to reduce the effort to a manageable amount. Otherwise, one would have to specify for each operating point a single objective which would lead to a large multi-objective optimization problem.

Within the new tool the setup of the optimization problem is supported: Especially the definition of the sum of least squares is prepared using the information of the mapping of the tags to the simulation streams or unit operations. At the time being no methods to check for the identi-

fiability of parameters, like in Lopez C. et al. [17], have been implemented, but would be a meaningful extension to avoid overfitting.

4 Optimal Design of Experiments and Robust Planning

There is a huge amount of literature available dealing with design of experiments and robust planning. In design of experiments [18, 19] model discrimination or parameter estimation is usually in focus and very often based on derivatives, which means it is normally only valid locally. The use of global sensitivity methods enlarges the validity range.

The structure of our process simulation software and probably also of other commercial simulation software does not allow using directly available tools for oDoE, like VPLAN [18]. But with the previously described task and the loop structure (see Tab. 1), we have now the possibility to combine multi-objective optimization with sensitivity analysis and to define further objectives for the experiments as will be discussed in this section and in the second example. This work is still in progress.

While we try to maximize sensitivities in optimal design of experiments the goal in robust planning is to minimize sensitivities. So both problems might be handled with the same tools. A factorial design is used for sampling the uncertain parameters, but the method is not restricted to this sensitivity method and can be applied in general with all methods of Tab. 2. However, some methods will be computationally intensive.

The overall goal of the optimal design of experiments is to reach the objectives of the experiments with a low number of investigations. Therefore, the first step is to define the objectives of the experiments. For example, if these experiments are used to maximize yield and product purity or to estimate unknown parameters. If both is of interest, then multi-objective optimization with decision support will give information about the trade-offs of the different tasks which are in general conflicting and will help to identify a good compromise.

Sensitivity analysis can be used in this context in different ways:

- After the selection of an operating point or process design, it can be investigated how certain process parameters are affected by uncertainties in other parameters, e.g., model parameters. For example, for a chosen column design (i.e., fixed number of stages and fixed diameter), it is possible to investigate for a specified product purity how reflux ratio or reboiler duty are affected by uncertainties in the binary VLE's (vapor-liquid equilibria) as represented by uncertainties in the activity coefficients. It also enables identifying for which parameters a reduction of uncertainties is necessary or beneficial. This method uses the standard approach for sensitivity analysis only.

- Alternatively, it is possible to calculate the sensitivities of some of the objectives during an optimization run and to monitor them afterwards within the decision support system. The different loops (see Tab. 1) provide this possibility. Here, also the different metrics to measure the information content of the optimal experiments can be monitored and investigated.
- Last but not least, sensitivities can be used as part of the optimization problem and can be either minimized or maximized depending on whether a robust planning problem or a design of experiment problem is studied. It is also possible to use the minimum (maximum) value of objectives estimated within the sensitivity analysis and to maximize (minimize) it. This would be a worst-case scenario (min-max problem [19]). Multi-objective optimization can be further used to simultaneously maximize the information content and minimize parameter correlation [20].

Summarizing this point, we conclude that INES brought the most prominent methods of robust and stochastic optimization into industrial practice, available to any user. These methods rely on applying a certain sampling strategy of the uncertain model parameters and processing the results further in the optimization loop. Also the chance-constraint programming approach [21], where the sampling is done according to probability distributions, can be straightforwardly incorporated in future work.

5 Solver

For solving the data reconciliation problem (see Sect. 3.2), sequential quadratic problem (SQP) based solvers NLPQLP and NLPISQ from Prof. Schittkowski [22, 23] can be selected. Additionally, the MISQP solver is selectable for the parameter estimation [24] for the case when a mixed-integer non-linear programming problem has to be solved. The user has the possibility to adjust the accuracy, the maximum number of function calls and further options to automatically reduce step length during optimization in case of diverging solutions.

6 Examples

6.1 Amine Plant

In the following, some of the tools for model validation, sensitivity analysis and parameter estimation will be demonstrated for an amine plant. The process includes an amination of an alcohol A. A scheme of the process is shown in Fig. 8. The alcohol A reacts with ammonia (NH_3) to form the primary amine P1. By further additions of A to P1, the secondary amine P2 and the tertiary amine P3 are formed

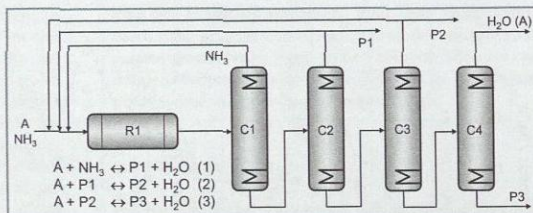


Figure 8. Scheme of the amine process.

(Fig. 8). Unreacted ammonia at the outlet of the reactor is separated in distillation column C1 and recycled. The distillation columns C2, C3 and C4 separate the products P1, P2, P3 and the by-product water. The products P1 and P2 can be partly recycled. This recycle as well as reaction conditions, e.g., feed ratio of alcohol and ammonia or temperature, affect the product distribution.

The goal of this process development is to allow process flexibility so that the product distributions can be adjusted to the actual market demands. To this end, suitable operating parameters must be identified. It was necessary to set up a model for the process including the reactor. The process was modeled in CHEMASIM (a detailed description of this process example is given in Burger et al. [16]). Note that this example is discussed qualitatively only and no details on the model are given here due to confidentiality. In a first step equilibrium constants from thermodynamic data like heats of formation and entropies at standard conditions have been used to calculate equilibrium constants for the reactions. Assuming that equilibrium is reached in the reactions, the reactor is modeled with these equilibrium constants.

Plant data for different operating conditions is available, in particular, reactor conditions, product recycles and resulting product distribution.

First, the equilibrium constants are used to calculate the product distributions to validate the model. Here, only one model is used and the operating data is read from a CSV file. The reactor temperature and the alcohol and ammonia mass flows as well as recycles flow rates for P1 and P2 are set to the measured values. In Fig. 9, a comparison between measured and calculated product mass flows for 15 different operating points is shown. Clearly, the model does not represent the data well, but at least the trend of the data is captured by the model though a large offset exists in products P1 and P3.

It is possible to combine model validation with data reconciliation as discussed above. The results of two different approaches are shown in Tab. 3. In the first approach for each operating point i the inlet flows in the simulation are allowed to deviate from the measured values. This is realized by introducing a factor d_{ij} for each flow j , which is allowed to vary between 0.95 and 1.05, i.e., the flows are

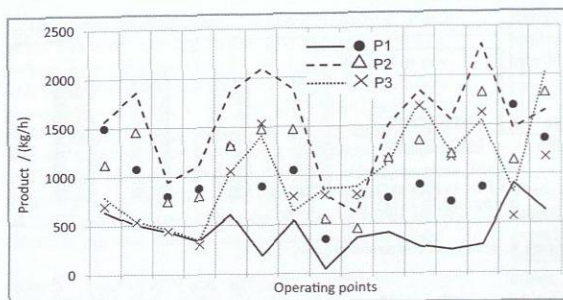


Figure 9. Model validation for the product distribution of the amine process at different operating points. Experimental: ● P1, △ P2, × P3, model: P1 (full line), P2 (dotted line), P3 (dashed line).

allowed to deviate by the typical accuracy of plant flow measurements, which is about $\pm 5\%$. For the 15 operating points four parameters in each loop are adjusted. In Tab. 3 only the arithmetic means $\bar{d}_i = \sum_{i=1}^N d_{ij}/N$, with N being the number of operating points, and the standard deviations are given.

In the second approach, only one set of 4 factors d_i are estimated simultaneously to all operating points, since typically in practice the 5 % accuracy not only reflects the measurement variances but also includes some offsets. In other words, one does not expect that one measurement deviates by +5 % in one operating point and by -5 % in another operating point. The results for these parameters (referenced as model validation with reduced data reconciliation) are also given in Tab. 3. It can be seen that there are no large differences between the means (av.) obtained from the first approach and the parameters from the second approach. Although the factors have all been changed nearly up to their bounds, the sum of least squares, LSQ, is only reduced by about 16 % in the best case. This clearly shows that data

reconciliation will not significantly change how model and data agree when an inadequate model is used.

In general, limited accuracy of thermodynamic data has a large impact on the equilibrium constants. The temperature dependence of the equilibrium constants in the considered temperature range is described in the simulation model by

$$\ln K_R = A_R + \frac{B_R}{T} \quad (10)$$

Herein A_R denotes the parameter which reflects the entropic part of the equilibrium constant, which is harder to determine. The subscript R is the index for the reactions. A sensitivity analysis is performed to find out which of the factors have the largest impact in order to decide which of these parameters A_R to adjust. For each of the parameters a factor d was introduced which allows a deviation from the original value by $\pm 10\%$. Since literature is available which shows large discrepancies in K_1 , the factor for this constant was allowed to vary in a larger range up to a factor of 6 of the original value.

The results of the sensitivity analysis are shown in an interactive sensitivity analysis support tool (Fig. 7). In this tool, it is possible for each operating point to see the impact of the different factors on several objectives like for example the sum of least squares (lsq) of all product flows (P1, P2 and P3) or the deviations in product P1 only denoted by DELTA_P1.

The schematic view of the interactive sensitivity analysis support tool consists of different areas. In the left part there is a 2D plot area and a slider view available which is similar to the one for the decision support in multi-objective optimization described in Burger et al. [16]. Here, in black the reference points and in gray all sampling points are given. Additionally, in the right part the sensitivities of the objec-

Table 3. Results of the model validation and parameter estimation of the amine plant with and without simultaneous data reconciliation (av. = average d_i of estimated factor overall operating points, std. dev. = standard deviation, LSQ = sum of least squares)

Factors d_i or d_j for j equal to	Model validation		Parameter estimation		
	–	with data reconciliation av. (std.dev.)	with reduced data reconciliation	–	with reduced data reconciliation
Feed A	–	0.970 (0.007)	0.970	–	0.994
Feed NH3	–	1.049 (0.003)	0.105	–	0.993
P1 recycle	–	0.950 (0.000)	0.950	–	1.050
P2 recycle	–	0.970 (0.031)	0.957	–	1.005
A_1	–	–	–	4.835	4.869
A_3	–	–	–	1.057	1.059
LSQ/10 ⁶	7.716	6.472	6.531	0.398	0.377

tives with respect to the uncertain parameters are shown. In the upper part a table gives the estimated sensitivities and in the lower part these sensitivities are visualized for the selected operating point for each objective (e.g., l_{sq} and Δ_{P3}). A box-whiskers plot [25] displays the distribution of the sample points and additionally bars show the sensitivities. The reference value from the initial simulation is shown as a black line. A red (here: dark gray) or blue (light gray) bar indicates an increase or decrease of the objective function with increasing parameter values if this indication can be obtained from the chosen sampling method. To this prototype visualization an averaged sensitivity overall operating points will be added.

The sensitivity analysis shows that both A_1 and A_3 reduce the sum of least squares while A_2 increases it. Since the simulation predicts the product flow of P2 already with good agreement, it seems that only A_1 and A_3 will be able to improve the distribution. So, A_1 and A_3 were selected to be estimated. The results are shown in Fig. 10 and Tab. 3. Thus, the deviations are reduced significantly (compare gray (without estimation) with black lines (with estimation)).

The parameter estimation is also combined with a simultaneous data reconciliation using the same four factors d_i as in the model validation (see above, denoted as "reduced data reconciliation" in Tab. 3) together with the factors for A_1 and A_3 to be estimated simultaneously to all operating points.

The results are given in Tab. 3. The sum of least squares is reduced compared to the case without data reconciliation, but not very significantly. In a diagram similar to Fig. 10, there would be no remarkable difference. Here, since the model with estimated parameters is able to describe the data, data reconciliation is not necessary. In our opinion the main purpose of data reconciliation is to verify if the data satisfies mass balances within their variances or accuracies. Compared to the computational effort, there is no great benefit to combine data reconciliation with model valida-

tion and parameter estimation. Thus, data reconciliation based solely on mass balances prior to model validation and parameter estimation seems to be sufficient. The user can decide if he prefers to use reconciled data or the original experimental values in these subsequent steps.

6.2 NQ Curve

For the separation of a gaseous mixture of methanol and water a distillation column as shown in Fig. 11 is designed. Sufficient vapor-liquid equilibria data is available in the literature, but there is some uncertainty in the data. However, the model agrees with the data to within the variance of the data as can be seen in Fig. 12 on the left side. Nevertheless, since methanol purity of up to 6 ppm is required, the impact of uncertainties in the activity coefficient at infinite dilution of water in methanol is of interest. The activity coefficients at infinite dilution are varied by $\pm 10\%$. This modification is realized with the Margules approach as a consistent model for the uncertainty in the Gibbs excess [11]. In the right part of Fig. 12 one can see the impact of

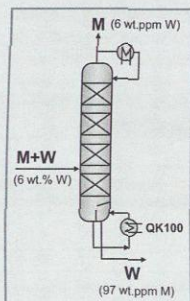


Figure 11. Distillation column for the separation of a methanol (M)-water (W) mixture.

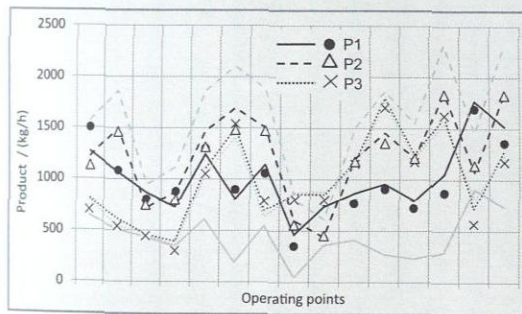


Figure 10. Model adjustment for the product distribution of the amine process at different operating points. Experimental: $\bullet$ P1, $\times$ P2, Δ P3, model: P1 (full line), P2 (dotted line), P3 (dashed line), black after parameter estimation, gray before parameter estimation.

this modification on the compositions of the vapor-liquid equilibria.

The classical approach in designing columns is to use NQ curves [26]. A NQ curve is a Pareto frontier representing all best compromises between the total number of theoretical stages N and the reboiler heat duty Q_{K100} . Here, only the number of stages and the feed stage are considered as parameters. The heat duty is a result of the fixed product specifications for top and bottom products. Since all parameters are integer variables, the Pareto frontier consists only of discrete points.

The uncertainty in the vapor-liquid equilibria introduced by the variation of the activity coefficient at infinite dilution has an impact on the necessary heat duty for some fixed number of total stages and feed stage. This can be investi-

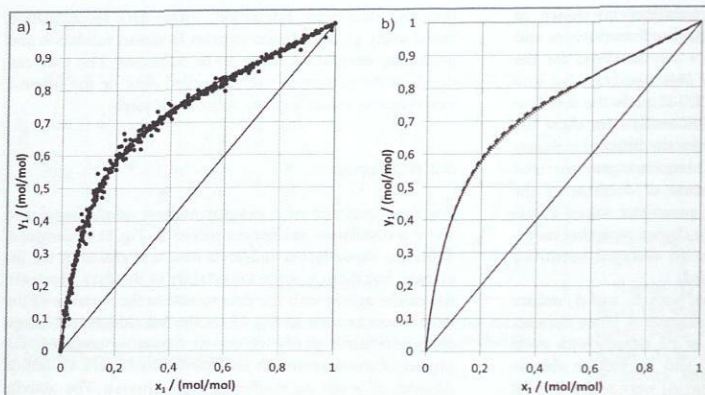


Figure 12. Vapor-liquid equilibria at 1.013 bar for the mixture methanol (1)-water (2). (a) Comparison of the model (full line) with available experimental data (full circles). (b) Impact of uncertainties in the limiting activity coefficient of water in methanol: original model (full line), 10% increased limiting activity coefficient (dashed line), 10% decreased limiting activity coefficient (dotted line).

gated simultaneously by sensitivity analysis. In Fig. 13 the resulting Pareto frontier is shown. The details of the visualization have already been described in detail [15, 16]. In the navigation tool the following different sensitivity measures

$$S_{1, \text{rel}} = \frac{f_u - f_l}{f_r} \quad (11)$$

$$S_{2, \text{rel}} = \frac{f_r - (f_u + f_l)/2}{f_r} \quad (12)$$

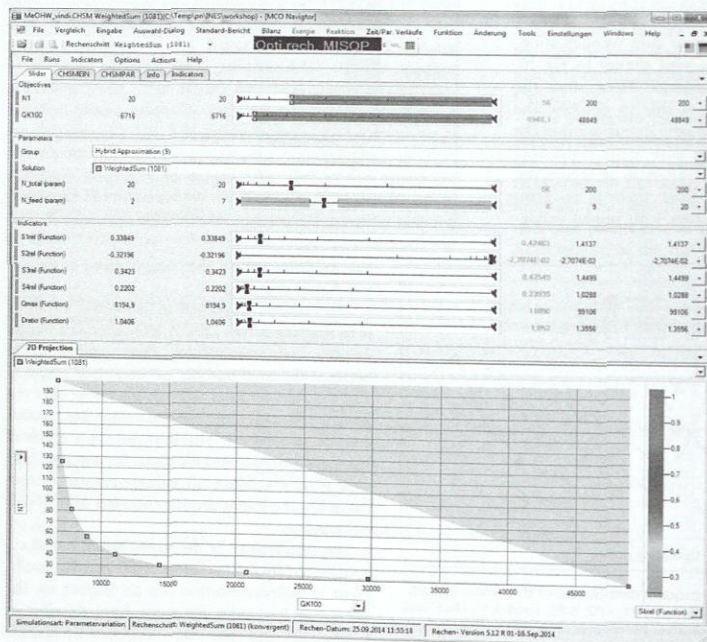


Figure 13. Screenshot of the decision support tool showing the results for the NQ curve for the methanol-water separation (cf. Fig. 11) together with the results of the sensitivity analysis for the uncertainties in the vapor-liquid equilibria (cf. Fig. 12).

$$S_{3,rel} = \sqrt{(S_{1,rel})^2 + (S_{2,rel})^2} \quad (13)$$

$$S_{4,rel} = \frac{\max_{i=u,l,r} (f_i - f_r)}{f_r} \quad (14)$$

f represents an objective function, in this case the reboiler duty Q_{K100} . Index u (l) represents the value at the upper (lower) bound, in this case $+10\%$ (-10%) and r is the reference case, i.e., without variation.

These sensitivity measures were chosen to represent sensitivities similar to the interactive sensitivity tool (see Fig. 7):

$S_{1,rel}$ represents the height of the bar relative to the reference case. $S_{2,rel}$ relates the distance of the reference case to the midpoint of the bar corresponding to the reference case. $S_{3,rel}$ combines both measures. $S_{4,rel}$ represents the relative distance of the largest reboiler duty to the reference case. With the largest reboiler duty it is in principle possible to achieve the separation specifications for all other cases. For this reason, only the largest positive deviation from the reference is considered and not the absolute deviation. It is interesting to know to which extent the reboiler duty has to be increased for the design to account for the VLE uncertainty as reflected by Fig. 12. $S_{4,rel}$ is selected to color code the points in the 2D plot (cf. Fig. 13). The relative sensitivity $S_{4,rel}$ varies between 22 and 103 % for the estimated Pareto points. The smallest values are reached at the lowest reboiler duties. The sensitivity $S_{4,rel}$ exhibits large values over the whole range so that it would be beneficial to reduce the uncertainty in the VLE by performing additional measurements. But it is doubtful that additional measurements really are able to decrease this uncertainty (see Fig. 12). An alternative is the consideration of the worst case to reduce the impact of uncertainties as will be discussed below.

The uncertainty in the VLE also has consequences on the load of the column or the sizing. If the sizing of the column diameter is based on a maximum allowed F -factor in the column, then the following expression can be used to compare the maximal column diameter for all cases with the reference case:

$$D_{ratio} = \sqrt{\frac{\max_{i=u,l,r} \left(\max_{j=1,\dots,N} \hat{V}_{i,j} \sqrt{\rho_{l,j}} \right)}{\max_{j=1,\dots,N} \hat{V}_{r,j} \sqrt{\rho_{r,j}}}} \quad (15)$$

In the shown range of the Pareto curve the diameter ratio is between 104 % and 135 %, where the highest values occur at the highest reboiler duties. At lower reboiler duties the increase in diameter is small or even negligible since this would only cause small increases in the F -factor. These small increases in the F -factor usually should be possible to handle if the selected maximum allowed F -factor was not at the limit of the operability range, i.e., if the design margin included some distance from the flooding curve of the used column internals.

This example shows how a simultaneous sensitivity analysis combined with a multi-objective optimization can be performed and yields useful information for the process design.

Since the reboiler duties for the varied activity coefficients are calculated, it is also possible to use the maximum value of Q_b , Q_u and Q_r and to minimize this value within the multi-objective optimization in addition to the total number of stages. This means that for all cases the separation is possible. The difference between the previous method and this robust planning method is shown in Fig. 14. The robust optimization needs more energy for the same number of total stages or a higher number of total stages for the same reboiler duty in the objective range where the curves of both methods overlap. Comparing the results for 56 total stages shows further differences as can be seen in Tab. 4. Here, the identified column designs differ in the last remaining parameter, the feed stage, which only can have discrete values. In the robust optimization the feed stage is lowered to reduce the necessary heat duty Q_{max} . If in the previous method also the sensitivity of the reboiler duty is taken into account in the reboiler design, then both designs based on Q_{max} are nearly identical. So, both methods will help to reduce the impact of sensitivities caused by uncertainties. To summarize the differences between the methods briefly: In the first method sensitivities are determined based on the design of the reference case, while in robust planning the design is optimized based on the worst case scenario.

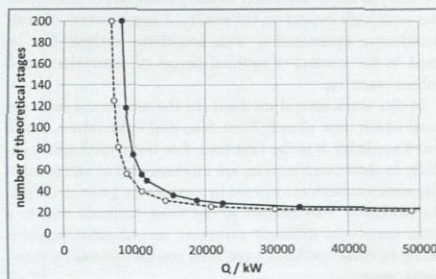


Figure 14. Comparison of the Pareto frontiers of the NQ curve for the methanol-water separation (cf. Fig. 11) with the original model (dashed line and hollow circles) with the results of the robust optimization (full line and full circles) taking into account the uncertainties in the vapor-liquid equilibria (cf. Fig. 12).

This small example already shows a potential application of the robust planning method. In other, more complex cases with more parameters, the differences in the design between both methods might be much more significant. Note that the method is not restricted to variations between the lower and the upper limit ("one at the time"), it is also possible to use each of the sampling methods given in Tab. 2.

Table 4. Feed stage position and reboiler duties for a design with 56 total stages (* denotes the result of the optimization for the reboiler duty).

	Multi-criteria Optimization with Sensitivity Analysis	Robust planning
Feed stage	8	7
Q_{K100} (reference) [kW]	8948*	8950
Q_{max} [kW]	11090	11068*

7 Conclusions

For the optimization of processes – offline [16] as well as online [27] – there is a need of high quality models describing the reality in the operating range of interest. Therefore, the use of available experimental data in model development has to be increased. There is a lack of tools supporting the process designer in the modeling, simulation and optimization workflow. The project INES was started to remedy these deficiencies and to develop an interactive interface between experiments and simulation.

Systematic tools supporting data selection and reconciliation based on data from plant information management systems facilitates these tasks. The use of selected operating data in model validation and adjustment will increase the understanding of model quality and its limitations. Sensitivity analysis helps to identify model parameters or uncertainties with high impact on the results. A combination of multi-objective optimization with sensitivity analysis can be used in the context of optimal design of experiments and robust planning.

In this work several methods for the mentioned tasks are used which have already been described in literature. But to our knowledge it is the first time that these methods, especially in their combination, are implemented in an industrially used simulation software to support the process designers workflow. This enables to use these methods now to a huge variety of different processes in industrial practice. Many of these methods have been complemented by interactive tools:

- In data selection, smart scaling enables the designer to remove outliers, identify stationary time periods for the storage of different steady-state operating points.
- Easy mapping of measurement tags to simulated state variables and grouping of unit operations using the process flow diagram facilitates data reconciliation based on the topology.
- Managing different operating points for model validation and adjustment (especially parameter estimation) is supported. Experimental data with simulation results can be compared using stream tables and process flow diagrams.
- It has been shown that sensitivity analysis is useful in many design tasks including investigation of the impact of uncertainties and identification of parameters with

high impact on the objectives of interest. This is supported by an interactive sensitivity analysis tool.

- Multi-criteria optimization can be connected to sensitivity analysis either to visualize sensitivities of the optimization results or to incorporate it into the optimization problem. Using results of the sensitivity analysis within optimization allows either to also maximize the information content of an experiment in addition to other objectives in optimal design of experiments or to design a robust process (optimization of the worst case scenarios).

Systematically supporting the process designer's workflow can increase model quality, which is very important for process scale-up and optimization, and improve the developed process. Moreover, it frees specialists from tedious and time-consuming elementary tasks and allows them to become more productive. Overall, it reduces time and cost in process development. In particular, runtimes of lab and mini-plant experiments can be shortened; production cost can be minimized by more robust process designs; risks in process design can be addressed earlier; time-to-market can be decreased.

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Abbreviations

KPSS	Kwiatkowski-Phillips-Schmidt-Shin
oDoE	optimal design of experiments
PIMS	plant information management systems
VLE	vapor-liquid equilibrium

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Paper V: Simulation and Multi-criteria Optimization under Uncertain Model Parameters of a Cumene Process [Asprion et al., 2017b]

Simulation and Multi-criteria Optimization under Uncertain Model Parameters of a Cumene Process

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Since experimentation is expensive with increasing computation power the significance of modeling, simulation, and optimization in process development has grown. Quite often in such models some parameters are uncertain, e.g., due to high variance in experimental data used for their estimation. Methods for investigating the impact of uncertain model parameters in the simulation and a new extension of an adaptive multi-criteria optimization method to account for these uncertainties are described and demonstrated based on a cumene process.

Keywords: Decision support, Multi-criteria optimization, Robust optimization, Sensitivity analysis, Stochastic optimization

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1 Introduction

The use of simulation models for an optimization with respect to sustainability criteria requires a combination of a thermodynamic process simulation with a sustainability evaluation (cost estimation and life cycle assessment) as shown in Fig. 1. Besides process parameters which include design and operation parameters, model parameters (e.g., interaction parameters of phase equilibrium models, parameters of kinetic, or equilibrium constants of reactions) as well as evaluation parameters (like e.g., costs of raw materials) have to be given. Many of these parameters are usually not known exactly but have some uncertainties. The impact of these uncertainties on the simulation results and especially on the most important objectives which are used for the optimization is of interest. Since the dependency of the objectives on uncertain parameters is usually not known, the task to investigate their impact is similar to a design of experiments.

One method which can be easily implemented within a process-simulation software is the application of sample points within the range of the uncertain parameters. Sample points are sets of uncertain parameters which will be called scenarios in the following. So in this contribution only finite numbers of scenarios for the optimization under uncertainty are considered. Infinite numbers of scenarios would lead to semi-infinite programming problems (e.g., Reemtsen et al. [1]) which are not considered in this contribution.

An alternative to sampling techniques is algorithmic (or automatic) differentiation (e.g., Griewank et al. [2]) to estimate the impact of uncertain parameters on simulation results by an appropriate linearization. However, this technique is not easy to use for process simulation software due to their complex structure and is therefore not used here.

The challenge is to get maximal information with limited effort (number of sample points). For this sensitivity analysis a lot of different methods are available (e.g., Saltelli et al. [3]) which greatly differ in accuracy and expense. While the use of this variety of methods is possible for investigating the impact on simulation, their implementation for the use within optimization is mostly restricted on methods with a very low number of sample points due to the problem size and calculation times.

To improve the modeling, simulation, and optimization workflow during process development, recently, several tools were implemented in BASF's inhouse simulation tool CHEMASIM due to the accessibility of the source code. However, the experience in respect to implementation, usability, and functionality gained does not depend on the choice of the process simulator or the company's environment and is therefore of general interest. A comprehensive description of the possibilities in CHEMASIM with some application examples is given in Asprion et al. [4]. For the above mentioned tasks for the investigation of the impact of uncertainty two options are of interest: (1) Sensitivity Analysis which supports the investigation of the dependencies of arbitrary objectives (selectable from the simulation outputs)

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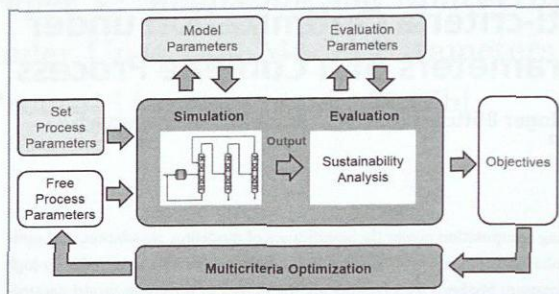


Figure 1. Scheme of process simulation and optimization and required parameters. The impact of uncertain parameters θ (selectable from set process parameters, model parameters as well as from evaluation parameters) on simulation and optimization results are investigated. Free process parameters are parameters p of the optimization problem.

on uncertain parameters for several different simulation inputs (e.g., reflecting different operating conditions). (2) The already existing multi-criteria optimization with an adaptive sampling scheme of the Pareto boundary (multicriteria optimization (MCO), Bortz et al. [5], Burger et al. [6]) which was extended to the use cases robust optimization and stochastic optimization. Those take uncertainties during optimization into account.

As shown in Fig. 1 the impact of uncertainties of many different parameters on simulation and optimization results might be investigated. For example, set process parameters like operating parameters (temperatures, pressures, mass flows, concentrations, etc.) and design parameters (number of theoretical stages of a column, etc.), but also model parameters can be defined as uncertain. Here an interface to physical properties (activity coefficients, vapor pressures, enthalpies, etc.) has been implemented into CHEMASIM. Using this interface, uncertainty is defined in the physical properties directly, e.g., limiting activity coefficient or vapor pressures than in interaction parameters or vapor pressure parameters (Burger et al. [7]).

In addition other model parameters like reaction parameters (equilibrium and kinetic constants) and mass transfer coefficients as well as enhancement factors can be perturbed for sensitivity analysis by applying factors on these properties. Furthermore, evaluation parameters like costs and some sustainability inputs might also be selected as uncertain parameters for investigation.

In the following some fundamentals of these methods will be described and then the application to the cumene production process will demonstrate some of the functionalities and their use within process development.

2 Sensitivity Analysis

The sensitivity analysis is a natural extension of a parameter variation to the case where the enumerated parameter

sets exhibit some kind of uncertainty – either in the enumerated parameters themselves or in any other model parameters. Thus, it is implemented as a parameter variation. The results are visualized in a graphical user interface together with interactive filter elements and statistical information.

Beyond this conventional use case, the sensitivity analysis allows the investigation of the impact of uncertain parameters on different objectives. Those can be selected after the sensitivity analysis run from the full set of simulated stream properties, heat streams, or self-defined functions. In the sensitivity analysis different operating conditions can be analyzed by a separate enumeration, which might reflect different operating conditions, e.g., different loads of a chemical plant.

Practical experience shows that it is necessary to compare different sampling schemes of the uncertain parameters in order to get reliable results from the sensitivity analysis. Therefore, different methods were implemented to estimate the impacts of the uncertain parameters. Since there is no easy functional dependency between objectives and uncertain parameters, the impacts have to be estimated by sampling the whole uncertainty range. There are in general two classes of methods: (1) Methods which determine the finite difference to estimate directly the impact of the individual parameters on the objective and (2) methods which estimate the contribution to the variance (i.e., the square of the standard deviation of a distribution) of the different parameters.

While the first class is always deterministic, for the second class there exist both stochastic and deterministic methods.

The results of both classes of methods are not directly comparable, while the first might also give negative values (anti-proportional impact), the stochastic methods only produces positive contributions with large values when the uncertainty produces large variances.

Details about the different sampling methods can be found in Saltelli et al. [3]. Tab. 1 shows the possible selections which have been implemented in CHEMASIM. The method of numerical integration using sigma points is

Table 1. Different selectable methods for sensitivity analysis in CHEMASIM.

Class	Method
Finite differences	One at a time [3]
	Full and fractional factorial design [3]
	Elementary effect method [3]
Variance-based indices	Quasi-Monte Carlo (Sobol sequence) [3]
	Numerical integration using sigma points [8]

based on sigma points calculated by using the fully symmetric numerical integration formulas [8].

The results can be investigated in a sensitivity navigator, where the properties for which sensitivities should be estimated, can be selected. There are a lot of different possibilities to analyze the generated data:

- Several 2D projections (or scatter plots, similar to the one in the MCO navigator described in Burger et al. [6]) with the possibility to choose a third property as color code of the investigated points. This can, e.g., be used to show the variability of an objective for different enumerated points. For example if they represent different measured operating points then it is possible to add the experimental data to this 2D projection.
- A slider view which allows to investigate the results of the sensitivity analysis by restricting values or navigation (moving sliders), similar to MCO [6].
- Sensitivity bar chart for each chosen objective to be investigated: Here in case of finite differences based sampling methods two different sensitivity measures are shown for each uncertain parameter. Furthermore, a box-whisker plot is included showing the full range, quantiles, mean values, and the reference (or nominal value).
- For vectorial properties like, e.g., temperature profiles of columns it is possible to see the sensitivities for the whole vector. This allows, e.g., to choose a position for the placement of a temperature sensor in a distillation column based on the largest sensitivity on process fluctuations as described, e.g., by Oldenburg et al. [9].
- Within the sensitivity navigator it is possible to calculate a relative gain array which can be used to identify possible good combinations of manipulated and controlled variables. (cf., e.g., Skogestad [10]).

3 Multi-criteria Optimization under Uncertainty

An existing multi-criteria optimization tool based on an adaptive method to calculate Pareto points (Bortz et al. [5]) was extended to account for uncertainties during optimization. As mentioned before, here only a finite number of scenarios (samplings) is considered. In this first implementation as sampling method for investigating the uncertainty range the factorial design was chosen. In principle it is possible to extend the application to other methods, but there is danger to get lost in the different methods and produce a large amount of different simulation and optimization runs. Therefore, a computationally relatively cheap method in terms of number of samplings was selected here. There are two different ways to consider the different scenarios (samplings). Either focus on the worst case and try to optimize this case, which is done in robust optimization (cf., e.g., [11] and [12]) or evaluate the different scenarios to calculate a mean (or expected value) and a variance to use them as

objectives within the multi-criteria optimization which is done in stochastic optimization (cf., e.g., [13] and [14]).

3.1 Robust Optimization

The goal of robust optimization is to identify a conservative design, which works for all scenarios without optimizing each scenario individually (parametric optimization, cf. Sect. 3.1.2). In this respect, conservative is a good result since none of the considered scenarios can lead to a worse design. In the following only this min-max robustness is considered. For examples of other kinds of robustness refer to [15]. Depending on the constraints of the optimization problem the robust optimization might lead to worse solutions than the individual scenarios. This leads to overconservative designs which will be more costly.

3.1.1 Unconstrained Robust Optimization

There are some questions arising with the definition of worst cases especially in the context of a multi-criteria optimization. Considered the case of an unconstrained single objective optimization problem, in which an objective f_2 should be minimized. If p denotes the parameter vector of the optimization problem and θ_s the vector of uncertain parameters for scenario s (proposed by the sampling method) then with

$$f_{i,s} = f_i(p, \theta_s) \quad (1)$$

The optimization problem can be formulated as follows:

$$\min_p \max_s f_{2,s} \quad (2)$$

So during optimization (here minimization) the maximum of f_2 of all scenarios has to be identified. This maximum which is unique in case of single-objective optimization (i.e., scenario with highest value of f_2) might be not in case of multi-objective optimization. That is demonstrated in Fig. 2 for a problem with 2 objectives f_1 and f_2 . There are

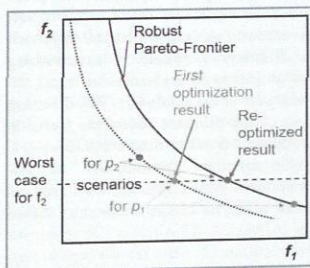


Figure 2. Problem with worst case of f_2 in multicriteria optimization: several solutions possible. Use of re-optimization to improve the solutions of extreme compromises: Identify worst case in f_1 at fixed value for worst case of f_2 .

two solutions with the same value $f_{2,s^*} = \min_p \max_s f_{2,s}$ which differ in the value for f_1 . If the objective was to minimize the worst value of f_1 as well; then the worst case scenario is the one with the higher value for f_1 .

In CHEMASIM a hybrid approach for the adaptive multi-criteria optimization is used (cf. Bortz et al. [5]). This starts with the identification of the extreme compromises (i.e., single-objective minimization of the different objectives). Since in these cases exactly the problem visualized in Fig. 2 may occur, a method for re-optimization is introduced. Starting from this point, a second optimization starts that should have f_{2,s^*} as an upper limit (included as constraint for all solutions):

$$\min_p \max_s f_{1,s} \quad (3)$$

$$\text{s.t.: } f_{2,s} \geq f_{2,s^*} \quad (4)$$

The analogous re-optimization problem is solved after identifying the extreme compromise (i.e., optimizing the function) for f_1 .

In case of more than two objectives the direction of this re-optimization is not unique. Here an equally weighted direction is used. So for the re-optimization after robust optimization of f_j the following problem is solved:

$$\min_p \max_s \sum_{i \in j} f_{i,s} \quad (5)$$

$$\text{s.t.: } f_{j,s} \geq f_{j,s^*} \quad (6)$$

Re-optimization is also beneficial for "normal" MCO problems, if, e.g., an objective is independent of one parameter. After optimizing this single objective this parameter might have an arbitrary value. In this case re-optimization can avoid starting the adaptive solution strategy from a dominated solution. There is no guarantee that this is the best solution but if a better one will appear the adaptive method will omit the dominated solution.

In a multi-criteria optimization the question about how to identify the worst case has to be answered as shown in Fig. 3 since there is not a single criterion to define the ranking of the cases like in single-objective optimization. Comparing scenario s_1 with s_2 in Fig. 3: s_1 is worse in f_2 but better in f_1 compared to scenario s_2 . In the adaptive approach for convex Pareto frontiers normally a sandwiching approach (cf. Bortz et al. [5]) is used which determines the direction of the thickest part of the sandwich. This direction defines the weights w_i of the different objectives f_i and in the adaptive process the next point of the Pareto frontier is determined by single-objective optimization of this weighted sum. So in robust optimization the maximum of the weighted sum of all scenarios has to be used as shown by Ehrgott et al. [16].

$$\min_p \max_s \sum_i w_i f_{i,s} \quad (7)$$

So here the weighted sum is used as a criterion for the ranking of the scenarios. The maximum defines the worst

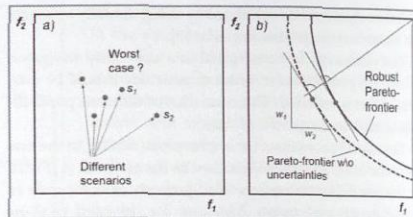


Figure 3. a) About the definition of worst case scenario in multi-criteria optimization: Scenario s_1 is worse in f_2 but better in f_1 compared to scenario s_2 . b) Determination of robust Pareto point by minimizing the maximum of the weighted sum of all scenarios in the sandwiching approach.

case for the minimization (Fig 3b). For the case of non-convex Pareto frontiers the Pascoletti-Serafini method is used for which a similar approach can be used.

3.1.2 Constrained Robust Optimization

In the following only inequality constraints are considered. Inequality constraints limit the feasible range for the optimization. If constraints are active after an optimization run, which means the equality holds, then the results for the objectives will in general be different from the unconstrained case. Therefore, constraints usually will influence the result of the optimization. During optimization it is in general not sufficient to consider only the constraints of the actual worst-case scenario which will be further optimized. Since it is not clear which scenario will finally (i.e., at the end of the optimization) be the worst case. A robust approach is to add the constraints for all scenarios to the optimization problem. This guarantees that the constraints are satisfied (if possible) by the final worst case scenario. That treatment of the constraints in general leads to a rather overconservative solution [15].

A different point of view is motivated by the fact that quite often, the different scenarios are independent from each other and the realization of one scenario will in general exclude the realization of the other. Therefore it is not realistic that the constraints for all scenarios have to be fulfilled simultaneously. It might be that there is even no solution with finite overlap between the feasible ranges defined by the constraints for the different scenarios. In this case, for each scenario a complete multi-criteria optimization has to be performed and it is only a posteriori possible to decide which scenario is the worst case. This is usually called parametric optimization (s., e.g., [17]). The therefore required automatic enumeration of the different scenarios is possible within the multi-criteria optimization setup. For this the uncertain parameters have to be enumerated. To get a full factorial design the step size for each uncertain parameter has to be equal to the distance between the upper and lower limits of this parameter.

If the limits in the constraints are also uncertain then their enumeration can be used to investigate the impact of these limits on the results of the multi-criteria optimization.

Among the implemented methods to take the constraints for the different scenarios in stochastic optimization into account there is also a method to define a probability that constraints are fulfilled – so-called chance-constraint approach [14] – which is not considered here.

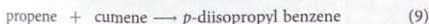
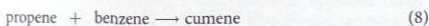
3.2 Stochastic Optimization

In stochastic optimization the objectives of the different scenarios should be weighted according to their probability to determine the expected value $E[\dots]$. Since normally the probability distribution is not known quite often equal weighting (uniform distribution) or normal distribution of the different scenarios are chosen which results in the mean value for the objective. One possibility is to replace an objective by its mean over all uncertainty scenarios. In some cases it might be interesting to reduce the variance (square of the standard deviation) of the distribution. Therefore, in the setup of the stochastic optimization it is alternatively possible to replace the objective by its standard deviation.

If inequality constraints are present in the stochastic optimization problem there are different possibilities to take them into account. Using also an expected value for the constraints will lead to solutions in which the active constraints are only fulfilled for 50 % of the scenarios in case of a normal distribution. This normally is not acceptable. In chance-constraint optimization (cf. [14]) it is possible to define a probability to which extent the constraints should be fulfilled. Here a version in which the constraints have to be fulfilled simultaneously for all scenarios similar to the proceeding for the robust optimization was used.

4 Cumene Process Example

A scheme of the cumene process is shown in Fig. 4. Benzene and propene containing 5 mol % of propane are used as feedstocks. The feeds are mixed with recycled, mainly unconverted benzene and fed into an evaporator. The mixture is then heated in a feed-effluent heat exchanger and subsequently heated up to temperatures above 330 °C. The reactor is a shell-and-tube reactor. The tubes are filled with catalyst and there the following reactions take place:



The model for the reaction rate is:

$$r_1 = k_1 c_{\text{propene}} c_{\text{benzene}} \quad (10)$$

$$r_2 = k_2 c_{\text{propene}} c_{\text{cumene}} \quad (11)$$

The kinetics are expressed by the Arrhenius ansatz:

$$k_i = k_{0,i} \exp\left(\frac{E_{A,i}}{RT}\right) \quad (12)$$

with:

$$k_{0,1} = 2.8 \cdot 10^7 \text{ L mol}^{-1}, E_{A,1} = 104\,251 \text{ J mol}^{-1} \quad (13)$$

$$k_{0,2} = 2.32 \cdot 10^9 \text{ L mol}^{-1}, E_{A,2} = 146\,873 \text{ J mol}^{-1} \quad (14)$$

The reaction heat is used to produce 40 bar(g) steam. The reactor outlet is cooled and flashed. Propane is removed with the overheads of the flash. In the first column of the process unconverted benzene is removed and recycled to the feed section of the reactor. The remaining bottoms are fed in a second column where cumene is the top product with a desired purity of 99.9 mol %. The design capacity target is 98 kt per year. The bottom product of the column contains the undesired side product *p*-diisopropyl benzene (*p*-dipb).

Details about the cumene process have been described by Luyben [18]. The fluid properties in the system are modelled with the Soave-Redlich-Kwong (SRK) equation of state with Peneloux volume correction [19]. Parameters of this model are given in Tab. 2. Based on a total cost (for 10 a with discounted operational expenditures, discount rate 11 %) minimization the design of the process shown in Fig. 4 has been determined, the gray parameters reflect the numbers which have been adjusted, the black ones were fixed during optimization.

Table 2. Parameters of the Soave-Redlich-Kwong equation of state for the binary system cumene + *p*-diisopropylbenzene. The binary interaction parameter is $k_{ij} = 0$.

	p_c [bar]	T_c [K]	ω [-]
cumene	32.00	638.35	0.3444
<i>p</i> -diisopropylbenzene	24.50	684.00	0.3587

The following assumptions are made for the basis of this design. The heat exchanger, pumps, and columns are designed for 120 % load, the reactor design is dimensioned for 105 % load, and the reactor tubes length and diameter are built as described by Luyben [18]). The heat exchanger are assumed with heat transfer coefficients (U -values) for gas of $60 \text{ W m}^{-2} \text{ K}^{-1}$ and for all others of $1 \text{ kW m}^{-2} \text{ K}^{-1}$, column height (2 stages per m + 5 m) and diameter ($F_{\text{max}} = 2 \text{ Pa}^{0.5}$), and costs for catalyst 9.2 € kg^{-1} , benzene 957 € m^{-3} , propene 192 € t^{-1} , steam 7.3 € t^{-1} , cooling water 1.8 ct m^{-3} , electricity 7.3 € MWh^{-1} , fuel gas 20 € MWh^{-1} , and boiler feed water 0.275 € m^{-3} . The catalyst life time is assumed as of 2 a: initial fill is included in investment, refill is part of operational expenditure, and credit for heating value (cf. [18]) of stream 7 and 9 has been taken into account.

Tab. 3 shows the results for the sizes of the heat exchangers. A stream table for this design is given in Tab. 4. Concerning the design there exist some uncertainty about the

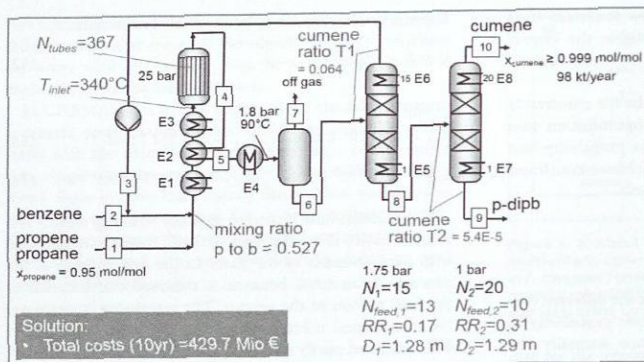


Figure 4. Principle of the cumene process with results of design optimization based on the model VLE2. Parameters during total cost minimization are shown in gray. Black values were fixed during optimization.

Table 3. Results of heat exchangers for the design of the cumene process based on model VLE2.

Heat exchanger	Area [m ²]	Utility	Heat Duty [kW]	T _{out} [°C]
E1	138	steam 40 bar(g)	3448	215.2
E2	705	–	1511	331.8
E3	15	electricity	104	340
E4	33	cooling water 25 °C	3320	90
E5	66	steam 40 bar(g)	1656	175.4
E6	30	cooling water 25 °C	1219	52.5
E7	47	steam 40 bar(g)	1174	217
E8	13	cooling water 25 °C	1330	151.6

Table 4. Stream table for the design of the cumene process based on model VLE2.

Stream	T [°C]	p [bar]	n [kmol h ⁻¹]	Mole fractions			
				propane	propene	benzene	cumene
1	25.0	25.2	104.4	0.05	0.95	–	–
2	20.0	25.2	99.1	–	–	1.0000	–
3	53.6	25.2	99.2	0.0582	0.0059	0.8719	0.0639
4	376.5	25	204.1	0.0539	0.0057	0.4396	0.4874
5	234.0	1.9	204.1	0.0539	0.0057	0.4396	0.4874
6	90.0	1.8	194.7	0.0297	0.003	0.4443	0.5089
7	90.0	1.8	9.4	0.5557	0.061	0.3419	0.0412
8	175.3	1.9	95.5	–	–	–	0.9711
9	217.0	1.1	2.6	–	–	–	0.0019
10	151.6	1	92.8	–	–	–	0.999

use of the correct vapor-liquid equilibrium (VLE) model and about the used kinetics. In Fig. 5 two different models (VLE1 and VLE2) to describe the experimental data of the VLE in the binary mixtures cumene/benzene and cumene/p-diisopropyl benzene are shown. Both VLE models differ in more than one model parameter but have been combined to one surrogate VLE model parameter to reduce the amount of scenarios to be considered during optimization under uncertainty. In the following the uncertainties of the kinetics as well as of the VLE model and their impact on simulation and optimization are investigated.

4.1 Application of Sensitivity Analysis

The design shown in Fig. 4 is based on the VLE2 model. In the following sensitivity analysis three uncertainties are considered:

- VLE model: either VLE1 or VLE2,
- uncertainty in kinetic constant $k_{0,1} \pm 10\%$,
- uncertainty in kinetic constant $k_{0,2} \pm 10\%$.

and compared to the nominal base-case: VLE model VLE2 and kinetic constants at their nominal values.

A factorial design is chosen as the sampling method. Since 3 parameters with 2 different values each are considered, $8 (= 2^3)$ scenarios are evaluated. Furthermore a variation of the load has been performed by multiplying the targeted capacity by a load factor which was chosen to be equal to 0.6, 0.8, 1, or 1.2. As can be seen in Fig. 6 for the whole loading range the cumene concentration is close to the targeted 99.9 mol%. Here no adaptations of the operating conditions were done, but also no operating limits of the designed plant were considered, which might change the picture.

For the VLE1 model all scenarios are significantly lower in the cumene concentration and it is unclear if the product quality can be achieved by adjusting the operating conditions

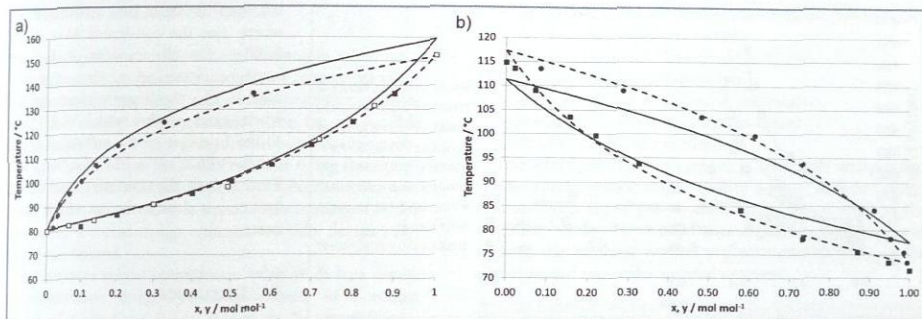


Figure 5. Vapor-liquid equilibrium (VLE) of a) cumene and benzene at 1 bar and b) cumene and *p*-diisopropyl benzene at 67 mbar: markers – experimental values, full lines – SRK model from ASPEN (model VLE1), dashed lines – modified model with corrected pure component fugacities (20 % increase for cumene, 20 % decrease for *p*-diisopropyl benzene, model VLE2).

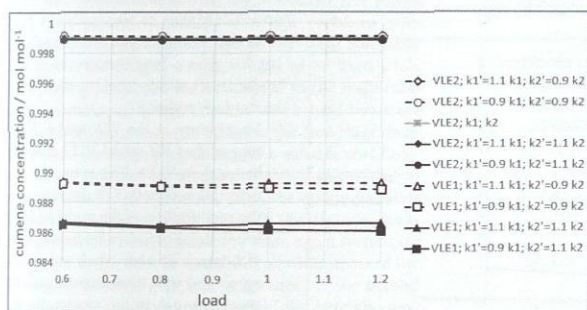


Figure 6. Results of the sensitivity analysis using a factorial design based on the parameter sets from the results of the process design (compare Fig. 4) for different loads. Uncertain parameters were the VLE model (1 or 2) and the kinetic constants ($\pm 10\%$).

within the limits of the designed plant. This question needs to be answered with optimization under uncertainty (s. next section).

4.2 Application of Optimization under Uncertainty

For the previously described cumene process it is investigated, if it is possible to adjust the operating conditions to achieve the desired product purity of 99.9 % under the given uncertainties.

For this optimization problem several operability constraints were introduced: (1) the logarithmic temperature difference in evaporators $< 30\text{ K}$ to avoid film boiling, (2) the maximum F -factor in columns is less than $2.1\text{ Pa}^{0.5}$ to avoid flooding and to maintain separation efficiency, (3) the liquid load in columns at top and feed stage is within 60 and 120 % of design load to stay in the typical liquid distributor operating range, and (4) the minimum temperature

difference in feed-effluent heat exchanger and condenser of the first column $> 1\text{ K}$ as a margin for calculation of logarithmic temperature difference.

The following objectives were chosen for the optimization: (1) minimize operational expenditures (discounted for 10 a) in relation to the amount of cumene produced (OpEx), (2) minimize global warming potential (GWP), (3) minimize load, and (4) maximize capacity.

OpEx and GWP are typical sustainability criteria. The GWP is a result (besides others like, e.g., resource demand, water use, etc.) of the life cycle assessment (s., e.g., [20]).

The last two objectives enable the simultaneous investigation of the minimal and maximal achievable load (= capacity/nominal capacity).

Here, the constraints have not to be fulfilled simultaneously for all scenarios, therefore, each scenario has to be optimized individually. As mentioned before, in the new MCO environment it is now supported to run individual MCO for several scenarios. Fig. 7 shows a 2D projection of the Pareto frontiers for the different scenarios. As can be seen for the cases with model VLE1 it is not possible to achieve a solution over the whole load range shown. For the worst case scenario (VLE1, $k_1' = 0.9 k_1$; $k_2' = 1.1 k_2$) less than 80 % of the nominal capacity could only be achieved. The results for the global warming potential (GWP) exhibit a similar trend and are not shown here.

In Fig. 8 these results are compared with the results of a robust optimization with the restriction that the constraints for all scenarios have to be fulfilled for each parameter set. Furthermore, it is compared with a stochastic optimization using the means for the operation expenditure and the global warming potential. For load and capacity, means could

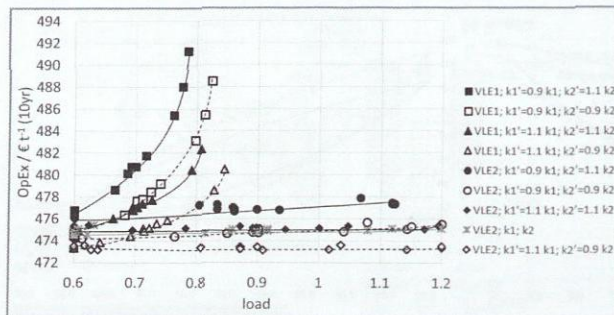


Figure 7. 2D projection (operational expenditure discounted for 10 years per ton of product (OpEx) vs load) of the Pareto frontier. Results of the enumerated MCO for optimization under uncertainty have been used for the cumene example: enumerated MCO (big symbols), robust and stochastic optimization. Lines are only for visualization (lower convex hull).

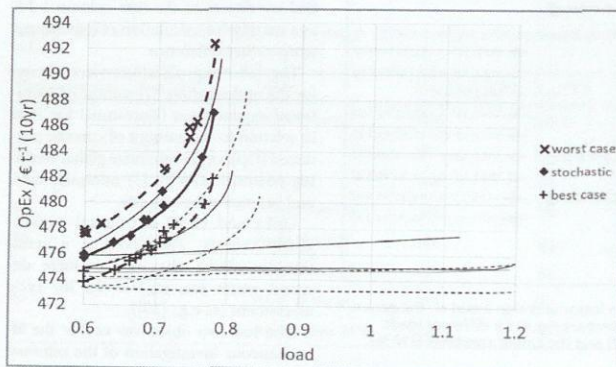


Figure 8. 2D projection (OpEx vs load) of the Pareto frontier. Here different methods for optimization under uncertainty have been used for the cumene example: enumerated MCO (lines cf. Fig. 7), robust optimization (worst case), stochastic optimization and best case optimization. Lines are only for visualization (lower convex hull).

also be used but since they are connected to the optimization parameter load, the means are identical to the parameter value.

The comparison of the different optimization methods (cf. Figs. 7 and 8) shows that robust optimization where the constraints have to be fulfilled for all scenarios s for the same operating parameters p is overconservative and the most costly solution. Stochastic optimization using the mean values in this case is close to the worst case of the enumerated MCO solutions. Probably this is due to the dominance of the constraints of the scenario VLE1 with $k_1' = 0.9 k_1$; $k_2' = 1.1 k_2$ in this problem and might be different in other optimization problems. The importance of the constraints is supported by the re-

sults of a best case minimization, where also the constraints have to be fulfilled for all scenarios s for the same parameter set p . Here, this best case is also significantly closer to the worse cases of the model VLE1 than to the best case of the individual MCO runs (VLE2, $k_1' = 1.1 k_1$; $k_2' = 0.9 k_2$). Furthermore, the maximum load of the best case is close to the one of the worst case.

5 Discussion

The design and the scenarios discussed for the cumene process are somehow artificial, but should rather demonstrate the use of the methods to account for uncertainty than to give guidelines how to design a cumene process. The following list gives a brief overview about the major issues which cause the example to be not fully realistic:

- Uncertainty in the VLE model: Fig. 5 suggest that the model VLE2 is much better than VLE1. This is true for the description of both VLE diagrams, but the modification of the model leads to lower vapor pressures for *p*-diisopropyl benzene at 1 bar which are not in agreement with measurements and are more relevant to the process. So for model VLE2 the separation in the last distillation column for the purification of the cumene to high purity (>99.9 mol %) is easier than it is in reality. Since the design is based on this model, the column is a limiting factor for the model VLE1 with the more realistic vapor pressure for *p*-diisopropyl benzene at 1 bar.
 - Choice of model type: In normal process design for the separation section at low pressure rather often a more accurate model based on Gibbs energy (e.g., an NRTL model) would be used than an equation of state or a modification like in model VLE2.
 - Constraints: The constraints for the distributors are often limiting. Especially for the top part of the first column very low liquid loads are present. Here, rather as internals trays would be used which offer a larger loading range for small liquid loads.
- In the discussed example the purification column seems to be the bottleneck of the design. The uncertainty in the kinetics can be compensated by loading ranges of the distillation section and the recycle.

6 Remarks and Improvements

The investigations considered in this example relied on a conventional design based on a total cost minimization for the nominal (un-perturbed) values of the uncertain parameters. Since usually a design should work for all possible uncertainties also a robust design could be used. One problem in this case is that the design rules for sizing the equipment, which form the basis for the cost estimation, are normally already conservative to cover all uncertainties. So for the use of a robust-design optimization new design rules would be required.

Furthermore robust optimization often leads to a costly, overconservative design. The requirements of a robust design of a plant are closely related to the possibility to adjust operating parameters for a chosen design to account for the uncertainty. Here, it is possible to extend the robust optimization in future to a two-stage stochastic programming with recourse formulation, e.g., Steinmel and Engell [21]: "[...] process synthesis and design problems with uncertain parameters naturally lead to two-stage stochastic problems as the design parameters have to be fixed while the operating parameters can be adapted to the realization of the uncertain parameters. The core idea behind two-stage stochastic programming is to optimize the first stage decisions (here, the design parameters) for a suitable cost function that is computed for an optimal choice of the second stage variables for each scenario. Thus, the option to counteract the uncertainties is anticipated in the decision, making the result much less conservative than, e.g., a worst-case design. The design must be feasible for all realizations of the uncertainty, however, only after adaptation of the second stage variables (operational parameters)." But here also new design rules would be necessary.

Further helpful improvements of the setup and execution of the multi-criteria optimization under uncertainty are:

- Inclusion of feasibility runs which ensure that each initial run during the optimization is based on a feasible parameter set.
- In some cases problems with the solver might arise which are probably to be caused by the linear dependence of the gradients of the constraints. This can be improved by the use of entropic smoothening (cf. [22, 23])

7 Conclusions and Outlook

The possibilities to analyze the impact of uncertainty on simulation and optimization are useful in many contexts.

- (1) To investigate the impact of uncertainty on simulation:
 - show variability of simulation results,
 - identify parameters which have to be determined with lower uncertainty
 - identify significant parameters for model adjustment or optimization,

- investigate different control concepts for process fluctuations (Oldenburg et al. [9]),
- Sensor placement (Oldenburg et al. [9]).
- (2) To be used within optimization:
 - show variability of optimization results,
 - stochastic and/or robust optimization,
 - optimal design of experiments.

The use of the different options in sensitivity analysis and multi-criteria optimization produce a lot of different simulations which are of great value for decision support of the engineer. Only by comparing different solutions and options the engineer reaches a good understanding of the situation and can make a sound decision.

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Symbols used

c	[mol L ⁻¹]	molarity (moles per volume)
E_A	[J mol ⁻¹]	activation energy
D	[m]	Diameter
f	[-]	objective
F	[Pa ^{0.5}]	F factor
k	[L mol ⁻¹]	kinetic constant
k_{ij}	[-]	binary interaction parameter
N	[-]	Number of feed stage, total stages or tubes
p	[-]	parameter
p	[bar]	pressure
r	[mol h ⁻¹ L ⁻¹]	reaction rate per volume
R	[J mol ⁻¹ K ⁻¹]	universal gas constant
RR	[-]	reflux rate
s	[-]	scenario
T	[K]	temperature
U	[W m ⁻² K ⁻¹]	heat transfer coefficient
w	[-]	weights

Greek symbols

θ_s	[-]	vector of uncertain parameters for scenario s
ω	[-]	acentric factor

Subscripts

C	at the critical point
feed	feed stage
max	maximal
p	parameter
*	worst case

Abbreviations

GWP global warming potential
MCO multi-criteria optimization
OpEx operational expenditure
p-dipb *p*-diisopropyl benzene
SRK Soave-Redlich-Kwong
VLE vapor-liquid equilibrium

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Paper VI: Stage-to-Stage Calculations of Distillation Columns by Fixed-Point Iteration and Application of the Banach Fixed-Point Theorem [Hoffmann et al., 2017]



Stage-to-stage calculations of distillation columns by fixed-point iteration and application of the Banach fixed-point theorem

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HIGHLIGHTS

- We present a novel approach for stage-to-stage calculations based on MESH equations.
- The transition from one stage to the next is formulated as a fixed-point problem.
- Fixed-point problems are solved by fixed-point iteration without using derivatives.
- Energy bounds are derived that guarantee the existence of a fixed-point.

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ABSTRACT

This work presents a novel approach for stage-to-stage calculations of distillation columns based on the MESH equations. No simplifying assumptions such as constant molar overflow are used. The transition from one stage to the next is formulated as a fixed-point problem, which can be solved by fixed-point iteration. Applying the Banach fixed-point theorem, bounds on the minimum energy requirement are derived. Within these bounds a solution to the fixed-point problem is proven to exist and convergence of the fixed-point iteration is guaranteed. Additionally, energy bounds are derived below which it can be guaranteed that no fixed-point exists. The stage-to-stage calculations are combined with an outer optimization loop in order to conduct process simulation and optimization. The approach is illustrated by examples.

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1. Introduction

Distillation is the most widely used technique for separating fluid mixtures. It is usually described by the equilibrium stage model based on the so-called MESH equations (material balances, equilibrium conditions, summation equations for the concentrations, heat (or better: energy) balances, see also Wang and Henke (1966)). Despite the important simplifications in this type of model, it is known to describe distillation processes reasonably well, so that it has successfully been used for distillation design for many decades, and there is no good reason to believe that this will change in the near future.

Describing distillation processes based on MESH equations leads to a large system of nonlinear equations with many unknowns and only few degrees of freedom, which has to be

solved in process simulation. As a result, the internal and external streams of the column are obtained (flow rate, composition, and temperature) for the steady state operation of the column. Furthermore, the heat flows in the reboiler and condenser are determined. For further reading, see e.g. Biegler et al. (1997) or Holland (1981).

Due to the inherent structure of the equilibrium stage distillation column model it is quite natural to decompose the system of equations and to consider stage-to-stage calculations of distillation columns instead of solving the underlying equations for all stages simultaneously. Early work in this field stems from Lewis and Matheson (1932) and Thiele and Geddes (1933) and is based on equation tearing. Holland (1963), Billingsley (1970), and Haas et al. (2007) enhanced the method of Thiele and Geddes and developed their so-called theta method. In the work of Friday and Smith (1964) different tearing techniques for solving the MESH equations were analyzed. Depending on the type of problem, the bubble-point method, a modification of the approach by Amundson and Pontinen (1958), or the sum-rates method, developed by Sujata (1961) in conjunction with the tridiagonal matrix formulation as

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Nomenclature

x	composition vector of the liquid phase based on mole fractions	i	counter for components
y	composition vector of the vapor phase based on mole fractions	L^n	molar liquid stream flow rate flowing from stage n to stage $n - 1$
$\dot{Q}_C$	condenser duty	n	counter for stages
$\dot{Q}_R$	reboiler duty	N_C	number of components
γ_i	activity coefficient of component i	N_F	feed stage
l	enthalpy of a liquid boiling mixture at given pressure	N_S	number of stages
v	enthalpy of a vapor dewing mixture at given pressure	p	pressure
$\mathcal{F}_{N_C}$	set of all physically meaningful compositions of a mixture	p_i^s	vapor pressure of pure component i
B	molar bottom stream flow rate	R	molar reflux flow rate
D	molar distillate flow rate	T	temperature
F	molar feed flow rate	V^n	molar vapor stream flow rate flowing from stage n to stage $n + 1$
h^l	molar liquid enthalpy	x_i	mole fraction of component i in the liquid phase
h^v	molar vapor enthalpy	y_i	mole fraction of component i in the vapor phase

described in [Burningham and Otto \(1967\)](#), was suggested. In more recent work, the sum-rates method was modified by Lucia and co-workers who developed a method that is good for both wide boiling and narrow boiling mixtures ([Sridhar and Lucia, 1989, 1990a,b; Lucia and Li, 1992](#)) and carried out an analysis of that method based on fixed-point iteration especially with regard to the uniqueness of the solution. [Rose et al. \(1958\)](#) developed the relaxation method that uses stage-to-stage calculations and computes the gradual changes in the stage and product compositions until a steady state is reached. This method was extended by [Ketchum \(1979\)](#) and [Mori et al. \(1987a,b, 1990\)](#), among others.

Besides methods that rely on equation tearing there also exist strategies that apply simultaneous Newton-type methods for the solution of the MESH equations ([Naphtali and Sandholm, 1971; Ishii and Otto, 1973; Vickery and Taylor, 1986](#)) including the inside-out method by [Boston and Sullivan \(1974\)](#). Such methods are frequently used in commercial process simulators where the user has to specify a precise value for each degree of freedom. After fixing the degrees of freedom, the simulation software tries to solve the resulting nonlinear system of equations where the number of variables equals the number of equations. At this point, convergence failures are common and usually it is not obvious whether they are due to poor starting values for Newton's method or due to unreachable specifications. These numerical problems may turn process simulation into a very time-consuming task. This is especially cumbersome in process optimization in which the underlying system of nonlinear equations has to be solved many times.

In contrast to using the full set of MESH equations, there exist also so-called shortcut stage-to-stage models, which use simplifying assumptions, mostly that of constant molar overflow (CMO). These methods are frequently used to trace the column profiles in the stripping and rectifying column section in order to determine the minimum energy demand. Because they neglect the energy balance and are easy to calculate, CMO methods are often used in conceptual synthesis problem, see, e.g. [Levy et al. \(1985\)](#), [Van Dongen and Doherty \(1985\)](#), [Levy and Doherty \(1986\)](#), [Julka and Doherty \(1990\)](#), [Zhang and Linninger \(2004\)](#), [Lucia et al. \(2006, 2008\)](#), and [Petlyuk et al. \(2015\)](#).

In this paper, a new approach for stage-to-stage calculations of distillation columns is presented and conditions for its guaranteed convergence are derived. To the best of our knowledge, such conditions have not been derived before. The presented approach does not use any simplifying assumptions, i.e. the full set of MESH equations is rigorously solved. The nonlinear system of equations,

which has to be solved for the transition from one stage to the next, is reformulated as a fixed-point problem following the method of [Welke \(2013\)](#). The fixed-point problem can be solved by fixed-point iteration. When conducting fixed-point iterations, derivatives only need to be computed for solving the vapor-liquid equilibrium. In the present work, this fixed-point problem is analyzed in detail. Applying the Banach fixed-point theorem, it is proven that a unique fixed-point exists and that the convergence to that point is guaranteed, if certain requirements on the energy, which are derived in the present paper, are fulfilled. If the energy is chosen below a certain bound, which is also derived in this work, there exists no fixed-point and hence no solution to the MESH equations.

Stage-to-stage calculations as presented in this work are used to solve a fixed-point problem for all stages of a distillation column but the last (either upward or downward calculation). Thus, all MESH equations for a distillation column are solved, except the component material balances of the last stage. Usually one column product (e.g. the bottom product) as well as the respective heat duty (e.g. the reboiler duty) are considered to be given in order to be able to conduct stage-to-stage calculations. Only in cases, these process variables are actually known before the simulation and an initial guess typically needs to be adapted. There the stage-to-stage calculations are embedded into an outer iteration loop, which is formulated as an optimization problem.

[Fig. 1](#) schematically shows this embedding with its different building blocks and how the stage-to-stage calculations fit into an overall concept for simulation and optimization of distillation columns. In a first step, the optimization problem for the simulation or optimization of a distillation column has to be initialized (cf. box (1)). This includes the choice of upward or downward stage-to-stage calculations and the initialization of the corresponding optimization variables. Additional specifications that represent the engineering demands can be included in a very flexible way as equality or inequality constraints in the optimization problem. If the considered distillation column should be optimal with respect to a predefined goal, a suitable objective function can be incorporated in the optimization problem formulation. In a first step, it should be checked whether the given optimization variables lead to convergent fixed-point iterations by comparison with the derived energy bounds (cf. box (2)). In cases in which the optimizer suggests input variables that would lead to divergent stage-to-stage calculations, the variables can be rejected and updated using an optimization algorithm (cf. box (6)). The original MESH system comprising typically hundreds of variables and equations is decomposed into an inner loop that solves almost all MESH

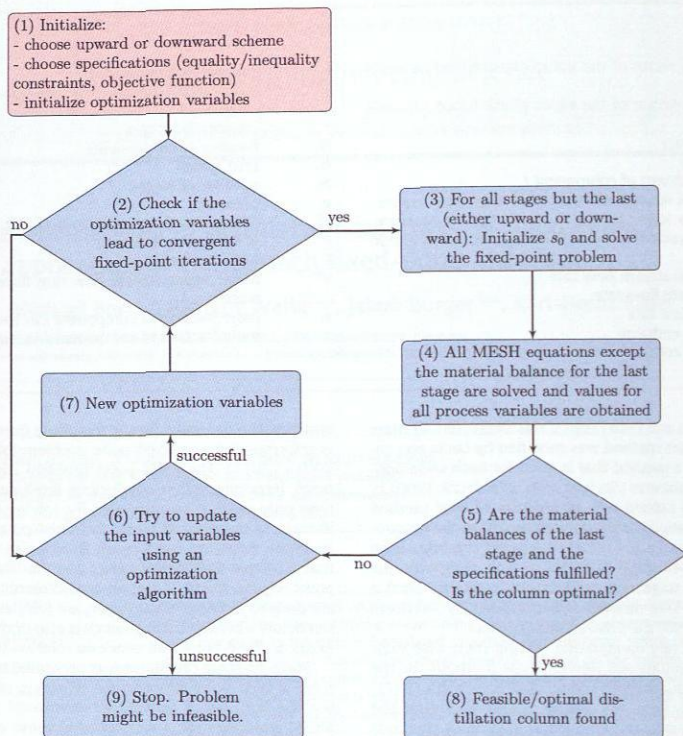


Fig. 1. Flow diagram for simulation of a distillation column embedded in an optimization problem.

equations except those for the last equilibrium stage of the column by using numerically robust stage-to-stage calculations (cf. boxes (3) and (4)) and an outer optimization loop where the MESH equations for the last stage are included as constraints (cf. box (5)). Within the inner loop a fixed-point problem has to be solved for all stages but the last and each iteration is initialized with a starting value s_0 . Within the outer loop, the input variables for stage-to-stage calculations (one column product and the respective heat duty) serve as optimization variables and are updated using the optimization algorithm (cf. box (6) and (7)) in a way that a feasible (or even optimal) column is obtained as a final result (cf. box (8)). If the optimization algorithms fails in updating the optimization variables the algorithms stops and the formulated optimization problem is either infeasible or the optimization algorithm failed in finding a solution (cf. box (9)).

This paper focuses on the convergence characteristics of the stage-to-stage calculations in the inner loop. Depending on the input variables, the stage-to-stage calculations may converge or diverge. Note that even if the fixed-point iteration converges for all stages but the last, the material balances of the last stage and the specifications are not necessarily fulfilled for an arbitrary choice of input variables. This is why the outer loop is required.

The remainder of this paper is organized as follows. Section 2 is devoted to the derivation of a fixed-point problem for the stage-to-stage calculations and the rigorous mathematical analysis of this

fixed-point problem. Convergence bounds for the stage-to-stage input variables are given. In Section 3 the extension to simulation and optimization of distillation columns using an outer optimization loop is described. In Section 4 the theoretical results from the previous sections are illustrated using distillations of binary and ternary mixtures as examples.

2. Stage-to-stage calculations using fixed-point iteration

The approach for stage-to-stage calculations of distillation columns, which is presented in the following, can be applied to multi-component systems with an arbitrary number of components and the conditions for guaranteed convergence can be evaluated in a completely analogous way for systems with a large or small number of components.

2.1. System of equations

The equilibrium stage model of a distillation column is schematically depicted in Fig. 2. There are indices i for the N_C components as well as indices n for the N_S stages. The distillation column is modeled as a cascade of stages with a reboiler duty $\dot{Q}_R > 0$ kW at the bottom and a condenser duty $\dot{Q}_C < 0$ kW at the top. For simplicity, a distillation column with one single feed on stage N_F ($N_F = 2$ in the

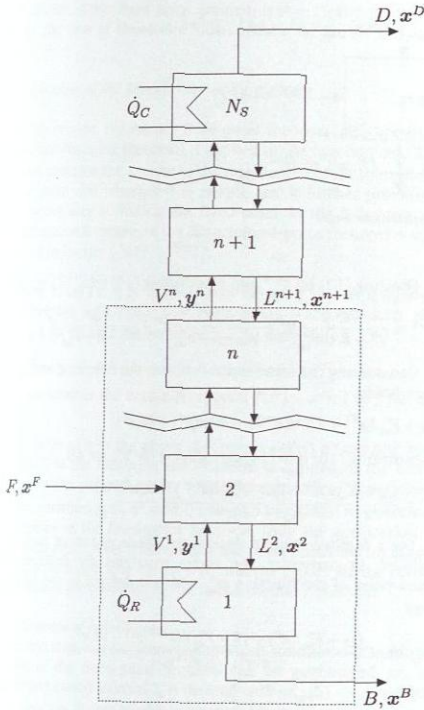


Fig. 2. Schematic of a stage-by-stage model of a distillation column with a single feed on stage $N_f = 2$, total condenser, and reboiler. The dotted box indicates the control volume, which is gradually extended.

example of Fig. 2) and without any side-draws is considered. The method described in the following can be extended to side-draws and multiple feeds in a straightforward manner.

The state of the feed stream is assumed to be completely defined, i.e. the molar feed flow rate F , the pressure p , and the mole fractions x_i^f of each component i are known. Furthermore, it is assumed that the feed stream is liquid boiling. That assumption is only used for simplicity and a generalization is possible. Each stage n has liquid and vapor streams flowing from it (with total molar flow rate L^n and V^n) and onto it (with total molar flow rate L^{n+1} and V^{n+1}) and is thereby connected to the stages above and below.

The extended Raoult's law is used for describing the vapor-liquid equilibrium (VLE) (see Appendix A) and it is assumed that for given pressure and composition of one of the phases in equilibrium the extended Raoult's law can be solved without any convergence failures. It is assumed that no second liquid phase (no LLE split) occurs along the column. Furthermore, $h^l(x, T)$ and $h^v(y, T)$ denote the enthalpies of the liquid and vapor phase, respectively, which depend on the composition of the phase and the temperature T .

Remark 1. Let the pressure p be given. For a liquid phase composition vector x that is in equilibrium with the corresponding vapor phase the temperature T^{VLE} in equilibrium can be determined by using extended Raoult's law. Define

$$l(x) := h^l(x, T^{\text{VLE}}). \quad (1)$$

Analogously, for a vapor phase composition vector y that is in equilibrium with the corresponding liquid phase T^{VLE} can be determined for a given pressure and we define

$$v(y) := h^v(y, T^{\text{VLE}}). \quad (2)$$

Thus, $l(x)$ and $v(y)$ are short notations for the molar enthalpy of phases of given composition in the liquid boiling and vapor dewing state respectively.

In this work, the enthalpy h_i^v of each component i as vapor at 298 K is set to 0 kJ/mol and the enthalpy of mixing is neglected in both phases. Inclusion of the excess enthalpy term in the numerical examples does not change the results significantly.

Here, the MESH equations are exemplarily stated for an equilibrium stage displayed in Fig. 3.

- Material balances

$$F x_i^f + L^{n+1} y_i^{n+1} + V^{n-1} x_i^{n-1} - L^n x_i^n - V^n y_i^n = 0, \quad \text{for } i = 1, \dots, N_C \quad (3)$$

- Equilibrium conditions

$$p_i^s(T^n) x_i^n \gamma_i(x^n, T^n) = p^n y_i^n, \quad \text{for } i = 1, \dots, N_C, \quad (4)$$

- Summation equations

$$\sum_{i=1}^{N_C} x_i^n = 1, \quad \text{and} \quad \sum_{i=1}^{N_C} y_i^n = 1 \quad (5)$$

- Energy balance

$$\dot{Q} + F h^l(x^f, T^f) + L^{n+1} h^l(x^{n+1}, T^{n+1}) + V^{n-1} h^v(y^{n-1}, T^{n-1}) - L^n h^l(x^n, T^n) - V^n h^v(y^n, T^n) = 0$$

$\dot{Q}$ is equal to zero in Eq. (6) on most stages as they are considered to be adiabatic. $\dot{Q}$ is non-zero for the lowest and the highest stage where reboiler and condenser, respectively, are located.

For the subsequent derivations we assume the following:

Assumption 1. Flow rates of internal column streams and mole fractions in the liquid and vapor phase are strictly larger than 0.

Assumption 2. Let the pressure p be given. For any composition of the gas (y) and the liquid phase (x) it is assumed that

$$v(y) - l(x) > 0. \quad (7)$$

For the general case, Assumption 2 cannot be proven, but it is plausible that it will hold for a big class of practical problems, cf. Appendix B.

2.2. Derivation of an equivalent fixed-point problem

A new approach is presented in which the full set of MESH equations is successively solved enabling a stage-wise calculation of distillation columns. It is either possible to calculate a column from the bottom to the top or the other way round. The upward calculation of a distillation column is described here, but the downward calculation is only briefly addressed in this section as both are similar. The remaining paper will, without loss of generality, mainly focus on upward calculations.

For the following considerations, it is assumed that process variables p , B , x^B , and $\dot{Q}_R$, as well as the specifications F and x^f of the liquid boiling feed stream on stage N_f , are given in order to

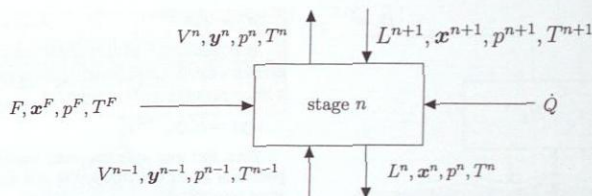


Fig. 3. Schematic of a single equilibrium stage.

calculate a column from the bottom to the top. The given variables should fulfill the following assumption:

Assumption 3. The values for B and x^b are chosen in such a way that

$$D := F - B > 0 \quad (8)$$

and

$$x_i^D := \frac{F x_i^F - B x_i^B}{F - B} > 0 \quad (9)$$

for all $i = 1, \dots, N_C$, i.e. the flow rate D and the composition x^D of a distillate stream that fulfills the material balance of the column should be positive.

One proceeds in the following way: The MESH equations for a control volume including the reboiler and the first stage of the distillation column are considered. The unknowns in the resulting system of equations are L^2 , x^2 , and y^1 (superscript numbers denote the stage in the present paper). The vapor stream leaving the first stage and the bottom stream, i.e. the liquid stream leaving the first stage, are in vapor-liquid equilibrium. Because the pressure p is given, the composition y^1 of the vapor phase can immediately be calculated using flash calculation. The unknowns L^2 , x^2 , and V^1 still need to be determined. For that purpose, the MESH equations for the considered control volume are reformulated as a fixed-point problem and solved by fixed-point iteration following the approach of Welke (2013). This gives values for L^2 , x^2 , and V^1 . The composition y^2 can then be calculated by solving the vapor-liquid equilibrium and a new fixed-point problem for the transition from stage 2 to stage 3 can be derived by extending the control volume by the second stage. In this way one can proceed upward the column.

In the following, the fixed-point problem for the transition from an arbitrary stage n to stage $n+1$ based on the MESH equations for a control volume including the reboiler and the lower part of the distillation column up to stage n as indicated by the dotted box in Fig. 2 is derived. The composition of the liquid phase x^n on stage n is assumed to be given from the previous step which also determines the composition of the corresponding vapor phase y^n . L^{n+1} , x^{n+1} , and V^n are the unknown process variables that have to be determined to proceed upward.

For the considered control volume shown in Fig. 2 the following total material balance holds:

$$F_{up}^n + L^{n+1} = V^n + B, \quad (10)$$

where F_{up}^n takes the column feed into account:

$$F_{up}^n := \begin{cases} 0 & \text{for } n < N_F, \\ F & \text{for } n \geq N_F. \end{cases} \quad (11)$$

Considering component material balances, it holds that

$$F_{up}^n x^F + L^{n+1} x^{n+1} = V^n y^n + B x^B. \quad (12)$$

Dividing (12) by L^{n+1} and substituting (10) into (12), we get

$$x^{n+1} = \frac{V^n}{V^n + B - F_{up}^n} y^n + \frac{B}{V^n + B - F_{up}^n} x^B - \frac{F_{up}^n}{V^n + B - F_{up}^n} x^F \quad (13)$$

Considering the same control volume the following energy balance holds:

$$\dot{Q}_R + F_{up}^n l(x^F) + L^{n+1} l(x^{n+1}) = V^n v(y^n) + B l(x^B). \quad (14)$$

Substituting (10) into (14) and solving for V^n , we get

$$V^n = \frac{\dot{Q}_R + F_{up}^n l(x^F) + (B - F_{up}^n) l(x^{n+1}) - B l(x^B)}{v(y^n) - l(x^{n+1})}. \quad (15)$$

For a feasible column design, the above equations have to be fulfilled. In particular, the above equations are fulfilled for a fixed-point of the function φ_{up}^n which is defined in the following way

$$\varphi_{up}^n(s) := \frac{\dot{Q}_R + F_{up}^n l(x^F) + (B - F_{up}^n) l(x^{n+1}(s)) - B l(x^B)}{v(y^n) - l(x^{n+1}(s))}, \quad (16)$$

where

$$x^{n+1}(s) = \frac{s}{s + B - F_{up}^n} y^n + \frac{B}{s + B - F_{up}^n} x^B - \frac{F_{up}^n}{s + B - F_{up}^n} x^F. \quad (17)$$

In a fixed-point s^* of φ_{up}^n it holds that $s^* = V^n$, cf. Eq. (13).

Fixing p , B , x^b , and $\dot{Q}_R$ enables an upward stage-to-stage calculation of a distillation column starting from the reboiler by subsequently solving the fixed-point problems for each stage.

Analogously, a sequence of fixed-point problems for the calculation of a distillation column from the condenser downward can be derived. In this case p , $\dot{n}^D := D x^D$, and $\dot{Q}_C$ are fixed and the vapor composition y^n on stage n is assumed to be given from which one can calculate the liquid composition x^n in equilibrium. The unknown values that have to be determined to proceed down the column are L^n , V^{n-1} and y^{n-1} . These values can be obtained by finding a fixed-point of the function

$$\varphi_{down}^n(r) := \frac{\dot{Q}_C + F_{down}^n l(x^F) + (D - F_{down}^n) v(y^{n-1}(r)) - D l(x^D)}{l(x^n) - v(y^{n-1}(r))}, \quad (18)$$

where

$$y^{n-1}(r) = \frac{r}{r + D - F_{down}^n} x^n + \frac{D}{r + D - F_{down}^n} x^D - \frac{F_{down}^n}{r + D - F_{down}^n} x^F \quad (19)$$

and

$$F_{down}^n := \begin{cases} 0 & \text{for } n > N_F, \\ F & \text{for } n \leq N_F. \end{cases} \quad (20)$$

The solution of this fixed-point problem is $r^* = L^n$. For the sake of brevity the case of downward calculation is no longer discussed here.

2.3. Application of the Banach fixed-point theorem

In this section, the Banach fixed-point theorem (also known as contraction mapping theorem) is applied to the function φ_{up}^n . This theorem provides the answer to the question whether there exists a fixed-point and whether it is unique and it further provides a constructive way of finding this fixed-point. In the following, the one-dimensional version of the Banach fixed-point theorem is used as stated in Forster (2013, p. 193):

Theorem 1. Let $I \subset \mathbb{R}$ be a closed interval and $f: I \rightarrow \mathbb{R}$ a differentiable function with $f(I) \subset I$. If there exists $0 \leq q < 1$ such that $|f'(x)| \leq q$ for all $x \in I$ the sequence $(x_n)_{n \in \mathbb{N}}$ defined by

$$x_n := f(x_{n-1}), \quad n \geq 1$$

converges towards the unique fixed-point $f(x^*) = x^* \in I$ of f for any $x_0 \in I$.

Any value of q in the above theorem is called a Lipschitz constant for f . In the following this theorem is applied to the fixed-point iteration defined by Eq. (16). More specifically, we study how the variables p , B , x^B , and $\dot{Q}_R$ have to be chosen to guarantee convergence of the fixed-point iteration. Only the application of the Banach fixed-point theorem to fixed-point problems for stages $n \geq N_F$ is discussed. The case $n < N_F$ and the proofs for the subsequent results are provided in the Supplementary Material.

2.3.1. Existence of a fixed-point

In a first step, one can show under which conditions at least one solution of the fixed-point problem can be guaranteed, i.e. an appropriate closed interval I_n is defined with $\varphi_{up}^{n+1}(I_n) \subset I_n$. Furthermore, one can derive conditions for which it is guaranteed that there exists no solution to the fixed-point problem. The uniqueness of the fixed-point is discussed at a later point in the present work.

It is shown in the Supplementary Material that a fixed-point with not only mathematical but also physical meaning can only occur in

$$M_n := (Dm_n; \infty), \quad (21)$$

where

$$m_n := \max_{i=1, \dots, N_C} \left(\frac{x_i^D}{y_i^n} \right). \quad (22)$$

Therein, x^D defined by Eq. (9) is the composition of the distillate and y^n is the composition of the vapor stream from stage n to stage $n+1$, cf. Fig. 2. In other words, for a physically reasonable fixed-point $s^* = V^n$ it holds that:

$$Dm_n < V^n < \infty. \quad (23)$$

The upper bound on V^n is obvious. The lower bound can also be reformulated as

$$Dx_i^D < V^n y_i^n, \quad \text{for all } i = 1, \dots, N_C. \quad (24)$$

It always holds that $m_n \geq 1$ due to the fact that both concentration vectors fulfill the summation equation.

Furthermore, a set I_n is defined in the following way

$$I_n := \left[\inf_{s \in M_n} \varphi_{up}^n(s); \sup_{s \in M_n} \varphi_{up}^n(s) \right]. \quad (25)$$

Additionally, a set

$$\mathcal{F}_{N_C} := \left\{ x \in \mathbb{R}^{N_C} \left| \sum_{i=1}^{N_C} x_i = 1, x_i > 0, i = 1, \dots, N_C \right. \right\} \quad (26)$$

is defined as the set of all physically meaningful compositions of a mixture. As $v(x)$ and $l(x)$ are bounded functions on $\mathcal{F}_{N_C}$ for fixed pressure the following result is obtained.

Lemma 1. Let $n \geq N_F$. If

$$\dot{Q}_R > \dot{Q}_R^{LB1,n} \quad (27)$$

with

$$\dot{Q}_R^{LB1,n} := B l(x^B) - F l(x^F) + D m_n v(y^n) + D(1 - m_n) \min_{x \in \mathcal{F}_{N_C}} l(x) \quad (28)$$

it holds that $\varphi_{up}^n(I_n) \subset I_n$ and the existence of at least one fixed-point in the closed interval I_n is guaranteed.

The derivation of the result in Lemma 1 and the corresponding proofs can be found in the Supplementary Material.

In order to evaluate Eq. (28) derived in Lemma 1 values for p , F , x^F , B , x^B , y^n , and m_n have to be given. Note that $\dot{Q}_R^{LB1,n}$ depends on the current value of y^n , which usually changes from stage to stage. A more general bound that requires less information on the choice of variables can also be derived:

Lemma 2. Let $n \geq N_F$. If

$$\dot{Q}_R > \dot{Q}_R^{LB2,n} \quad (29)$$

with

$$\dot{Q}_R^{LB2,n} := B \left(\max_{x \in \mathcal{F}_{N_C}} l(x) - \min_{x \in \mathcal{F}_{N_C}} l(x) \right) + D m_n \left(\max_{x \in \mathcal{F}_{N_C}} v(x) - \min_{x \in \mathcal{F}_{N_C}} v(x) \right). \quad (30)$$

the existence of at least one fixed-point in the closed interval I_n is guaranteed. It always holds that

$$\dot{Q}_R^{LB2,n} \geq \dot{Q}_R^{LB1,n}. \quad (31)$$

The more general bound $\dot{Q}_R^{LB2,n}$ depends only on p , F , B , m_n , and on the physical properties of the specific components in the considered system. The maximum and minimum values of the liquid and vapor enthalpy functions only have to be calculated once for a mixture by using an arbitrary optimization strategy. This can be done in a pre-processing step of process simulation. Enthalpy functions of one phase often exhibit only small changes on $\mathcal{F}_{N_C}$ when compared to enthalpy changes between liquid and vapor phase. Thus the more general bound is expected to be close to the actual bound and not much more pessimistic.

Unfortunately, the quotient m_n cannot be bounded from above due to the fact that y_i^n can be arbitrarily small and therefore it is not possible to derive a more general bound on $\dot{Q}_R$ that does not depend on y^n .

So far, bounds on $\dot{Q}_R$ were derived such that the existence of at least one solution is guaranteed for the derived fixed-point problem. Similarly, one can show for which choices of $\dot{Q}_R$ there exists no fixed-point with physical meaning and thus no solution of the MESH system.

Lemma 3. Let $n \geq N_F$. If

$$\dot{Q}_R \leq \dot{Q}_R^{UB1,n} \quad (32)$$

with

$$\dot{Q}_R^{UB1,n} := B l(x^B) - F l(x^F) + D m_n v(y^n) + D(1 - m_n) \max_{x \in \mathcal{F}_{N_C}} l(x) \quad (33)$$

the function φ_{up}^n has no fixed-point in I_n .

The proof of this lemma is provided in the [Supplementary Material](#).

Again, a more general bound on $\hat{Q}_R$ that does no longer depend on x^f and x^b can be derived:

Lemma 4. Let $n \geq N_f$. If

$$\hat{Q}_R \leq \hat{Q}_R^{UB2,n} \quad (34)$$

with

$$\hat{Q}_R^{UB2,n} := B \left(\min_{x \in \mathcal{F}_{N_C}} l(x) - \max_{x \in \mathcal{F}_{N_C}} l(x) \right) + D m_n \left(\min_{x \in \mathcal{F}_{N_C}} v(x) - \max_{x \in \mathcal{F}_{N_C}} l(x) \right). \quad (35)$$

the function φ_{up}^n has no fixed-point in I_n . It always holds that

$$\hat{Q}_R^{UB2,n} \leq \hat{Q}_R^{UB1,n}. \quad (36)$$

In this case, it is possible to formulate a similar result independently of the quotient m_n :

Lemma 5. Let $n \geq N_f$. If

$$\hat{Q}_R \leq \hat{Q}_R^{UB3,n} \quad (37)$$

with

$$\hat{Q}_R^{UB3,n} := B l(x^b) - F l(x^f) + D v(y^n) \quad (38)$$

the function φ_{up}^n has no fixed-point in I_n .

An even more general upper bound on $\hat{Q}_R$ is derived:

Lemma 6. Let $n \geq N_f$. If

$$\hat{Q}_R \leq \hat{Q}_R^{UB4} \quad (39)$$

with

$$\hat{Q}_R^{UB4} := B \left(\min_{x \in \mathcal{F}_{N_C}} l(x) - \max_{x \in \mathcal{F}_{N_C}} l(x) \right) + D \left(\min_{x \in \mathcal{F}_{N_C}} v(x) - \max_{x \in \mathcal{F}_{N_C}} l(x) \right). \quad (40)$$

the function φ_{up}^n has no fixed-point in I_n . It always holds that

$$\hat{Q}_R^{UB4} \leq \hat{Q}_R^{UB3,n}. \quad (41)$$

The bound $\hat{Q}_R^{UB4}$ does no longer depend on y^n and can therefore be determined based on the knowledge of p , F , B , and the physical properties of the considered system.

If the results of [Lemmas 1 and 3](#) are combined with given information on the feed and bottom stream it is possible to conduct a feasibility study. On the one hand, it is possible to derive a bound on $\hat{Q}_R$ above which a fixed-point can be guaranteed and on the other hand one can deduce a minimum value for $\hat{Q}_R$ below which no solution to the MESH system exists.

Combining the previous results one can additionally derive the following result:

Lemma 7. Let $n \geq N_f$. If

$$\hat{Q}_R^{UB1,n} < \hat{Q}_R \leq \hat{Q}_R^{LB1,n} \quad (42)$$

it is neither possible to guarantee nor to exclude the existence of a fixed-point.

The lower and upper bound on $\hat{Q}_R$ stated in [Lemma 7](#) define an interval for which it is not possible to state anything about the existence of a fixed-point using the presented approach. This interval has length

$$\hat{Q}_R^{LB1,n} - \hat{Q}_R^{UB1,n} = D(m_n - 1) \left(\max_{x \in \mathcal{F}_{N_C}} l(x) - \min_{x \in \mathcal{F}_{N_C}} l(x) \right) \quad (43)$$

which is usually very small.

2.3.2. Uniqueness of the fixed-point and convergence of the fixed-point iteration

So far, the existence of a fixed-point in the interval I_n with $\varphi_{up}^n(I_n) \subset I_n$ was discussed. If one can additionally show that there exists some $0 \leq q < 1$ such that

$$|(\varphi_{up}^n)'(s)| \leq q$$

for all $s \in I_n$ the fixed-point $s^* \in I_n$ is unique and the sequence $(s_k)_{k \in \mathbb{N}}$ defined by $s_{k+1} := \varphi_{up}^n(s_k)$ converges to this fixed-point for any $s_0 \in I_n$.

In a first step, an expression for the derivative of φ_{up}^n is derived for $n \geq N_f$:

$$(\varphi_{up}^n)'(s) = (\varphi_{up}^n(s) - D) \frac{\nabla l(x^{n+1}(s)) (x^{n+1})'(s)}{v(y^n) - l(x^{n+1}(s))}. \quad (44)$$

Computing the derivative of Eq. (17) yields

$$(x^{n+1})'(s) = \frac{1}{s - D} (y^n - x^{n+1}(s)). \quad (45)$$

If (45) is inserted into (44) we obtain

$$(\varphi_{up}^n)'(s) = \frac{\varphi_{up}^n(s) - D}{s - D} \cdot \frac{\nabla l(x^{n+1}(s)) (y^n - x^{n+1}(s))}{v(y^n) - l(x^{n+1}(s))}. \quad (46)$$

Before considering the general case, two special cases are discussed.

(a) $n \geq N_f$ and $D = 0$:

It follows that $x^{n+1}(s) \equiv y^n$ and

$$\varphi_{up}^n(s) \equiv \frac{\hat{Q}_R}{v(y^n) - l(y^n)}. \quad (47)$$

From this one can conclude that $(\varphi_{up}^n)'(s) \equiv 0$.

(b) $\hat{Q}_R \rightarrow \infty$

In this case it holds

$$\lim_{\hat{Q}_R \rightarrow \infty} \varphi_{up}^n(s) = \infty \quad (48)$$

and hence also

$$\liminf_{\hat{Q}_R \rightarrow \infty, s \in I_n} \varphi_{up}^n(s) = \infty \quad (49)$$

and

$$\limsup_{\hat{Q}_R \rightarrow \infty, s \in I_n} \varphi_{up}^n(s) = \infty. \quad (50)$$

This yields

$$\lim_{\hat{Q}_R \rightarrow \infty} \max_{s \in I_n} |(\varphi_{up}^n)'(s)| = 0 \quad (51)$$

due to the fact that

$$\lim_{\hat{Q}_R \rightarrow \infty} \max_{s \in I_n} |x_i^{n+1}(s) - y_i^n| = 0, \quad \text{for all } i = 1, \dots, N_C. \quad (52)$$

Hence, one can always get an arbitrarily small upper bound on $(\varphi_{up}^n)'$ by increasing $\hat{Q}_R$.

In both cases $(\varphi_{up}^n)'$ is identical to 0. Due to continuity reasons it is possible to deduce that in case (a) there exists $\varepsilon > 0$ such that for all $D < \varepsilon$ it holds $|(\varphi_{up}^n)'(s)| \leq q < 1$. Similar results can also be derived for (b).

For the general case it is possible to derive a bound on $\hat{Q}_R$ such that $|(\varphi_{\text{up}}^n)'(s)| \leq q$ holds. The derivation is provided in the [Supplementary Material](#). For this general bound a new parameter called $\tilde{c}$ is introduced whose value can be chosen in a suitable way such that $q < 1$ as one can see from the following results:

Lemma 8. Let $n \geq N_f$ and

$$\hat{Q}_R > \hat{Q}_R^{LB1,n,\text{unique}} \quad \text{or} \quad \hat{Q}_R > \hat{Q}_R^{LB2,n,\text{unique}}, \quad (53)$$

with

$$\begin{aligned} \hat{Q}_R^{LB1,n,\text{unique}} &:= B l(\mathbf{x}^B) - F l(\mathbf{x}^F) + D \max_{\mathbf{x} \in \mathcal{F}_{N_C}}(\tilde{c}, m_n) v(\mathbf{y}^n) \\ &\quad + D(1 - \max(\tilde{c}, m_n)) \max_{\mathbf{x} \in \mathcal{F}_{N_C}} l(\mathbf{x}) \geq \hat{Q}_R^{LB1,n} \end{aligned} \quad (54)$$

and

$$\begin{aligned} \hat{Q}_R^{LB2,n,\text{unique}} &:= B \left(\max_{\mathbf{x} \in \mathcal{F}_{N_C}} l(\mathbf{x}) - \min_{\mathbf{x} \in \mathcal{F}_{N_C}} l(\mathbf{x}) \right) \\ &\quad + D \max(\tilde{c}, m_n) \cdot \left(\max_{\mathbf{x} \in \mathcal{F}_{N_C}} v(\mathbf{x}) - \min_{\mathbf{x} \in \mathcal{F}_{N_C}} l(\mathbf{x}) \right) \geq \hat{Q}_R^{LB2,n}. \end{aligned} \quad (55)$$

Then it holds that

$$\begin{aligned} |(\varphi_{\text{up}}^n)'(s)| &= \left| \frac{\varphi_{\text{up}}^n(s) - D}{s - D} \cdot \frac{\nabla l(\mathbf{x}^{n+1}(s))(\mathbf{y}^n - \mathbf{x}^{n+1}(s))}{v(\mathbf{y}^n) - l(\mathbf{x}^{n+1}(s))} \right| \\ &\leq \frac{\min_{\mathbf{x} \in \mathcal{F}_{N_C}} v(\mathbf{x}) - \min_{\mathbf{x} \in \mathcal{F}_{N_C}} l(\mathbf{x})}{\left(\min_{\mathbf{x} \in \mathcal{F}_{N_C}} v(\mathbf{x}) - \max_{\mathbf{x} \in \mathcal{F}_{N_C}} l(\mathbf{x}) \right)^2} \\ &\quad \cdot \frac{2}{\tilde{c} - 1} \max_{1 \leq i < j \leq N_C, \mathbf{x} \in \mathcal{F}_{N_C}} \left| \frac{\partial l}{\partial x_i}(\mathbf{x}) - \frac{\partial l}{\partial x_j}(\mathbf{x}) \right| =: q(\tilde{c}). \end{aligned} \quad (56)$$

The bound in (56) only depends on the parameter $\tilde{c}$ and the physical properties of the multi-component mixture at given pressure p . The value for $\tilde{c}$ can always be chosen in such a way that $|(\varphi_{\text{up}}^n)'(s)| \leq q(\tilde{c}) < 1$. Therefore there exists a unique fixed-point in I_n and convergence of the sequence $(s_k)_{k \in \mathbb{N}}$ defined by $s_k := \varphi_{\text{up}}^n(s_{k-1})$ towards this fixed-point is guaranteed for any $s_0 \in I_n$. The fixed-point iteration thus has guaranteed convergence if $\hat{Q}_R$ is chosen above the limit in Eq. (55). This limit depends on the choice of p, F, B , the current value for m_n , the physical properties of the considered system and the parameter $\tilde{c}$. As indicated in Lemma 8, the energy bounds that guarantee uniqueness of the fixed-point are at least as restrictive as those energy bounds that only guarantee the existence of at least one fixed-point.

Remark 2. If $N_C \leq 3$ the factor 2 in Eq. (56) can be replaced by 1.

2.4. Rate of convergence

In this section, the rate of convergence of the corresponding fixed-point iteration is considered. In case $\tilde{c}$ is chosen in such a way that $|(\varphi_{\text{up}}^n)'(s)| \leq q(\tilde{c}) < 1$ holds, it is known by definition that the fixed-point iteration converges at least linearly. The question is now, whether higher order convergence can also be proven. A necessary condition for convergence of order $p \geq 2$ is that for a fixed-point s^* it holds:

$$(\varphi_{\text{up}}^n)^{(k)}(s^*) = 0, \quad \text{for all } k = 1, \dots, p-1. \quad (57)$$

In the fixed-point s^* it holds

$$(\varphi_{\text{up}}^n)'(s^*) = \frac{\nabla l(\mathbf{x}^{n+1}(s^*))(\mathbf{y}^n - \mathbf{x}^{n+1}(s^*))}{v(\mathbf{y}^n) - l(\mathbf{x}^{n+1}(s^*))}. \quad (58)$$

Hence, the derivative in the fixed-point equals zero if

$$\nabla l(\mathbf{x}^{n+1}(s^*))(\mathbf{y}^n - \mathbf{x}^{n+1}(s^*)) = 0, \quad (59)$$

which is in general not the case. However, Eq. (59) is the necessary condition for higher order convergence. Therefore, the rate of convergence for the considered fixed-point iteration is generally linear.

3. Extension to simulation and optimization of distillation columns

Assuming constant pressure on all stages of a distillation column yields a MESH system with $N_{\text{var}} = N_S \cdot (2N_C + 3) + 3$ process variables and $N_{\text{eq}} = N_S \cdot (2N_C + 3)$ model equations, which means that $N_{\text{var}} - N_{\text{eq}} = 3$ degrees of freedom remain for the combined MESH system. However, if $p, F, \mathbf{x}^F, B, \mathbf{x}^B$, and $\hat{Q}_R$ are given, then the column will be over-specified and an arbitrary choice of these variables will in general not lead to a physically feasible solution. Hence, a strategy is needed to find a feasible choice for the input variables for stage-to-stage calculations. In the following, it is assumed that the process variables $\hat{\mathbf{n}}^B := B\mathbf{x}^B$, and $\hat{Q}_R$ can be adapted in a suitable way by using an outer optimization loop as sketched in Fig. 1. The solution to this problem is briefly discussed here. It will be presented in detail in further work.

When calculating a distillation column stage-to-stage starting from the reboiler upward one proceeds until the fixed-point problem for the transition from stage $(N_S - 1)$ to stage N_S is solved and the composition $\mathbf{x}^D$ of the distillate is obtained. We write $\mathbf{x}^D(\hat{\mathbf{n}}^B, \hat{Q}_R)$ in order to stress the dependence of $\mathbf{x}^D$ on the choice of variables $\hat{\mathbf{n}}^B$, and $\hat{Q}_R$. The component material balance for the last stage the distillation column is not enforced during upward calculation of the distillation column, and thus also the material balance the entire column is not enforced. This means that $\mathbf{x}^D(\hat{\mathbf{n}}^B, \hat{Q}_R) \mathbf{v}$ in general not fulfill:

$$F\mathbf{x}^F = B\mathbf{x}^B + (F - B)\mathbf{x}^D(\hat{\mathbf{n}}^B, \hat{Q}_R), \quad (6)$$

where the relation $F = B + D$ was used. In order to obtain a feasible column design, $\hat{\mathbf{n}}^B$ and $\hat{Q}_R$ have to be adapted in a way such that Eq. (60) is fulfilled. The problem is formulated as an optimization problem of the following form:

$$\begin{aligned} \min_{\hat{\mathbf{n}}^B, \hat{Q}_R} \quad & 0 \\ \text{s.t.} \quad & F\mathbf{x}_i^F = B\mathbf{x}_i^B + (F - B)\mathbf{x}_i^D(\hat{\mathbf{n}}^B, \hat{Q}_R), \quad i = 1, \dots, N_C - 1. \end{aligned} \quad (61)$$

This optimization problem is of size $N_{\text{opt}} = (N_C + 1)$ in terms of optimization variables. The number of constraints in (61) is $N_{\text{constr}} = (N_C - 1)$ (the component material balance for the component N_C is fulfilled due to construction in case the component material balances for the $(N_C - 1)$ remaining components are fulfilled). Thus, the optimization problem is small compared to the large number of model equations and process variables in the underlying system of MESH equations. Those MESH equations that are not incorporated explicitly as constraints in the optimization problem are already enforced during the upward or downward calculation of the distillation column, which is carried out in each iteration step of the optimization algorithm. In the general case, it is also possible to impose additional equality or inequality constraints, for example desired product purities.

As long as the constant objective function 0 is used and no additional specifications (e.g. product purities) are given, this approach only finds an arbitrary solution to the underlying system of MESH equations. Thus, the optimization solver will output the first feasi-

ble solution found, which strongly depends on the chosen initial values for the optimization variables and the specific implementation of the optimization algorithm. In order to obtain a distillation column that is optimal with respect to a non-constant objective function, e.g. the reboiler duty, one can simply replace the constant objective function in the optimization problem (61) by the objective function of interest. It is of big advantage that in order to optimize a process there is no need for a feasible column design as a starting point and hence it is not necessary to perform process simulation in advance. This facilitates simultaneous process simulation and optimization.

Conceptual methods for distillation-based flowsheets that determine feasible column products can be used to generate a good initial guess for the values of the flow rate and composition of a product stream. Examples of such conceptual methods have been mentioned in the Introduction.

A sequential quadratic programming (SQP) approach is used in this paper for solving the nonlinear optimization problems (see Han (1977) and Powell (1978) for the origin of this method and Nocedal and Wright (2006) for more recent work in this field).

Although, the focus of this work lies on the simulation and optimization of distillation columns, these ideas could also be extended to other (simple and stage-based) units such as flash units, reactors, heat exchangers, decanters, extraction columns, absorption columns, or even Petlyuk distillation columns (Wolff and Skogestad, 1995). As prerequisite, suitable algorithms are needed for the different units that facilitate the calculation of all process variables. Again, the idea is to decompose the original system of MESH equations into a subsystem that can be solved with guaranteed convergence based on a particular set of given process variables and to include the remaining MESH equations in the optimization problem as constraints. The number of additional optimization variables and constraints depends on the specific unit.

Numerical results

The numerical examples shown in this section only serve as an illustration for the theoretical ideas presented in Section 2 and 3. At this point, our aim is to identify opportunities of the approach but we do not claim to prove superiority compared to existing methods.

4.1. A numerical example for stage-to-stage calculations

In this section, the results from Section 2 are illustrated by a numerical example. The example separation problem is fairly simple and constructed so that stage-to-stage calculations can be discussed without considering the outer optimization loop.

4.1.1. Separation problem

The separation of a binary mixture of acetone (AC) and chloroform (CF) is considered. The binary system exhibits a heavy-boiling azeotrope which lies at $x_{AC}^{azeo} = 0.3454$ mol/mol at 1 bar. Acetone shall be obtained as distillate of a distillation column with completely defined binary feed on stage 20 counted from bottom. The variables used in this example are given in Table 1. In this example, the bottom product of the distillation column is chosen to be close to the azeotrope. Furthermore, the desired minimum acetone purity in the distillate is $x_{AC}^D = 0.9964$ mol/mol.

Several questions are answered here: Is it possible to conduct stage-to-stage calculations for the input variables given in Table 1, i.e. does Q_R fulfill the minimum energy requirements? Is it possible to achieve the desired purity of acetone in the distillate? And how many stages are needed in the rectifying part of the distillation column to achieve the desired purity of acetone? The physical

Table 1

Variables for stage-to-stage calculations of a distillation column for a binary mixture of acetone (AC) and chloroform (CF).

Variable	Value
p/bar	1
$F/(\text{kmol/h})$	1
$x^F/(\text{mol/mol})$	0.5 AC 0.5 CF
N_F	20
$B/(\text{kmol/h})$	0.78
$x^B/(\text{mol/mol})$	0.36 AC 0.66 CF
Q_R/kW	25

property model used for the calculation including enthalpy data needed to derive the energy bounds is given in Appendix A.

4.1.2. Energy bounds derived with the Banach fixed-point theorem

The energy bounds that were derived in Section 2.3 can be applied to verify that the choice of Q_R in Table 1 enables upward calculation of the column.

As an example, a stage n above the feed is considered with $y_{AC}^n = 0.6$ mol/mol. This gives $m_n = 1.661$. Based on these values and the process variables in Table 1 the bounds $\hat{Q}_R^{LB1,n}$, $\hat{Q}_R^{LB2,n}$, and $\hat{Q}_R^{UB1,n} - \hat{Q}_R^{UB4}$ derived in Section 2.3 can be calculated (cf. Eq. (28), (30), (33), (35), (38) and (40)). The results are given in Table 2.

In order to be able to evaluate $\hat{Q}_R^{LB1,n,unique}$ and $\hat{Q}_R^{LB2,n,unique}$ (cf. Eq. (55) and (54)) information on an appropriate choice of $\tilde{c}$ is needed. For that purpose, the function $q(\tilde{c})$ (cf. Eq. (56)) is plotted in Fig. 4 for the system acetone and chloroform at 1 bar.

From this figure one can conclude that $\tilde{c} \approx 1.09$ suffices in order to guarantee $q(\tilde{c}) < 1$, which gives us uniqueness of the fixed-point and convergence of the fixed-point iteration. With this choice of $\tilde{c}$ it is now possible to determine the two remaining energy bounds. In this exemplary case, it holds

$$\max(\tilde{c}, m_n) = \max(1.09, 1.661) = 1.661, \quad (62)$$

and thus the energy bounds that guarantee uniqueness are not more restrictive than the bounds that guarantee existence of a fixed-point and it holds $\hat{Q}_R^{LB1,n} = \hat{Q}_R^{LB1,n,unique}$ and $\hat{Q}_R^{LB2,n} = \hat{Q}_R^{LB2,n,unique}$, cf. Table 2. Note that in this special case where all information for the computation of $\hat{Q}_R^{LB1,n}$ and $\hat{Q}_R^{LB2,n}$ is available the gap between $\hat{Q}_R^{LB1,n}$ and $\hat{Q}_R^{UB1,n}$ where we can neither guarantee, nor exclude a fixed-point is very small. One can conclude that for the value of Q_R chosen in Table 1, a fixed-point is guaranteed and the transition from stage n to $n+1$ is possible.

Applying the McCabe-Thiele method under the assumption of constant molar overflow to this binary example, the minimum energy that is needed in order to obtain the desired acetone purity in the distillate (using an infinite number of stages) is determined to be

Table 2

Energy bounds exemplarily evaluated for $y_{AC}^n = 0.6$ mol/mol and the variables given in Table 1.

Bound/kW	Value
$\hat{Q}_R^{LB2,n} = \hat{Q}_R^{LB2,n,unique}$	3.197
$\hat{Q}_R^{LB1,n} = \hat{Q}_R^{LB1,n,unique}$	3.007
$\hat{Q}_R^{UB1,n}$	2.972
$\hat{Q}_R^{UB2,n}$	2.781
$\hat{Q}_R^{UB3,n}$	1.791
$\hat{Q}_R^{UB4}$	1.614

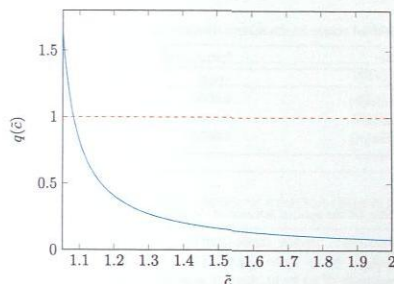


Fig. 4. Function $q(\bar{\epsilon})$ is plotted for the system acetone and chloroform at 1 bar. The dotted line at $q(\bar{\epsilon}) = 1$ indicates for which values of $\bar{\epsilon}$ one can be sure to have a derivative which is bounded by $q(\bar{\epsilon}) < 1$.

$$\dot{Q}_{R,\min} = 16.63 \text{ kW.} \quad (63)$$

If this result is compared with the energy bounds stated in Table 2 one can conclude that stage-to-stage calculations cannot only be conducted for physically feasible choices of the reboiler duty but also for choices of $\dot{Q}_R$ that are far below $\dot{Q}_{R,\min}$.

4.1.3. Number of stages

For the variables in Table 1 the number of stages needed for the separation is determined. Stage-to-stage calculations are terminated if the mole fraction of acetone in the liquid phase exceeds 0.9964 mol/mol. In this binary example 30 stages are required. The result is depicted in Fig. 5.

4.1.4. Convergence properties of the fixed-point iteration

As mentioned above, the transition from one stage to the next is conducted via solution of a fixed-point problem. The rate of convergence is generally linear as shown in Section 2.4. Nevertheless, the fixed-point iteration converges within a small number of iterations in this example due to a small Lipschitz constant in the order of magnitude 10^{-5} for the function φ_{up}^1 . For the variables in Table 1 only two fixed-point iterations are needed for the transition from stage 1 to stage 2 in order to obtain a desired accuracy of at least 10^{-6} . The starting value s_0 is taken from the interval $M_1 = (0; \infty)$ (cf. Supplementary Material) and chosen to be 100 in this example. The iterations are listed in Table 3 and a graphical representation is given in Fig. 6. The function φ_{up}^1 is almost constant. Hence, the first iterate s_1 is already extremely close to the fixed-point.

In Section 4.1.3 it was shown that 30 stages are needed to obtain a distillate with acetone purity greater than 0.9964 mol/mol for stage-to-stage calculations based on the input variables given in Table 1. In Fig. 7 the number of iterations steps needed for the transition from stage n to stage $n+1$, for $n = 1, \dots, 30$ are depicted. In the majority of all cases, only two iterations are needed and for a small number of transitions three iterations are conducted.

Clearly, the convergence properties of the fixed-point iteration, in general, depend on the considered system. This means, that the Lipschitz constant could also be significantly larger and, hence, more iterations would be required. However, all systems investigated so far have shown similar convergence properties as the one discussed here.

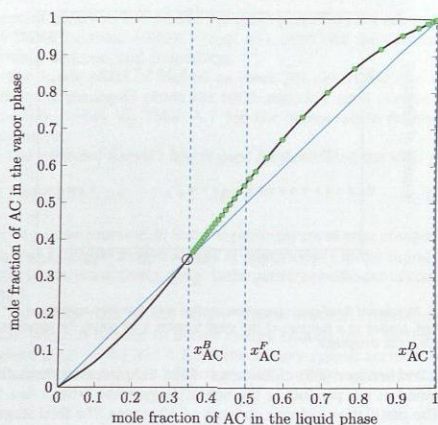


Fig. 5. Column profile in a McCabe-Thiele plot for the example in Table 1. The large circle depicts the azeotrope of the binary system and the vertical line on the right indicates the desired acetone purity in the distillate.

Table 3

Iteration steps for the transition from stage 1 to stage 2 of a distillation column until an accuracy of at least 10^{-6} is reached. Values for the required input variables can be obtained from Table 1.

Iteration	Value
s_0	100
s_1	3.07258
s_2	3.07254

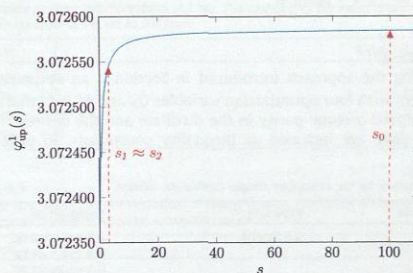


Fig. 6. Function φ_{up}^1 plotted for process variables in Table 1. The iteration steps for s are shown, whereas s_1 and s_2 cannot be distinguished in the figure.

4.2. A numerical example for the outer optimization loop

In this second numerical example it is illustrated how the outer optimization loop works. For this purpose, an optimization problem is formulated for a single distillation column with ternary feed. Process specifications are introduced as inequality constraints and an objective function is minimized.

4.2.1. Separation problem

Consider as an example a simple distillation column with completely defined ternary feed containing acetone (AC), chloroform

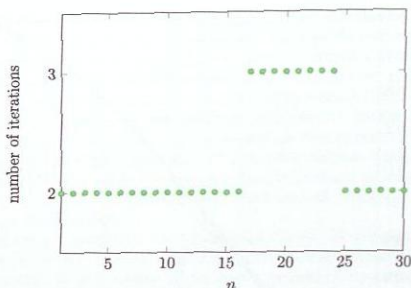


Fig. 7. Number of fixed-point iterations needed until a desired accuracy of 10^{-6} is reached, plotted as a function of the stage number n for which the transition to stage $n+1$ is computed.

(CF), and benzene (BE), cf. Table 4 and Fig. 8. Again, acetone shall be obtained as top product at the operating pressure 1 bar.

The distillation column consists of 30 stages. The feed stage is 15 counted from the bottom. A certain minimum purity and a certain minimum yield of acetone in the distillate are required. This is incorporated using inequality constraints, cf. Table 8. Note again that the use of inequality constraints is only possible because process simulation is embedded in an optimization problem.

Furthermore, the reboiler duty of the distillation column is incorporated in the problem formulation as objective function, which is to be minimized. This example comprises more than 250 process variables. The final optimization problem reads:

$$\begin{aligned} \min_{\mathbf{n}^B, \mathbf{Q}_R} \quad & \mathbf{Q}_R \\ \text{s.t.} \quad & Fx_i^F = Bx_i^B + (F-B)x_i^D(\mathbf{n}^B, \mathbf{Q}_R), \quad i = \text{AC, CF} \\ & x_{AC}^D \geq 0.99 \text{ mol/mol} \\ & \dot{n}_{AC}^D \geq 1.2 \text{ kmol/h.} \end{aligned} \quad (64)$$

4.2.2. Results

Using the approach introduced in Section 3 an optimization problem with four optimization variables $\mathbf{Q}_R$ and $\mathbf{n}^B$ is formulated. The desired acetone purity in the distillate and the desired minimum yield are included as inequality constraints. In order to

Table 4
Specifications for the exemplary simple distillation column.

Stream	Flow rate	Composition
F	3.6 kmol/h	0.4 mol/mol AC 0.3 mol/mol CF 0.3 mol/mol BE
D	≥ 1.2 kmol/h AC	≥ 0.99 mol/mol AC

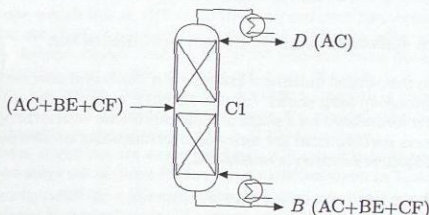


Fig. 8. Schematic distillation column with ternary feed containing acetone (AC), chloroform (CF), and benzene (BE).

Table 5
Initial and final values for the optimization variables.

Variable	Initial Value	Final Value
Q_R /kW	100.0	45.8
$\dot{n}_{AC}^D$ /kmol/h	0.6000	0.2400
$\dot{n}_{CF}^D$ /kmol/h	0.6000	1.0796
$\dot{n}_{BE}^D$ /kmol/h	0.6000	1.0683

Table 6
Stream table for the optimal solution of the column depicted in Fig. 8.

Stream	F	D	B
$\dot{n}$ /kmol/h	3.6	1.21	2.39
x_{AC} /mol/mol	0.4	0.9900	0.1005
x_{CF} /mol/mol	0.3	0.0004	0.4521
x_{BE} /mol/mol	0.3	0.0096	0.4474

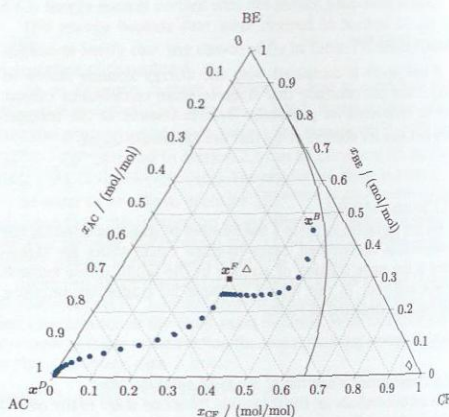


Fig. 9. Composition profile of the liquid phase of the column in Fig. 8 with minimal reboiler duty. The black curve indicates the distillation boundary in the system. The triangle represents the initial value for the bottom composition according to Table 5 and the diamond represents the initial value according to Table 7.

obtain the remaining process variables the distillation column is computed stage-wise starting from the bottom. The fixed-point iterations that need to be solved on each stage converge again within two or three iterations. In this example, the initial values for all three molar flow rates of the bottom stream are first arbitrarily chosen to be 0.6 kmol/h. The initial value for the reboiler duty is 100 kW. The distillation column with minimal reboiler duty is calculated in 40 iterations of the optimization solver. The initial values as well as the final values for the optimization variables are summarized in Tables 5 and 6 (stream table). The composition profile of the liquid phase of the optimal column is depicted in a ternary diagram in Fig. 9.

Fig. 9 shows that the system has a distillation boundary. In order to illustrate the robustness of the approach with respect to poor initial values, the alternative initial values for the composition of the bottom stream are chosen differently and the calculations are repeated. The initial composition of the bottom product is specified in Table 7 and shown in Fig. 9. This composition clearly lies in another distillation region than the feed and the desired distillate. However, even with these poor initial values the optimization solver finds the distillation column with minimal reboiler duty within

Table 7

Initial values for the optimization variables with the composition of the bottom product in the wrong distillation region.

Variable	Initial Value
Q_{10}/KW	100.0
$\dot{n}_{10}^{\text{L}}/(\text{kmol/h})$	0.0450
$\dot{n}_{10}^{\text{V}}/(\text{kmol/h})$	1.7100
$\dot{n}_{10}^{\text{B}}/(\text{kmol/h})$	0.0450

41 iterations. The solution is independent from the chosen starting values.

Note that a generic SQP optimization solver (related to the implementation of Schittkowski (2009)) was used to solve the optimization problem, which was not adapted to task.

5. Conclusion

An approach for stage-to-stage distillation calculations based on given values for a particular set of input variables was presented and analyzed. This set consists of the molar flow rates of a product stream and the heat duty at one end of the column. Using this approach, no additional process variables need to be specified on each stage of the column. For the transition from one stage to the next a fixed-point problem is derived, which is equivalent to the corresponding MESH equations and can be solved via fixed-point iteration. The approach has several advantages: using the Banach fixed-point theorem, convergence of the fixed-point iteration can be guaranteed within wide ranges of the input variables, and, though the convergence is in general only linear, experience shows that it converges within two or three iterations when applied to typical distillation problems. The robustness of the approach is further enhanced by the fact that the convergence of the underlying fixed-point iteration is not limited to physically feasible choices of input variables for stage-to-stage calculations. In case the heat duty is chosen below certain bounds it is a priori possible to exclude the existence of a fixed-point.

Stage-to-stage calculations based on fixed-point iteration are used as building block to derive a novel approach for flexible and robust simulation of distillation columns and distillation-based flowsheets. In this approach, process simulation is embedded in an optimization problem with a small number of optimization variables and equality or inequality constraints and the possibility of including flexible specifications. Most MESH equations are solved by stage-to-stage calculation with guaranteed convergence. Only the small number of remaining MESH equations that are not solved by stage-to-stage calculations need to be included as constraints in the optimization problem.

This concept can be advantageously used in several ways for example for simultaneous process simulation and optimization due to the fact that no feasible solution is required as starting point for the optimization. Furthermore, process initialization can be facilitated by specifying only the engineering demands and without the need of fixing all degrees of freedom. The required framework is given in this paper and the different building blocks are illustrated with examples. Possible extensions will be topic of subsequent work.

Although we did only illustrate our method by the examples of a conventional distillation column, these ideas can also be transferred to columns with multiple feeds and side draws or to other stage-based units.

Appendix A. Physical property models of the example systems

The pure component properties required for the simulation are: vapor pressure, enthalpy of vaporization, ideal gas heat capacity at

constant pressure. The models for these properties are taken from the DIPPR Database (DIPPR Project 801, 2005) for the substances acetone, benzene, and chloroform.

The vapor phase is treated as ideal. For describing the non-ideality of the liquid phase the NRTL model is used (Renon and Prausnitz, 1968), cf. Table A.1 for the temperature-dependent parameters.

The extended Raoult's law is used for describing the VLE

$$p_i^S(T) x_i \gamma_i(\mathbf{x}, T) = p y_i, \quad i = 1, \dots, N_c \quad (\text{A.1})$$

where p is the pressure, p_i^S is the vapor pressure of pure component i , x_i and y_i are the mole fractions of component i in the liquid and vapor phase, respectively, and γ_i is the activity coefficient of component i .

The caloric data for the binary system acetone, chloroform at 1 bar, which is needed to derive energy bounds from Section 2.3 is given in Tables A.2 and A.3. For the ternary system acetone, benzene, and chloroform at 1 bar that caloric data is given in Tables A.4 and A.5.

Table A.1

NRTL model parameters for the description of the vapor-liquid equilibrium in the ternary system acetone, benzene, chloroform with $\tau_{ij} = a_{ij} + b_{ij}/(T/\text{K})$. Parameters are taken from Aspen Plus, V8.8 (2014).

Component i Component j	Acetone Chloroform	Acetone Benzene	Benzene Chloroform
a_{ij}	0.9646	-0.1015	0
a_{ji}	0.5382	0.4224	0
b_{ij}	-590.026	306.0663	313.0115
b_{ji}	-106.4216	-239.9009	-375.4311
α_{ij}	0.3	0.3	0.47

Table A.2

Minimum and maximum values of molar liquid and vapor enthalpy for a system containing acetone and chloroform at 1 bar. The enthalpy of the vapor phase at 298 K of each component i is set to 0 kJ/mol.

Type	Value/(kJ/mol)
$\max_{\mathbf{x} \in F_{N_c}} l(\mathbf{x})$	-26.513
$\min_{\mathbf{x} \in F_{N_c}} l(\mathbf{x})$	-27.212
$\max_{\mathbf{x} \in F_{N_c}} v(\mathbf{x})$	2.7970
$\min_{\mathbf{x} \in F_{N_c}} v(\mathbf{x})$	2.3823

Table A.3

Caloric data needed for the derivation of energy bounds. The values are computed for the system consisting of acetone and chloroform at 1 bar.

Type	Value/(kJ/mol)
$\max_{\mathbf{x} \in F_{N_c}} \frac{\partial l}{\partial x_1}(\mathbf{x})$	-29.379
$\min_{\mathbf{x} \in F_{N_c}} \frac{\partial l}{\partial x_1}(\mathbf{x})$	-30.825
$\max_{\mathbf{x} \in F_{N_c}} \frac{\partial v}{\partial x_1}(\mathbf{x})$	-28.514
$\min_{\mathbf{x} \in F_{N_c}} \frac{\partial v}{\partial x_1}(\mathbf{x})$	-31.055
$\max_{\mathbf{x} \in F_{N_c}} \left \frac{\partial l}{\partial x_1}(\mathbf{x}) - \frac{\partial v}{\partial x_1}(\mathbf{x}) \right $	2.3013

Table A.4

Minimum and maximum values of molar liquid and vapor enthalpy for a system containing acetone, benzene, and chloroform at 1 bar. The enthalpy of the vapor phase at 298 K of each component i is set to 0 kJ/mol.

Type	Value/(kJ/mol)
$\max_{\mathbf{x} \in F_{N_c}} l(\mathbf{x})$	-25.718
$\min_{\mathbf{x} \in F_{N_c}} l(\mathbf{x})$	-27.468
$\max_{\mathbf{x} \in F_{N_c}} v(\mathbf{x})$	5.0052
$\min_{\mathbf{x} \in F_{N_c}} v(\mathbf{x})$	2.3823

Table A.5

Caloric data needed for the derivation of energy bounds. The values are computed for the exemplary multi-component system consisting of acetone, benzene, and chloroform at 1 bar.

Type	Value/(kJ/mol)
$\max_{w \in F_{N_c}} \frac{\partial h}{\partial x_i}(x)$	-29.290
$\min_{w \in F_{N_c}} \frac{\partial h}{\partial x_i}(x)$	-31.383
$\max_{w \in F_{N_c}} \frac{\partial h}{\partial x_j}(x)$	-28.439
$\min_{w \in F_{N_c}} \frac{\partial h}{\partial x_j}(x)$	-39.593
$\max_{w \in F_{N_c}} \frac{\partial h}{\partial x_k}(x)$	-28.679
$\min_{w \in F_{N_c}} \frac{\partial h}{\partial x_k}(x)$	-32.261
$\max_{w \in F_{N_c}} \left \frac{\partial h}{\partial x_i}(x) - \frac{\partial h}{\partial x_j}(x) \right $	9.0983
$\max_{w \in F_{N_c}} \left \frac{\partial h}{\partial x_i}(x) - \frac{\partial h}{\partial x_k}(x) \right $	2.8133
$\max_{w \in F_{N_c}} \left \frac{\partial h}{\partial x_j}(x) - \frac{\partial h}{\partial x_k}(x) \right $	8.6858

Appendix B. Comments on Assumption 2

Let all pure components be sub-critical at the studied conditions and the pressure be given. The interval

$$T^{\text{lower}} < T < T^{\text{upper}} \quad (\text{B.1})$$

gives the temperature range in which the mixture exhibits a VLE. T^{lower} is the boiling point of the lightest-boiling pure component or azeotrope, T^{upper} the one of the highest-boiling pure component or azeotrope.

Let the vapor phase enthalpy $h^v(T)$ of all pure components i be normalized to 0 at the temperature T^{lower} .

If for every pure component i it holds that

$$\Delta h_{v,i}(T^{\text{lower}}) > \int_{T^{\text{lower}}}^{T^{\text{upper}}} c_{p,i} dT, \quad (\text{B.2})$$

then Assumption 2 is fulfilled as $h_i^l < 0$ and $h_i^v > 0$. Thereby, $\Delta h_{v,i}$ denotes the enthalpy of vaporization of pure component i , and $c_{p,i}$ the saturated liquid heat capacity of the pure component at constant pressure. Typically the enthalpy change induced by the heat capacity (right hand side of Eq. (B.2)) is small compared to the enthalpy change induced by phase transition (left hand side of Eq. (B.2)). Thus, Assumption 2 is plausible.

For bad choices of reference points the bounds in the proofs have to be chosen slightly more conservatively. Therefore, the references have to be chosen carefully for every system. For many example systems that have been investigated, Assumption 2 is valid for a trivial choice of the reference (e.g. $h_i^v > 0$ at 298 K).

It may be possible to find a system that serves as a counterexample. Even in that case, a fixed-point is most likely to exist and the fixed-point iteration will usually converge. However, these properties can no longer be proven in the mathematically rigorous way described in the paper.

Appendix C. Supplementary material

Supplementary data associated with this article can be found, in online version, at <http://dx.doi.org/10.1016/j.ces.2017.02.006>.

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Paper VII: Multi-criteria Optimization of an Industrial World-Scale Process [von Kurnatowski et al., 2017]

Multi-criteria Optimization of an Industrial World-Scale Process

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Dedicated to Prof. Dr.-Ing. Günter Wozny on the occasion of his 70th birthday

Commercially available flow sheet simulators cannot perform optimization runs with more than one criterion. To overcome this problem, the flow sheet simulator CHEMCAD is combined with an external optimization solver, and the Excel VBA client is used to arrange inter-process communications. The resulting tool for multi-criteria optimization in chemical process engineering is applied to two separation problems. First, a dividing-wall column is used as a theoretical example to test different starting points and different scalarization techniques. Second, a significant decrease in energy demand is achieved for a real continuous world-scale facility.

Keywords: Adaptive scalarization, CHEMCAD, Flow sheet simulation, Multi-criteria optimization, Process engineering

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1 Introduction

A development engineer working in the chemical industry typically has to take a variety of objectives into account, such as operational costs and product yield. These objectives are often conflicting, e.g., it may be difficult or impossible to improve the economics and the product quality of a process at the same time. Moreover, the objectives depend on a variety of factors, the so-called design variables, suitable values which need to be determined in an iterative procedure involving computer simulations. Consequently, it is natural to treat chemical process design as a multi-criteria optimization (MCO) problem. Flow sheet simulations are widely used for development in process engineering, but, unfortunately, the commercially available flow sheet simulators are unable to perform optimization runs with more than a single criterion. This can be overcome either by integrating an MCO framework into a flow sheet simulator [1] or by exploiting an external programming interface. The latter approach is used in this work to realize multi-criteria optimization with CHEMCAD.

Process designs of interest allow for an improvement in one objective, only if a worsening in at least one other objective is accepted. In the context of multi-criteria optimization, such designs are called Pareto-optimal [2] and they combine to the Pareto set. In the objective space, this hypersurface separates feasible from infeasible regions, and thus, it is also called Pareto frontier. A feasible point in objective space located aside this frontier is said to be dominated. To calculate a single point on the Pareto set, a suitable algo-

rithm is required. The popular class of deterministic optimization solvers represents one possible way to tackle optimization problems, see [3,4] for details and exemplary applications. These methods make use of derivatives to converge fast and with high precision. However, due to their local nature, algorithms of this type may get stuck in local extrema and they require a large number of objective function evaluations. Deterministic algorithms for global optimization exist, too, even for the case of nonlinear problems [5]. Apart from that, stochastic algorithms exist [6]. Their concept is to sample bigger parts of the objective space and check for optimality, which is less prone to getting trapped locally but also less time-efficient.

A practical approach to find Pareto sets is to couple a flow sheet simulation to a numerical algorithm for multi-criteria optimization. In this way, the advantages of commercial flow sheet simulators are exploited, i.e., the provided models for unit operations and thermodynamics as well as the component property data are used, whereas their

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deficiencies concerning multi-criteria optimization are overcome. In an earlier application of this approach, Zobel et al. integrated CHEMCAD V together with a stochastic optimization solver based on an evolutionary algorithm for mixed-integer nonlinear programming (MINLP) problems [7], and they successfully applied it to a rectification problem from industrial practice. Vazquez-Castillo et al. used a genetic algorithm to optimize a process incorporating dividing-wall columns simulated in Aspen Plus [8]. Otte et al. connected a MATLAB implementation of the molecular-inspired parallel tempering (MIPT) algorithm for global optimization to CHEMCAD via its object linking and embedding for process control (OPC) interface for the purpose of retrofitting a separation process [9]. The cited paper also provides a wide overview of publications on combinations between flow sheet simulators and external optimization solvers. In a recent report, Sundberg et al. compared the performance of three different optimization solvers during the optimization of a flow sheet for methanol synthesis implemented in UniSim [10]. For additional applications of this method to process optimization, see [1, 11, 12].

The optimization problem to calculate a single Pareto point uses a scalarization rule to combine the objectives to a single scalar function f , which is passed to the optimization solver. A common scalarization strategy is the ϵ -constraint method [13, 14]. Convex optimization problems allow for weighted scalarizations [15], which sum up the objectives f_i multiplied with individual factors w_i . The weights w_i are non-negative numbers and they sum up to 1. A simple approach in the case of only two objectives is to choose w_1 from an equidistant sequence of numbers covering the unit interval, and w_2 is set to $1 - w_1$. This procedure is illustrated in Fig. 1a. The figure sketches the objective space for an optimization problem with two objectives f_1 and f_2 , both of which shall be minimized. The dotted line marks the Pareto frontier. The rightmost Pareto point and the leftmost Pareto point are the points where all but one weighting factors are zero. They are the extreme compromises and are calculated as part of any Pareto approximation. Using equidistant weights allows for a fixed choice of the total number N of Pareto points. However, it also brings about some disadvantages: first, it is a-priori unknown how many points are required to approximate the Pareto set with a given accuracy, because its shape is unknown. Second, since weights have to be chosen for all dimensions of the objective space, the equidistant choice of weights exhibits a much higher complexity if there are more than two objectives.

As a consequence, adaptive methods such as the sandwiching algorithm are required to overcome these deficiencies. A detailed explanation of this algorithm can be found in [1, 16, 17]. It enables the calculation of Pareto sets with a well-defined approximation quality and with the corresponding lowest possible number of Pareto points, and hence, with a minimum of computing time. This is exemplified in objective space in Fig. 1b. The inner approxima-

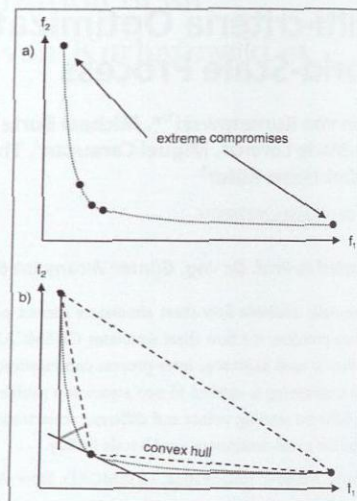


Figure 1. Discrete approximation of a Pareto set (dotted line) for two objectives f_1 and f_2 , a) using equidistant weights with five points, b) using the sandwiching algorithm. The Pareto set is incorporated between the outer approximation (solid lines) and the inner approximation which is part of the convex hull (dashed lines). The gray line indicates the thickness of the “sandwich” as a quantitative measure of accuracy.

tion, which consists of the facets spanned by the Pareto points, and the outer approximation, which is formed by the hyperplanes passing through the Pareto points with the weights determining the normal vector, enclose the real but unknown Pareto set. The sandwiching quality has to be chosen in advance, and it corresponds to the length of the gray line in the figure. The non-convex case requires different approximation strategies, such as the hyperboxing algorithm, and different scalarizations, such as the Pascoletti-Serafini scalarization [18]. However, that lies beyond the scope of the examples treated in this work. For details on combining sandwiching and hyperboxing, the reader is referred to [1].

This article is organized as follows: Sect. 2 describes the numerical tool used for multi-criteria optimization and explains in detail, how the flow sheet simulation CHEMCAD is coupled to the MCO routines. Subsequently, in Sect. 3.1, a theoretical test process is constructed, based on a dividing-wall column fed with a mixture of hexane, n-heptane, and octane. A multi-criteria optimization problem with equidistant weights is solved for this process to validate the method and the influence of the starting point is investigated. The second case studied here is a model of a world-scale process (Sect. 3.2) with the principal purpose of separating a mixture of two components (see Sect. 3.2). This facility is running at high capacity in industrial practice. It is treated using the

sandwiching algorithm, and significantly better process designs are found with the MCO method.

2 Computational Framework

Commercial flow sheet simulation tools in general cannot perform automated multi-criteria optimization runs. For this particular purpose, the simulation engine has to be linked with additional optimization functionalities. Fig. 2 shows the basic architecture of the framework. MS Excel is chosen as a front-end component here for several reasons: on the one hand, it is available to the majority of development engineers, and it is comfortable to have a graphical user interface, especially a familiar one. On the other hand, results of the multi-criteria optimization shall be conveniently connected to pre-existing data, which is often stored in Excel files.

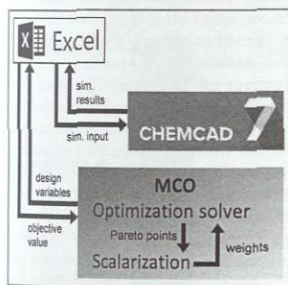


Figure 2. Architecture of the computational framework with MS Excel as front-end component and CHEMCAD as flow sheet simulation. Black arrows indicate data transfer.

The starting point in the development process of the framework was the native CHEMCAD-Excel VB client, which is provided with the CHEMCAD installation. This is a macro-enabled Excel workbook with a set of subroutines to control CHEMCAD simulations. It already contains a basic user interface with buttons, e.g., to establish the connection to CHEMCAD, to load a specific flow sheet, to send changes in the simulation variables to CHEMCAD, and to trigger simulation runs. More important, it includes macros which transfer all the flow sheet data concerning streams and unit operations to Excel worksheets. These macros are automatically triggered after loading or running a simulation and, hence, the full set of process data is always available in Excel. The underlying technology is a COM (component object model) interface, a Microsoft standard platform for interaction between different programs. In this respect, CHEMCAD acts as a COM server and Excel is the client program. The programming language in the framework is VBA (Visual Basic for Applications), an object-orientated scripting language. The flow sheet simulation is

available in the code as an object with different interfaces providing information about and control over different process characteristics such as streams, unit operations, or component properties. No additional reference to a CHEMCAD library needs to be set in the client program, because CHEMCAD is registered to the operating system as a COM server during the installation procedure. CHEMCAD 7 is used in this work. The simulations were executed in the sequential modular mode and the underlying systems of equations were solved using the direct substitution method. The maximum number of flow sheet iterations was chosen as 200.

Here, the VB client provided by CHEMCAD was extended by several features. First, the required optimization solvers and the sandwiching algorithm for adaptive scalarization [1, 17] are linked to the Excel COM client by referencing the respective type libraries (tlb), which themselves access corresponding dynamically linked libraries (dll). The employed optimization solvers are NLPQLP (nonlinear programming with non-monotone and distributed line search) for ordinary nonlinear problems and MISQP (mixed-integer sequential quadratic programming) for mixed-integer problems [19]. These solvers are based on a gradient technique, which requires the calculation of derivatives of the objective function with respect to the design variables. These derivatives are calculated numerically using finite difference quotients. Calculations of gradients take a lot of simulation runs. However, these additional runs usually converge very fast, because the design variables are only changed by the small value of the accuracy parameter of the derivatives. The solvers use penalty terms in the objective function to handle constraints. Equality and inequality constraints can be dealt with. The NLPQLP is used for optimization unless integer design variables are defined in the problem. In that case, the MISQP solver is chosen automatically. The solvers are embedded in a loop, in which they are alternately fed with gradients to determine the direction of steepest descent and with values of the objective function for a line search along a fixed direction.

A second extension to the CHEMCAD-Excel VB client is the automatic output of the column profiles of all rectification columns in the flow sheet to Excel. The pressures, temperatures, total and component-wise flow rates, mass densities, and the F factors are listed for each stage. As a result, these quantities can be used as part of an objective function. Especially the F factor is an important indicator for process engineers, which is not calculated by CHEMCAD itself. A user does not need to be familiar with VBA, because a graphical interface to specify the optimization problem was set up in Excel for this purpose. It consists of three tables to define the objectives, the design variables including their boundaries, and the constraints. In addition to that, there is a panel to view the optimization status and to control the optimization process. Excel formulas are used to connect the variables in the corresponding tables to the worksheets which are used to transfer data to and from CHEMCAD.

When a design variable has to be updated, its formula is parsed to determine its original data cell. Then the new value is written in this cell and finally sent to CHEMCAD.

In the typical workflow, a flow sheet is first loaded into the framework and subsequently the optimization problem is specified in the graphical interface. In principle, the tool can handle an arbitrary number of objectives. The Pareto approximation is started by a mere click on a button. The information flow during the calculations is sketched in Fig. 2. Simulation data from CHEMCAD is written to Excel from where it is used to get objective function and gradient information for the optimization solver. The optimization solver then suggests new values for the design variables which are transferred back to CHEMCAD again via Excel. There is no direct interaction between CHEMCAD and the multi-criteria optimization part. After the extreme compromises have been determined, the objective space is rescaled such that the values of the objectives lie in dimensionless intervals between 1 and 2 (not 0 and 1 to avoid entering negative quadrants in case of non-convexity). Then, the sandwiching algorithm calculates the weight factors for the next Pareto point in the rescaled space. The objective function is calculated as the weighted sum.

The sandwiching quality was set to 1.05 for this work, i.e., the real Pareto frontier will be located within a 5 % interval next to the linearly interpolated hyperplanes between the calculated Pareto points. Once the Pareto approximation is finished, the output contains the convergence parameters as well as detailed information about all the stream data, unit operation data, and the column profiles for each calculated point. Note that the simulation tool included is generic, i.e., within the framework, CHEMCAD could be replaced by a different simulation module, which does not even have to be a flow sheet simulator if the context is different. Only the subroutines organizing the data transfer between Excel and the simulation engine would have to be rewritten since the employed interfaces are engine-specific. The presented framework does not contain a method to deal with non-convex Pareto sets, but a convexity check is performed by taking the center of mass for the design variables of Pareto points spanning a facet, calculating the corresponding objectives, and checking on which side of the approximated Pareto frontier the resulting point in objective space lies. No indication of non-convex Pareto sets occurred in the optimization problems solved in this work. If it was the case, a hyperboxing approximation scheme could be applied [1].

3 Method Validation and Application to a Real World-Scale Process

3.1 Dividing-Wall Column

In the first test of the multi-criteria optimization framework, a flow sheet consisting of a dividing-wall distillation column is applied. Its purpose is to separate a ternary mix-

ture with only one unit operation. The concept can even be extended to reactive distillation, as reported, e.g., by Ehlers et al. recently [20]. The facility is supposed to have only a single dividing wall and, hence, it is modeled as a prefractionator [21], i.e., with two standard distillation columns, only the second one of which has a reboiler and a condenser.

The flow sheet is displayed in Fig. 3. The columns C1 and C2 consist of 20 and 60 stages, respectively. The liquid recycle stream from the upper side drain (stream 7) and the vaporous recycle stream from the lower side drain (stream 8) of the second column represent the material inputs to the column section left of the wall. The vertical position of the dividing wall is in the middle of the unit, i.e., from stage 20 to 40. Thus, stream 7 is drained from stage 20 and stream 8 is drained from stage 40 of C2, stream 5 is fed to stage 20 and stream 6 is fed to stage 40 of C2. Streams 7 and 8 enter C1 at its top and bottom stage, respectively.

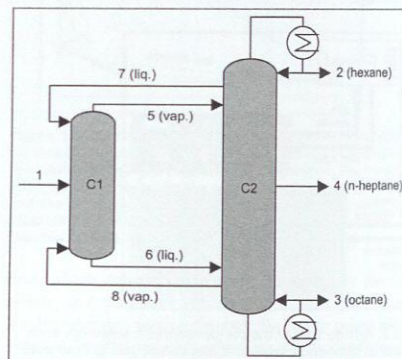


Figure 3. Flow sheet for the single dividing-wall column modeled as a prefractionator. Feed stream 1 contains equal parts of hexane, *n*-heptane, and octane, which are supposed to be separated in the product streams.

The system is fed with a ternary mixture of hexane, *n*-heptane, and octane. The feed rate of each component is 333 kg h^{-1} , resulting in an overall feed rate of 999 kg h^{-1} . Product stream 2 consists mainly of the low boiling substance hexane, stream 4 consists mainly of *n*-heptane, and stream 3 has a high octane concentration. For specification of the central side drain (stream 4), its total mass flow rate is set to a fixed value of 330 kg h^{-1} . The upper side drain (stream 7) and the lower side drain (stream 8) are specified by total mass flow rates of 400 and 500 kg h^{-1} , respectively. If related to the total liquid and vapor flows inside C2 on the corresponding stages, these rates determine the material splits, which result from the particular position of the dividing wall inside the column. However, this particular flow sheet simulation turned out to have better convergence properties if the flow rates rather than the splits are specified for the side drains. The split ratios can be calculated a

posteriori from the simulation output, and the split ratio of the liquid molar flows at the top of the dividing wall varies between 0.86 and 32.64 for the working points calculated in this section. The recycle tolerances were set to 10^{-5} and the flash tolerance was set to 10^{-7} . The vapor heat capacities were calculated using the corresponding DIPPR (Design Institute for Physical Properties) equation, and NRTL (non-random two-liquid) was used as the vapor-liquid equilibrium (VLE) model for calculation of K values in this work. For this example, the required interaction parameters were taken from the CHEMCAD internal property data base.

The optimization problem has two design variables, two objectives, and two constraints. The design variables are the total mass flow rate from the bottom of column C2, varied between 200 and 400 kg h⁻¹, and the reflux ratio of C2, varied between 1 and 80. These are the free variables, which are supposed to be manipulated by the optimization solver to obtain Pareto optimality. Their boundaries are not chosen from an economic point of view here. Instead, the test is supposed to sample a broad interval in the design space of the problem. The first objective is to maximize the molar flow rate N_h of *n*-heptane in stream 4. It is equivalent to maximizing the mole fraction of *n*-heptane in this stream, because its total flow rate is kept constant. The second objective is to have a minimal reboiler duty Q_{rebr} to keep the energy demand of the process low. Furthermore, the mole fractions of hexane in the head product and of octane in the bottom product are required to be at least 90%. From a practitioner's point of view, this is not a very strong requirement since product purities of 90% are often insufficient in process engineering. However, it is going to have a notable impact on the optimization results, as discussed below.

Tab. 1 gives an overview of the multi-criteria optimization problem as well as the different starting values applied for the Pareto approximation. The problem is solved using the NLPQLP solver. The solver accuracy is set to 10^{-6} and the solver quadratic programming (QP) accuracy for the underlying quadratic programming problem is set to 10^{-5} for this example. The calculations of gradients should be less precise than the simulation outputs. Hence, the accuracy of the derivatives is set to 0.01 % of the corresponding design variable with a forced lower bound of 10^{-9} for the absolute value. This choice follows the performance test described in the NLPQLP documentation.

Table 1. Optimization problem and tested starting values for the discrete Pareto approximation in the case of the single dividing-wall column fed with a mixture of hexane, *n*-heptane, and octane. N_h is the molar flow rate of *n*-heptane in the product stream, and Q_{rebr} is the reboiler duty.

Variable	Type	Bounding interval	Starting point 1	Starting point 2	Starting point 3
bottom drain [kg h ⁻¹]	Design variable	[200, 400]	350	370	350
reflux ratio [-]	Design variable	[1, 80]	20	20	40
N_h [kmol h ⁻¹]	Objective, maximize	-	3.1535	2.9539	3.1535
Q_{rebr} [kW]	Objective, minimize	-	632.88	592.98	1231.67

For a first test, no adaptive scalarization strategy is used. Instead, the weighting factors multiplying each objective in the scalar objective function are chosen from an equidistant sequence of numbers covering the unit interval and the total number of desired Pareto points is set to $N = 6$. The results of the optimization runs are shown in Fig. 4, which depicts the calculated Pareto points in the 2D objective space of the problem. The filled symbols mark the starting point for each optimization run, whereas markers without filling indicate the Pareto points themselves.

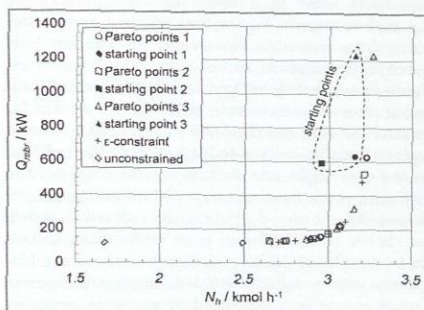


Figure 4. Pareto-optimal points of the single dividing-wall column modeled by a prefractionator flow sheet fed with a mixture of hexane, *n*-heptane, and octane plotted in the 2D objective space. N_h is the molar flow rate of *n*-heptane in the product stream, which shall be maximized, and Q_{rebr} is the reboiler duty which shall be minimized. Filled symbols mark the starting points of the optimization run for each point, unfilled symbols mark Pareto points calculated with equidistant weights. Plus signs represent comparative results from the ϵ -constraint method (no further constraints) with starting point 1. The diamond symbols correspond to an unconstrained optimization with starting point 1.

Three different starting points for the Pareto samplings were tried, marked by different shapes, in order to investigate their impact on the optimization procedure. In addition, an ϵ -constraint technique, marked by plus signs in Fig. 4, was tested. That patch was calculated without further constraints. For starting points 2 and 3, the maximum number of recycle iterations in CHEMCAD had to be increased to 400 for convergence reasons. Apparently, in all runs, the

Pareto-optimal points are placed on the same imaginary line, and the boundary of the feasible region in objective space is indeed identified in the figure. However, by moving the starting point to higher reboiler duties, from squares over circles to triangles, the Pareto point representing the extreme compromise with full weight on N_h and zero weight on the heat input is shifted to much higher reboiler duties, revealing the Pareto frontier in the top right region of the diagram. This results from the fact that the frontier is almost parallel to the vertical axis in this part of the objective space and, hence, Q_{rebr} can be significantly reduced by only a small decrease in N_h . Small variations in an objective can arise from numerical inaccuracies or from the local nature of the optimization method.

The diamond symbols in Fig. 4 correspond to a comparative calculation without constraints. The lower bound of the reflux ratio had to be increased to 2.3 for this patch to avoid divergent simulations. Since starting point 1 was used here again, the upper right extreme compromise is the same as in the circled patch. But in contrast to the constrained optimizations, the reboiler duty could be reduced to values below 120 kW for the leftmost point in the unconstrained patch, because lower product purities in the head and bottom drains enable working with less heat input. However, this improvement is accompanied by a notable worsening in the second objective N_h .

3.2 World-Scale Separation Process Running in Industrial Practice

In this subsection, the multi-criteria optimization tool is applied to a real world-scale separation process. The facility is operated at high capacity, and thus, a decrease in operational expenditures is particularly desirable, since it implies a big economic advantage. The setup consists of two distillation columns with one forward connection and two recycle streams, as shown in Fig. 5. Only the first column has a reboiler, whereas C2 works with the heat input from stream 4. C1 is modeled with 53 equilibrium stages and C2 is modeled with 34 stages. The feed stream (stream 1) is a mixture of two components, and the main task of the process is to separate these two components. The bottom drain of C1 and the side drain of C2 are specified by fixed flow rates. The forward connection (stream 4) is chosen as the cut stream in the sequential modular solution scheme, which is applied by CHEMCAD by default.

An unconstrained multi-criteria optimization procedure with five design variables and two objectives is conducted. The objectives are a maximal product

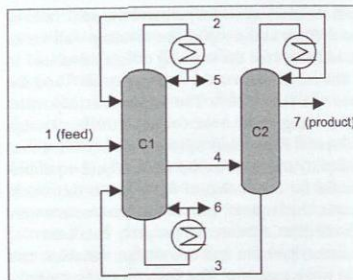


Figure 5. Flow sheet representation of the industrial world-scale facility for separation of two components. Only C1 has a reboiler and C2 works with the heat input from stream 4. Stream 7 is the main product stream.

purity x_{prod} and a minimal reboiler duty Q_{rebr} of the first column, which represent conflicting criteria. The design variables and their boundaries are listed in Tab. 2. Two of the variables in this problem are of integer type: the feed stage of the upper recycle stream 2 into C1 and the product withdrawal stage for stream 7. Hence, the MISQP solver was used to solve the optimization problem. Its accuracy and the QP accuracy were set to 10^{-4} , and the derivatives were calculated with an accuracy of 0.1%. The specifications for the two applied starting points differ only in the vapor split for stream 4. Thus, there are two respective values in the corresponding cell in Tab. 2.

According to experience, recycle streams can be one of the reasons for a flow sheet simulation to become prone to convergence issues. Therefore, it is mandatory to carefully determine the boundaries for each design variable via individual test simulations before solving the multi-criteria optimization problem. Otherwise, simulation divergences may occur, that are difficult to track down from inside Excel. In fact, the tool contains a homotopy functionality [22], but this cannot compensate divergences due to thermodynamic infeasibility and, more important in this case, it does not apply for mixed-integer problems, because the concept of homotopy in process engineering is based on

Table 2. Design variables with their corresponding initial values and boundaries in the multi-criteria optimization problem for the industrial world-scale process separating two components.

Design variable	Initial value	Lower boundary	Upper boundary
Reflux ratio C1 [-]	7.5	6	20
Head drain C2 [kg h ⁻¹]	100	1	400
Vapor split for stream 4 [-]	Starting point 1: 1.5 Starting point 2: 1.2	1	2
Feed stage for stream 2 into C1 [-]	41	30	53
Product drain stage [-]	12	1	34

reducing step sizes, which cannot be realized for integer variables. However, in case of exclusively continuous design variables, *homotopy* strongly improves the convergence behavior of the tool. For line searches in the objective space, the concept is implemented intrinsically by the optimization solver, and for gradient calculations, it was added manually to the VBA code.

Fig. 6 shows the results of the Pareto approximation. The sandwiching algorithm was used with the approximation quality (see Fig. 1b) chosen such that the Pareto set will be located within a 5% vicinity of the convex hull. Again, Pareto points are indicated by unfilled symbols and starting points are indicated by filled symbols. Beyond a product purity x_{prod} of 99.6%, the Pareto frontier becomes very steep. This leads to the effect, that in the patch marked by circles (starting point 1) the extreme compromise with full weight on x_{prod} is found at higher Q_{rebr} than in the patch for the second starting point marked by squares, since starting point 1 is located at higher Q_{rebr} . The recycle tolerances were reduced to 10^{-6} to avoid dominated points as result. This measure has also been encouraged in [10], where the application of different starting points in objective space is recommended, too. The flash tolerance was set to 10^{-8} .

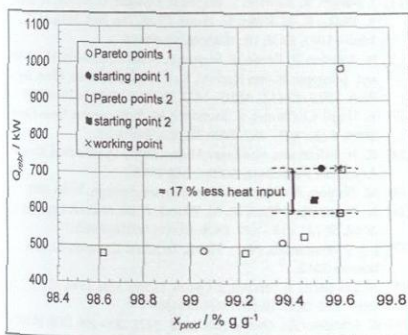


Figure 6. Results from multi-criteria optimization for the world-scale process separating two components. x_{prod} is the product purity, which shall be maximized, and Q_{rebr} is the reboiler duty, which shall be minimized. Filled symbols mark the starting points of the optimization run for each point, unfilled symbols mark Pareto points calculated with the sandwiching algorithm. The cross marks the working point of the real process before optimization. It is clearly dominated.

The Pareto points at $x_{\text{prod}} = 99.61\%$ and $Q_{\text{rebr}} = 591\text{ kW}$ clearly dominate the current working point of the process, indicated by the cross. The multi-criteria optimization suggests an *alternative working point* with slightly higher product purity and a significant decrease in energy demand of about 17%. The improvement could not have been found without using MCO techniques. To transfer these numerical results into practice, the principal changes to be applied to

the design variables are a switch of the feed stage for stream 2 into C1 and of the product drain stage.

4 Conclusion

The combination of the flow sheet simulator CHEMCAD with a multi-criteria optimization framework proved to be a powerful tool for process design problems in chemical industry. MS Excel as a COM client is a suitable platform to interlink the different components, while it provides a familiar and comfortable front end. It requires the simulator to have a programming interface to set up a connection to the scalarization algorithm and the optimization solver. In the case of CHEMCAD, the optimizer provided by the product itself may also be used, because it can be triggered externally. Once the interface is under control, the concept is very useful during the design period of completely new industrial processes. Apart from that, it can also be used to retrofit existing facilities, which eventually suggests alternative points of operation. Cases from both categories are studied in this work.

If a weighted sum approach is used as scalarization strategy, one has to be aware of the fact that its limitation lies in the convexity properties of the Pareto set underlying the optimization problem. Only convex regions of the objective space can be explored when using this particular scalarization technique. For a relatively simple flow sheet such as the prefractionator, different segments of the Pareto set are revealed in the regions of extreme compromises, depending on where the starting point or the initial guess for the solution is chosen in objective space. This behavior can occur if the scalar objective function exhibits a rather weak dependence on the design variables or if the Pareto frontier is very flat or very steep in the sampled region. When applying local optimization techniques, different starting points should always be tried to ensure that the Pareto set has been located correctly. In this respect, if numerous Pareto approximations have to be calculated, the sandwiching method as an adaptive algorithm is particularly advantageous because of its time efficiency. Another important point to mention is the boundaries set on the design variables during the optimization procedure. They need to be determined carefully in advance by test simulations to avoid infeasible regions and convergence issues.

The application of the MCO concept in the revision of processes, which are already running and which perhaps have already been running for a long time, is advisable, too. It might, e.g., result in a decent reduction of operational expenditures, especially when the facility is working at high capacity. In this work, it is demonstrated that for a world-scale separation process, multi-criteria optimization suggests an alternative design with the heat consumption reduced by about 17% compared to the current state at approximately the same product flow rate. The example shows that this solution would not have been discovered without MCO.

We thank Jan Schöneberger from Chemstations Europe for impeccable support with the programming interfaces of CHEMCAD.

Symbols used

f	[-]	scalar objective function
f_i	[-]	value of the i th objective
N	[-]	total number of points in a discrete Pareto approximation
N_h	[kmol h ⁻¹]	molar flow rate of n -heptane in the product stream of the dividing-wall column
Q_{rebr}	[kW]	reboiler duty
w_i	[-]	weighting factor of the i th objective in the weighted sum
x_{prod}	[% g g ⁻¹]	product purity of the world-scale process for separation of two components

Abbreviations

COM	component object model
DIPPR	Design Institute for Physical Property Research
dll	dynamically linked libraries
MCO	multi-criteria optimization
MINLP	mixed-integer nonlinear programming
MIPT	molecular-inspired parallel tempering
MISQP	mixed-integer sequential quadratic programming
NLPQLP	nonlinear programming with non-monotone and distributed line search
NRTL	non-random two-liquid
OPC	open platform communications
QP	quadratic programming
tlb	type libraries
VBA	Visual Basic for Applications
VLE	vapor-liquid equilibrium

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Paper VIII: Decision Support by Multicriteria Optimization in Process Development: An Integrated Approach for Robust Planning and Design of Plant Experiments [Bortz et al., 2015b]

Decision Support by Multicriteria Optimization in Process Development: An Integrated Approach for Robust Planning and Design of Plant Experiments

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Abstract

In simulation-based process design, model parameters, like thermodynamic data, are affected by uncertainties. Optimized process designs should, among different other objectives, also be robust to uncertainties of the model parameters. In industrial practise, it is important to know the trade-off between an increase in robustness and the other objectives – like minimizing costs or maximizing product purities. This contribution describes a practical procedure how to incorporate robustness as an objective into a multicriteria optimization framework. The general procedure is illustrated by a concrete example. Finally, we argue that the same approach is useable for an optimal design of plant experiments.

Keywords: Optimization, robust design, sensitivity analysis, Pareto solutions

1. Introduction

Models for computer-aided process design contain a multitude of physical, chemical and, when it comes to cost functions, also economical and sustainability related parameters. Often these parameters have either been estimated by model adjustment to experimental data, or their values are given by experience. In both cases, these values are not known exactly, but rather within specific uncertainty ranges (we prefer using the term uncertainty range to confidence interval. The term confidence interval has a statistical meaning that is not needed in our discussion). The impact of these ranges on the output functions can be estimated by sensitivity analysis (Saltelli et al. 2008). In sensitivity analysis, different sampling-techniques for scenarios in the space of the uncertain model parameters are available to obtain insight into the importance and the size of the resulting uncertainty ranges in the output functions of the model. The application of Monte-Carlo sampling (e.g. in Xin et al., 2000) demonstrated the importance of analysing the uncertainties in the calculated process designs.

On the other hand, the engineer aims at understanding the influence of the available process parameters on the output functions. This is essential in order to arrive at a process design in the space of process parameters that meets certain criteria in the space

of the output functions. Generally, these optimization problems contain different, often conflicting objectives, like cost and quality measures. In this situation, Multicriteria optimization is a well-established tool to arrive at best compromises (Pareto solutions) between conflicting criteria (adaptive sampling strategies combined with deterministic optimization algorithms have been demonstrated by Bortz et al. (2014)). Navigating the Pareto solutions then visualizes the trade-offs interactively to the planner (Asprion et al. 2011).

In this contribution, we aim at including the sensitivities with respect to uncertain model parameters as further objectives into a multicriteria optimization setting. We call this procedure Robust Planning (RP). The result of RP will be the quantification of trade-offs between increasing robustness to uncertain model parameters and the other objectives. This approach complements the definitions of robust optimization (for a review, see Ben-Tal et al. (2009)) and chance-constraint programming (Ostrovsky et al. 2009). In these approaches, the focus is on an absolute definition of robustness in the sense that solutions can be classified as either robust or non-robust. Our strategy however puts emphasis on the compromise one has to accept in order to arrive at a more robust solution compared to a more sensitive one.

It turns out that in practice, optimal experimental design (OED) is supported in a similar multicriteria setting: On the one hand, the model should be accurate for process designs which are practically relevant (e.g. at low costs, high product qualities). Thus, experiments should preferably be carried out at these designs. On the other hand, in order to reliably estimate model parameters, experiments are favored at which measurable output functions are sensitive to the respective model parameters. A common approach discussed in literature (Franceschini and Macchietto 2008) - focuses on the maximization of different sensitivity measures. Therefore, one defines scalar measures of the sensitivity matrix encoding the sensitivity of certain output functions to relevant model parameters. However, these scalarizations of the sensitivity matrix lead not only to contradictory results (Telen et al., 2012), but also constitute a weighting of matrix entries which has to be known *a priori*. In practice, however, this knowledge does not exist, leading eventually to a loss in optimization potential.

A possible solution suggested in this contribution consists in following a similar route as sketched above for robust process design: For each measurable output function of interest, an adequate sensitivity measure is proposed as one objective to be maximized, among others which also have to be met during the experiment. By doing so, the trade-off between sensitivity, i.e. reliable estimates of model parameters, and good representation of the designs which are practically most relevant is quantified. On this basis, the planner can decide for a process design that realizes the compromise that best suits the current situation. Thus in our approach, RD and OED merely differ in the way how sensitivity measures are treated: As objectives to be minimized for RD, or as objectives to be maximized for OED.

The article is structured as follows. In Section 2 it is described how robustness can be incorporated into a conventional optimization problem. Section 3 contains the illustration of this approach by an example. The article ends with the conclusion in Section 4.

2. Sensitivity as an optimization objective

Sensitivity analysis is used here to quantify the uncertainty range of an output function with respect to given distributions over uncertainty ranges of thermodynamic model

parameters around their reference values. During RP (OED), process parameters are to be adjusted such that, among others, adequate robustness measures derived from the uncertainty ranges of certain output functions are maximized (minimized).

Our starting point is a conventional optimization problem that has been set up and solved, i.e.

- the engineer has chosen one or more meaningful objectives $f_i, i = 1, \dots, N_{obj}$ from the output functions and relevant process parameters $p_j, j = 1, \dots, N_{proc}$;
- one or more (Pareto-) optimal solutions have been obtained by some optimization method. These are given by design points $S_\alpha, \alpha = 1, \dots, N_{sol}$, with corresponding objective function values $f_{i,ref}(S_\alpha)$. The index *ref* means that the model parameters $x_k, k = 1, \dots, N_{mod}$, are fixed to certain reference values $x_{k,ref}$.

If one now wants to take into account the uncertainty ranges in the x_k one merely has to find out which compromise one has to accept in order to arrive at more (for RP) or less (for OED) robust solutions compared to the $f_{i,ref}(S_\alpha)$. The following steps are recommended:

- Carry out a conventional sensitivity analysis for a set of design points $P_\beta, \beta = 1, \dots, N_{points}$, where for each design point a sampling in the N_{mod} -dimensional space of the x_k is done. In order to keep the numerical effort manageable, scenario samplings that scale linearly with N_{mod} , like one-at-a-time or factorial design (Saltelli et al., 2008), should be used. The P_β should contain the original Pareto points S_α , but do not have to be restricted to them; it is advisable to include some more points, for example, by enumerating points in a suitable neighbourhood around the designs of the Pareto points. The result will be uncertainty ranges in f_i for each P_β resulting from the uncertainty of model parameter x_k with lower values $f_{i,k-}(P_\beta)$ and upper values $f_{i,k+}(P_\beta)$. Thus an average relative deviation with respect to the reference value $f_{i,ref}(P_\beta)$ follows:

$$\Delta_{f_i,k}(P_\beta) := \frac{1}{f_{i,ref}(P_\beta)} \sqrt{\frac{1}{2} \left[(f_{i,k-}(P_\beta) - f_{i,ref}(P_\beta))^2 + (f_{i,k+}(P_\beta) - f_{i,ref}(P_\beta))^2 \right]} \quad (1)$$

This is the measure for robustness used in this contribution. It quantifies the impact of x_k on the objective function f_i at P_β and tends to zero if both $f_{i,k-}$ and $f_{i,k+}$ approach $f_{i,ref}$. Without trade-off between the original objectives and minimizing (RP) or maximizing (OED) this measure, then one can stop here.

- If there are trade-offs, one includes the corresponding $\Delta_{f_i}(P_\beta)$, into the original optimization problem. In each iteration step during the optimization, a sensitivity sampling has to be done in order to calculate the $\Delta_{f_i}(P_\beta)$.

It is important that one restricts oneself to the most important *conflicting* objectives in this procedure. The strength of multicriteria optimization is in quantifying trade-offs between best compromises (Pareto-solutions). Objectives that correlate should not be defined as single objectives in the procedure: This would lead to numerical inefficiency and to hiding valuable information.

3. Example

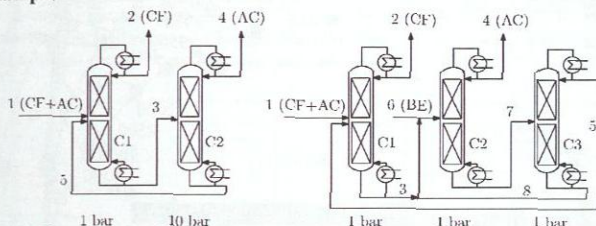


Figure 1: Flow sheets of the pressure-swing (left) and entrainer (right) distillation processes for separating chloroform (CF) and acetone (AC). The entrainer is benzene (BE).

In this section, we want to compare two types of distillation processes for separating a binary mixture of chloroform and acetone into pure components. As these two substances form a maximum boiling azeotrope, a separation in a simple single distillation column is not possible. Two variants for separating the azeotropic mixture are considered: the first is a pressure-swing distillation which takes advantage of the pressure dependency of the azeotrope. In the second one, an entrainer (benzene) is used to influence the phase behavior in a way which makes a separation by distillation feasible. The flow sheets for these two variants are shown in Fig. 1. In Bortz et al. (2014), a comparative multicriteria study of these two variants has been performed with three conflicting objectives: Minimizing the total heat duty and maximizing the product purities in the product streams, i.e. the purity of Acetone in streams 4 and the purity of Chloroform in streams 2; as design parameters, the reboil and split ratios of the columns were taken.

Here we aim at including the robustness of the separation with respect to uncertainties in the VLE data as additional objective that is to be minimized. A NRTL model was taken to model the VLE of the mixtures with reference model parameters given in Bortz et al. (2014). An inspection of original VLE measurements in the Dortmund Data Bank (Onken et al., 1989) revealed that assuming uncertainty ranges in the activity coefficients at infinite dilution, $\gamma_{AC,CF}^{\infty}$ and $\gamma_{CF,AC}^{\infty}$, by $\pm 10\%$ around their reference values models the accuracy of experimental data well. A Margules approach (Mathias 2014) was then used to incorporate the uncertainties into the corresponding VLE model. A sensitivity analysis using one-at-a-time-sampling was then performed for a large set of possible design points to analyze the impact of the uncertainty ranges in both $\gamma_{AC,CF}^{\infty}$ and $\gamma_{CF,AC}^{\infty}$. It turned out that the influence of $\gamma_{CF,AC}^{\infty}$ on the objective functions is negligible. Thus in the following, we focus on the impact of the uncertainty range of $\gamma_{AC,CF}^{\infty}$. To keep computational costs moderate, a one-at-a-time-sampling is used here as well to calculate $\Delta_{f_{i,j} \gamma_{AC,CF}^{\infty}}(P_{\beta})$, i.e. in Equation (1), one sets $f_{i,k}(P_{\beta}) = f_i(P_{\beta})|_{\gamma_{AC,CF}^{\infty}-10\%}$ and $f_{i,k+1}(P_{\beta}) = f_i(P_{\beta})|_{\gamma_{AC,CF}^{\infty}+10\%}$. With this set-up, the sensitivity in the product purities of the original Pareto-points was calculated. It turned out that the effect on the Acetone purity dominates the effect on the Chloroform purity by one order of magnitude; furthermore, both effects are highly correlated. Therefore, we restrict ourselves to the uncertainty of the Acetone purity, $\Delta_{AC, \gamma_{AC,CF}^{\infty}}$, in the following, which we note by Δ_{AC} . Its values for the original Pareto points are shown in Fig. 3.

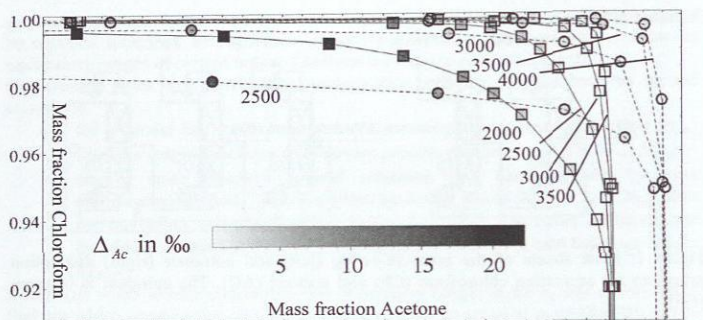


Figure 3: Pareto points for entrainer distillation (squares) and pressure swing distillation (circles) for different heat duties in kW (numbers next to the Pareto sets), calculated by a sandwiching algorithm as in Bortz et al. (2014) maximizing the mass fractions of the two product purities: mass fraction of Acetone (Chloroform) in stream 4 (2)). The grey code denotes the relative uncertainty of the acetone purity.

From the results shown in Fig. 3, two conclusions can be drawn. First, increasing the Acetone purity is not conflicting with its robustness. On the other hand, an increase in the Chloroform purity leads to a decrease in its robustness, which can, however, be counterbalanced by an increase in the heat duty. Thus, in order to achieve certain robustness, one either has to invest sufficient energy, or make a compromise in the Chloroform product purity. This leads to the question how to quantify the trade-off between robustness and product quality.

This question is answered by minimizing Δ_{Ac} as a fourth objective. Since, as argued above, this objective is conflicting with the minimization of the heat duty and the maximization of the Chloroform purity, it can be included into the original Multicriteria framework by introducing appropriate upper bounds and redoing the original problem again. The result is presented in Fig. 4.

Fig. 4 shows the highest possible increase in robustness that can be achieved by accepting a compromise in the Chloroform purity. This gain in robustness at relatively moderate heat duty is similar in value to the robustness obtained by significant increase in the energy invest. Furthermore, Fig 4 demonstrates that the entrainer distillation tends to be more robust to uncertainties of $\gamma_{AC,CF}^{\infty}$ at less energy invest.

4. Conclusions

We presented a practical guideline how to include robustness as one objective among others in a multicriteria optimization framework. If the goal consists in finding robust designs, then robustness as an objective is to be maximized. However, in the framework of optimal experimental design, it is to be minimized. The guideline consists of three steps, starting from the original optimization problem, followed by a sensitivity analysis of the original Pareto points, possibly including an interesting neighbourhood, and leading to the inclusion of robustness as a further objective only where conflicts with the other objectives occur. In order to play to the strength of the multicriteria approach, one should restrict oneself to the representatives of the most important conflicting

objectives. The planner then obtains the trade-offs between the objectives. The practicability of our approach was demonstrated by a comparative study between two distillation types, leading to new insights into the competition between maximal product quality, minimal energy invest and maximal robustness.

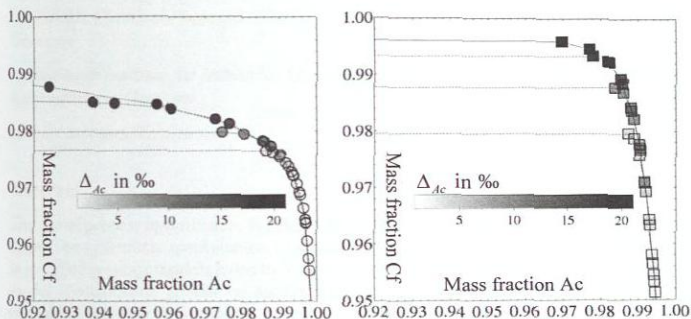


Figure 4: Pareto points for constant heat duty (left panel: 2500 kW, pressure swing distillation; right panel: 2000 kW, entrainer distillation) and bounds on Δ_{Ac} , namely $\Delta_{Ac} \leq 2\%$, 5% , 13% (curves from bottom to top; the grey level is the same in both panels). The uppermost curve represents the case unrestricted in Δ_{Ac} .

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Paper IX: Graybox Models - New Opportunities for the Optimization of Entire Processes [Asprion et al., 2017a]

Graybox Models - New Opportunities for the Optimization of Entire Processes

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Abstract

The use of process optimization is often limited due to missing models for certain process steps. The systematic combination of available operating data with previous knowledge in so called graybox models helps to bridge this gap. Following the concept of incremental model identification it will be shown how the workflow has been integrated into a simulation software environment. It will be applied to a cumene process.

Keywords: graybox models, validity range, process simulation, process optimization.

1. Introduction

The importance of simulation of entire processes increases in chemical process development. The interaction of experiments (e.g. from a mini-plant) with simulations is beneficial for both. The simulation model helps to improve process understanding especially about the relevant impact factors including their complex relationships and for this reason may support the design of experiments and the evaluation of experimental results. On the other hand experiments may be used for the validation or if necessary for the adjustment of the simulation model. The goal is to obtain a validated simulation model which might be used for process optimization. Besides a mere cost driven optimization the use of multi-criteria optimization (see for example Bortz et al. 2014, Burger et al. 2014) gains in significance especially in respect of competing sustainability objectives.

One problem for simulations are process units, where rigorous models are lacking or where the effort for the setup of such a model is too expensive. Examples are reactors and decanters. Consider the following procedure for reactors: For each individual operating point, the yield can be adjusted so that the simulation model describes this operating point. However, a reliable prediction of other operating points with such models is in general not possible - especially when recycles to the reactor inlet are present. Graybox models based on measured operating data are able to eliminate such "blind spots". In contrast to a purely empirical, statistical evaluation with so-called blackbox modeling a lot of previous knowledge is available, which can be used for the setup of graybox models. In this paper the workflow of the method will be described and demonstrated for a Cumene process.

2. Graybox modeling for process simulation

The approach implemented in BASF's in-house simulation software CHEMASIM is following the concept of incremental model identification (cf. for example Bardow and Marquardt, 2004). The use of the approach was already demonstrated by Kahrs and Marquardt (2009), but is to our knowledge the first time implemented into a software environment for industrial use to support the workflow of graybox modeling.

The key idea of graybox modeling in process simulation is to use available operating data of the process to generate a model for a process step with a missing rigorous model. To obtain this data-driven model, a vast number of possible methods from supervised machine learning exist. Quite often however, the inputs and outputs of the process step to be modeled are not measured or not easily determined from other measurements. So before the modeling for the process step can start these missing data will be estimated based on measured operating data with the help of the already available rigorous model (so-called soft-sensoring).

Therefore the first step in graybox modeling is data selection. The goal is to identify many different representative steady-state operating conditions. Methods to support this data selection step have been described before (Asprion et al., 2015). At its end, a set of good operating data is available. The application and validity range of the graybox model will crucially depend on the number of different operating points and the variance in the operating variables (set points).

For the soft-sensoring step, a simple surrogate model reflecting all necessary input and output streams of the process step to be modeled is included into the simulation model. For example, in case of generating a data-driven model for an extraction step a component split might be used as a simple surrogate model. In a second step variables of this simple model besides other operating variables of the rigorous part of the simulation model for the entire process (e.g. reflux ratios and heat duties of distillation columns) will be adjusted to each measured operating point to minimize a weighted sum of least squares between measured and simulated properties. For the example with an extraction step, the partition coefficients of the components will be the optimization variables besides other operating variables of all other process steps in the simulation model of the entire process.

After this soft-sensoring step for the set of operating points all inputs and outputs of the process step to be modeled are available. This data is at least fulfilling the heat and mass balances. Of course it is also possible to add additional knowledge. If for example for an extraction like mentioned above some partition coefficients are already known, they might be included in the simple model and do not have to be adjusted in the soft-sensoring step. After the soft-sensoring step having all input and output data at hand, it is possible to just focus on this data, to analyze it and to set up a data-driven model.

To support the user in the modeling step different methods have been implemented to analyze the data. This includes correlation analysis (Pearson and Spearman) to identify if linear correlations or monotonic relationships between potential model properties exist. A principal component analysis helps to identify how much of the data can be described by a linear model of the principal components. 2D projections together with a slider concept similar to the one described by Burger et al. (2014) to filter data is useful to identify trends.

The data-driven model for a set of selected inputs and outputs itself is defined by the user and might be either a parametric, empirical model or non-parametric like a neural network. Apart from the model itself, emphasis is put on judging its reliability. Therefore,

different options have been implemented: Cross-validation, confidence intervals of the estimated parameters and prediction errors. The models are automatically exported in a defined format so that they can be used as user-defined modules in the flowsheet-simulator together with the already existing process model.

The validity range of the data-driven model is described based on convex hulls (see e.g. Kahrs and Marquardt, 2008) and on statistical indicators like the prediction error. In our work, inputs are normalized and a function describing the distance of the center is generated. This function is exactly equal to zero at the convex hull, greater than zero outside and less than zero inside the convex hull. This function can easily be used directly or as part of a function for a constraint in optimization and ensures that the model will be used only inside or within a user defined percentaged extension of the validity range.

3. Graybox modeling for a Cumene process

For an application test an available simulation model for a cumene process (Asprion et al., 2016) has been used as a virtual plant. In contrast to the scheme shown in Fig. 1 the original process model included a tubular reactor consisting of ten segments with a known kinetic for the formation of cumene and the side product p-di-isopropyl-benzene (DIPB). This original model has been used to generate artificial plant data reflecting different combinations of operating variables covering a load range from approx. 68 to 115%. To this artificial data random noise has been added to produce data with standard deviation of 3% for flow (F), 0.01 bar for pressure (P), 1 K for temperature and 0.001 mol/mol for analytical (Q) measurements. An overview of the available process data range and the selected data points is shown in Fig. 2. The 20 operating points have been selected in order to cover a wide operating window.

The goal of the test was to identify a graybox process model including a data-driven model for the tubular reactor. Therefore, in the first step as a simple surrogate model a continuous stirred reactor including the two above mentioned reactions was selected. As sketched and described in Figure 1 besides the operating variables, the yields Y_1 and Y_2 of the two reactions and the heat flow Q were adjusted for each selected operating point.

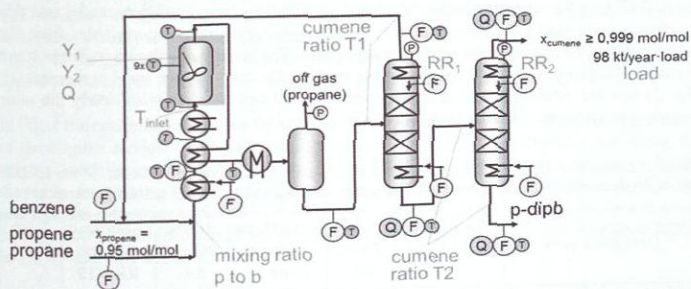


Figure 1: Available measurements and variables of the cumene simulation model for the graybox modeling of the reactor: In the soft-sensoring step for each operating point besides the operating variables (T_{inlet} , mixing ratio propene to benzene, cumene ratios T1 and T2, reflux ratio RR_1 and RR_2 , load) the yields Y_1 and Y_2 as well as the heat duty Q are adjusted to minimize the weighted sum of least squares between measured and simulated properties. Circles indicate measurements: F - mass flow, T - temperature, p - pressure, Q - quality here molar concentration.

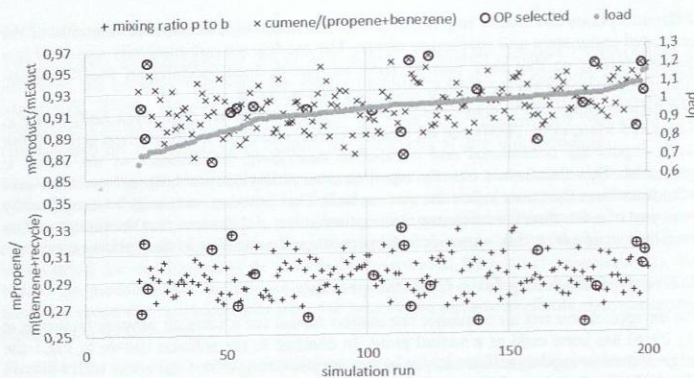


Figure 2: Available and selected artificial operating data of the cumene process. Selection was performed to achieve a high variance in the shown properties.

In Table 1 and Figure 3 the results of soft-sensing step are shown in comparison to the original operating conditions to generate the artificial operating data. As can be seen the data is identified with good agreement although there was noise added to the artificial data. Especially the large deviations in the yield are not caused by the method but by the measurement noise as has been verified using data without noise (results not shown here). The results for the yields are used to train a neural network consisting of sigmoid functions ($\alpha=2$) with one layer (no hidden layers). As input for the network only the molar flow and the molar concentrations of propene and benzene at the outlet have been used. Outputs which have to be described by the network are the yields for the cumene and the DIPB formation as well as the outlet temperature. Since the inlet temperature was nearly constant in the selected operating points ($342 \pm 2^\circ\text{C}$), it was neglected as input and set to 342°C . The neural network has been included in the simulation model and this graybox model was used in a first test to determine the operating variables from the measurements of the used set of operating points. The results are shown in Table 1 and Figure 3. As can be seen this model is able to describe the yields in good agreement (cf. Fig. 3) and the operating variables are identifiable from the data with nearly the same accuracy as in the previous soft-sensing step (see Tab. 1).

Table 1: Deviations from the original operating variables of the cumene process for the selected points. Results of soft-sensing step and adjustment with graybox model including neural network

Deviations in %		T_{inlet}	Mixing Ratio p to b	Reflux Ratio RR_1	Logarithmic Cumene Ratio T_1	Reflux Ratio RR_2	Logarithmic Cumene Ratio T_2	Load
Soft sensing	Average	0.	0.09	-0.24	0.37	1.73	-1.01	-0.73
	Standard	0.19	1.53	2.36	3.71	2.08	2.66	0.91
Neural Network	Average	-0.15	0.23	-0.01	-0.03	1.69	-1.08	1.21
	Standard	0.24	1.62	2.48	3.94	2.03	2.68	1.01

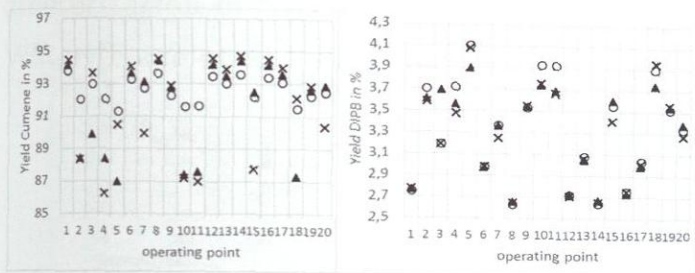


Figure 3: Results for the yields for the formation of Cumene and DIPB of the selected operating points: O original model, X soft sensing step and ▲ graybox model (including neural network) of the entire process with adjusted operating variables

Since the goal of the graybox modeling is the completion of the simulation model for process optimization, it is interesting to see the results in comparison to the reality or here for this artificial example in comparison to the original model (cf. Asprion et al., 2016: case with model VLE2; k1; k2).

For this reason a multi-criteria optimization considering the following objectives has been performed:

- Minimize operational expenditure (discounted for 10 y) in relation to the amount of cumene produced (OpEx)
- Minimize global warming potential (GWP)
- Minimize load
- Maximize capacity

The first two objectives are typical sustainability criteria while the last objectives ensure a simultaneous investigation of the minimally and maximally achievable capacity or load. The variables of the optimization are shown in Fig. 1 and there have been several constraints added to reflect the operating limits of the plant (for details see Asprion et al., 2016). In the graybox model a constant inlet temperature of 342 °C is assumed. In this application example the validity range of the model was not included as a constraint.

In Fig. 4 the optimization results for the graybox model are shown in comparison to those of the original model. The trend in OpEx vs load is a little bit different when using the graybox model compared to the original model. The differences in the trends are probably caused by the training set which included lower yields of cumene in the lower load range and also the negative deviations up to 4% (see Fig. 3) caused by the noise are more frequent in the lower load range. However, the maximal deviations in the objectives OpEx and GWP are only about 0.5 %.

To check the quality of the operating conditions (i.e. the optimization variables) resulting from the optimization of the graybox model, for five selected loads at minimal OpEx the variables from the graybox model were used as input for the original model for verification. The results are also shown in Figure 4 as filled, black circles. As can be seen the deviations are of the same order of magnitude. So the prediction of optimal operating conditions for the cumene process based on this simple graybox model is possible.

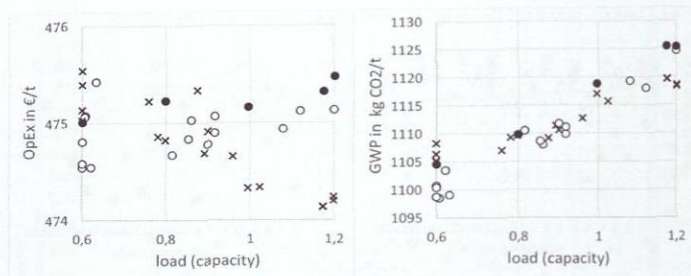


Figure 4: Comparison of the multi-criteria optimization results of the original model (O: cf. Asprion et al., 2016: Fig.7, VLE2; k1;k2) and the graybox model (X) using a neural network. ● Selected verification runs with the original model using operating variables from the optimization with the graybox model including a neural network.

4. Conclusions

Due to a missing model for certain process steps often process simulations are incomplete and therefore cannot be used for optimization of the entire process. The development of graybox models based on available operating data helps to overcome these limitations. The systematic implementation of tools to support the setup of graybox models into the workflow facilitates the use of such methods and gives new opportunities for the optimization of entire processes. The example of the cumene process has shown how this could help to identify optimized process conditions. The method and the workflow of graybox modeling as well as the results and their limitations will be discussed in the presentation.

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Paper X: Multi-Criteria Optimization for Parameterization of SAFT-Type Equations of State for Water [Forte et al., 2017a]

Multi-Criteria Optimization for Parameterization of SAFT-Type Equations of State for Water

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Finding appropriate parameter sets for a given equation of state (EoS) to describe different properties of a certain substance is an optimization problem with conflicting objectives. Such problem is commonly addressed by single-criteria optimization in which the different objectives are lumped into a single goal function. We show how multi-criteria optimization (MCO) can be beneficially used for parameterizing equations of state. The Pareto set, which comprises a set of optimal solutions of the MCO problem, is determined. As an example, the perturbed-chain statistical associating fluid theory (PC-SAFT) EoS is used and applied to the description of the thermodynamic properties of water, focusing on saturated liquid density and vapor pressure. Different options to describe the molecular nature of water by the PC-SAFT EoS are studied and for all variants, the Pareto sets are determined, enabling a comprehensive assessment. When compared to literature models, Pareto optimization yields improved models. © 2017 American Institute of Chemical Engineers AIChE J, 64: 226–237, 2018

Keywords: PC-SAFT, multi-criteria optimization, pareto optimization, parameter estimation, water

Introduction

Most applications in chemical engineering require an accurate description of more than one physical property. The development of physical property models for the simultaneous description of different physical properties is, however, not a simple task. The model adjustments to different physical properties are in conflict, as the optimal description of one property will usually not coincide with that for another property. Of course, for a truly ideal model, there would be no such conflict, but in reality, it is there for many reasons, among which is the unavoidable simplification of the real world by the model.

Already the definition of optimality is not trivial in the case of conflicting objectives. Leaving aside the problem of the ambiguity of defining goal functions and assuming that these are given for the different objectives, there will usually be no single optimal model, but rather a set of optimal models which represent best compromises between the different goals. This is well known to developers of thermodynamic models: once a certain stage of the modeling process is reached, further improvements in one objective are only possible at the expense of a deterioration in others.

The approach to find best compromises in a multi-objective or multi-criteria optimization (MCO) problem dealing with conflicting objectives is known as Pareto optimization, after the Italian economist Pareto.¹ A Pareto-optimal solution of such a problem is one for which an improvement of any of the objectives is not possible without worsening at least one other objective. The set comprising all these solutions is the Pareto set, often referred to as the Pareto frontier of the MCO problem.

The use of MCO has received considerable attention in recent years in different areas of chemical engineering such as process design, operation and control.^{2–5} There are many methods available for solving MCO problems and many of them involve the optimization of a “scalarization” function, or a function of the original objectives, by a suitable single-criteria optimization technique (SCO). A series of such SCO problems will have to be solved to find the Pareto-optimal solutions. The classical approach uses a weighting scalarization approach, where the objectives are combined based on certain weighting factors, which have to be chosen in advance. The difficulty in the task is to define a systematic and efficient way to define those weights. Different weighting approaches can be found in the literature, such as the so-called weighted sum, the weighted global criterion, the weighted product and the exponential weighted.⁶ Other common classical approaches are the ϵ -constraint, where the MCO problem is converted into an SCO only for one objective and the rest are treated as constraints, and goal programming methods, where the total deviation from goals defined for each objective is optimized. Other

Additional Supporting Information may be found in the online version of this article.

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methods make use of stochastic optimization techniques including evolutionary approaches, such as genetic algorithms, swarm approaches and adaptations of simulated annealing.^{6–8} In contrast to deterministic approaches, stochastic methods do not require gradient information. These approaches have the common characteristic of not requiring to solve a sequence of SCO problems, and are insensitive to the structure of constraints and objective functions. They may however sample large areas of the search space and therefore can be computationally expensive.^{6–8}

The classical method for parameterizing thermodynamic models remains the use of single-objective optimization techniques.^{9–11} The different objectives are weighted and lumped into one goal function which is then minimized, yielding a single optimal model parameter set. MCO has however recently been used for parameterizing force fields to describe thermodynamic properties of fluids^{12–14} and there is a work on the application of MCO to parameterizing an excess Gibbs free energy model.¹⁵

The present work is, to the best of our knowledge, the first application of MCO to parameterizing equations of state. Equations of state are important tools for describing properties of fluids and widely used in chemical engineering and other fields. The accuracy of the description of the fluid properties by an equation of state (EoS) crucially depends on its parameterization. The methodology presented here is also interesting for comparing different equations of state or molecular descriptions. As an example, we use the perturbed-chain statistical associating fluid theory (PC-SAFT),^{16,17} which is one of the different flavors of the statistical associating fluid theory (SAFT),^{18,19} for reviews see Refs. 20–24. In PC-SAFT the molecules are modeled as chains of dispersive spherical segments with optimal sites to mimic hydrogen-bonding interactions. An extension of the PC-SAFT theory incorporating a contribution accounting for dipolar interactions²⁵ is also considered here.

In the examples which we use to illustrate the MCO approach, the PC-SAFT EoS is used to model two properties of water, namely the saturated liquid density and vapor pressure. Water is characterized by a peculiar behavior,^{26,27} which is a consequence of the complex interplay of intermolecular forces that define its structure.^{28,29} The choice of an adequate physical model is therefore not trivial (see Refs. 30,31 for comprehensive reviews of water models appropriate for use in analytical theories), and understanding the influence of short-range attractive forces (hydrogen-bonding) and long-range electrostatic (primarily dipole–dipole) interactions on the structure and thermodynamic properties of water is essential.³² Accounting for molecular features such as the presence of a permanent dipole moment and the formation of hydrogen bonds obviously requires complex models with different parameters which have to be suitably determined.

We first discuss an adaptive sampling scheme to calculate a finite set of Pareto points the interpolation of which optimally approximates the Pareto set with a given accuracy, and describe a numerical algorithm which is particularly suited for the present application. The PC-SAFT formalism (and a polar extension of the EoS) is then briefly introduced, including the adjustable parameters that can be employed to model water. The objective functions, which are used in the following to parameterize PC-SAFT for water, are then defined and the adaptive MCO algorithm is carried out to determine the Pareto sets for different PC-SAFT molecular descriptions of water.

The results enable a comprehensive comparison and assessment of these variants. Finally we compare the Pareto-optimal solutions found in the present work with PC-SAFT water models from the literature and show that for each studied molecular variant, better models were found than those which were previously available.

Methodology

Pareto terminology

The dimension of the objective space is given by the number of conflicting objective functions which are used. A point in the objective space is characterized by the values of the different objective functions. The Pareto frontier represents the set of optimal solutions in the objective space. In our example, it shows how well the studied EoS can represent the studied set of properties. For each element in the objective space, there exists an element in the parameter space. The dimension of the parameter space is the number of parameters of the studied model and each element of the parameter space corresponds to a certain parameterization of the model. The Pareto frontier has an image in the parameter space which indicates where the optimal parameter sets lie. For parameters that have a physical meaning this is in itself interesting. As the relation between the points on the Pareto frontier and the points in the parameter space is known, the user can directly select a model of a desired quality (the compromise which is best suited for his application) in the objective space and get the corresponding parameters from the image of that point in the parameter space.

Approximation of the Pareto frontier

An adaptive algorithm to calculate the Pareto points is used. It has previously been applied to product and process design^{33–37} and parameter estimation for molecular simulations,¹⁴ and consists of a hybrid approach^{33,38} which aims at calculating a minimal number of Pareto points, the linear interpolation of which approximates the Pareto frontier within a predefined tolerance or quality. The hybrid method is based on a sandwiching algorithm to sample convex regions and a hyperboxing scheme to sample non-convex regions of the Pareto set. In both cases a scalarization of the objectives is performed to calculate each Pareto-optimal point by a single-objective optimization. Within the sandwiching scheme a weighted-sum scalarization is employed³⁹ whereas within the hyperboxing approach a Pascoletti-Serafini scalarization⁴⁰ is used. In this work only problems with two objectives are considered. The algorithm for this case, and assuming that the objectives are to be minimized, is briefly summarized here. For a more comprehensive explanation the reader is referred to the original works.^{33,38}

In broad terms the algorithm first uses the sandwiching approximation method to create successively inner and outer approximations to the Pareto frontier. The inner approximation is found from the bounding facets (line segments in two dimensions) of the convex hull (set of convex-linear-combinations) of the Pareto points. See Figure 1a) for a sketch: each facet coincides with the line segment connecting two neighboring points and the set determines the corners of the convex hull. The latter constitutes the approximation to the Pareto frontier sketched. The outer approximation is represented by supporting tangential hyperplanes (line segments in two dimensions) of the Pareto frontier at the calculated points.

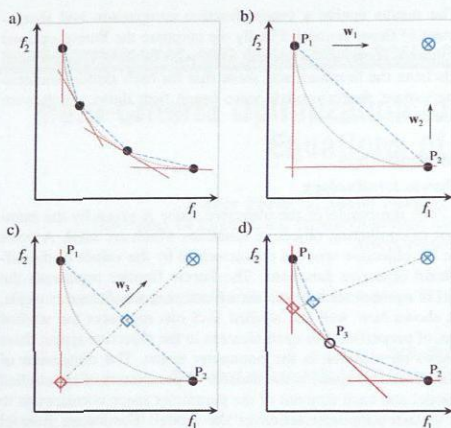


Figure 1. Sketch of the sandwiching method for two objectives f_1 and f_2 .

Filled circles denote Pareto points, dashed blue lines and solid red lines represent, respectively, the inner and the outer approximation, dotted gray curves are the (unknown) Pareto frontier, open black circles are new Pareto points calculated in the step represented, and open blue and open red diamonds are, respectively, the inner and outer intersection points used to compute the approximation quality. [Color figure can be viewed at wileyonlinelibrary.com]

Each new Pareto point is calculated using the weighted sum scalarization which, for objective functions denoted generically as f_i , is formulated as

$$\min_{\Omega} \sum_{i=1}^Q w_i f_i(\Omega), \quad (1)$$

where Ω represents the vector of parameters to be estimated, w_i are certain weights and Q is the dimension of the problem ($Q = 2$ in this case). The weight vectors coincide with the normals to the supporting tangential hyperplanes of the Pareto set at each calculated point. Pareto points are sequentially added as long as the difference between the outer and the inner approximation (the sandwich) is beyond the threshold fixed by the desired approximation quality. The progress of the algorithm, including the selection of weights and the calculation of the approximation quality is explained in more detail along the sketches shown in Figures 1a–b as follows:

1. Obtain the extreme compromises (Pareto points P_1 and P_2 in Figure 1b) optimizing the weighted sum with weight vectors $w_1 = (1, 0)$ and $w_2 = (0, 1)$, respectively. These two Pareto points are used to set the Nadir point, given as the worst value for each objective.
2. Find the inner and outer approximation to the Pareto frontier (see Figure 1b).
3. The Nadir point is employed as a reference to determine the quality of the current approximation σ_s . This is calculated as the ratio between the distances from the Nadir point (N) to the outer (O) and inner (I) intersection points (see Figure 1c) as $\sigma_s = ON/IN$. When more Pareto points

have been added, the ratio between outer and inner distances is computed for each facet. The maximum value is taken as the quality of the current approximation and the corresponding facet is selected for step 4.

4. If the quality of the current approximation is worse than the predefined tolerance, continue with step 5, otherwise stop.
5. Calculate a new Pareto point within the selected facet. This Pareto point will be determined in a further weighted-sum optimization using a weight vector w_3 (see Figure 1c) normal to the inner approximation. The facet will be replaced by two new facets around the Pareto point (cf. Figure 1d). The algorithm continues again with step 2.

Once the predefined approximation quality for the sandwiching is achieved, the convexity of the facets obtained is checked and non-convex regions are then treated within the hyperboxing scheme. Again new Pareto points are sequentially added as long as the difference between the outer and inner approximation to the non-convex regions is worse than the predefined approximation quality for this scheme. For an explanation of the convexity check and the hyperboxing scheme the reader is referred to the original works.^{33,38}

PC-SAFT EoS

In PC-SAFT the Helmholtz free energy is expressed as a sum of the following contributions,^{16,17} including an additional polar term A^{DP} ,²⁵:

$$A = A^{Ideal} + A^{HC} + A^{Disp} + A^{Assoc} + A^{DP}, \quad (2)$$

where A^{Ideal} is the free energy of an ideal gas, A^{HC} is the free energy of a hard-chain reference, A^{Disp} is the contribution due to dispersion interactions between the chain-like molecules and A^{Assoc} is the contribution due to association interactions. A^{DP} is incorporated following the work of Gross and Vrabec²⁵ to account for dipolar interactions among non-spherical molecules. During the execution of this work some inconsistencies in the formulation of the PC-SAFT association term in the literature were found. Some details about the particular formulation of the EOS used here are given in the Supporting Information.

An associating molecule is described within PC-SAFT by the number of segments m , the diameter of the segments σ , the energy of the dispersion interactions ϵ , the energy of the hydrogen-bonding interaction $\epsilon_{a,b}^{HB}$ between association site types a and b , and the reduced volume available for bonding $K_{a,b}^{HB}$ between those. The polar term does not necessarily require any additional parameter to be adjusted, since experimental values for the dipole moment μ can be used, following the original work.²⁵ Here we will consider models in which the dipole moment is neglected (i.e., the original PC-SAFT EoS is used), as well as scenarios where the dipole moment is set to experimental values (for the gas phase, as will be commented later) or used as an additional parameter.

Definition of the optimization problem

Two competing objective functions are used in the present work. They quantify deviations between the model and experimental data in two important properties, which are often used for estimating model parameter, namely the saturated liquid density ρ_{liq} and the vapor pressure p_v . The objective functions are defined as follows,

Table 1. Bounds Chosen for the PC-SAFT-Intermolecular Model Parameters (and the Polar Extension, Where Relevant) During the Optimizations

	m	$\sigma/\text{\AA}$	$\varepsilon/(k_B\text{K})$	$\varepsilon_{H,b}^{\text{HB}}/(k_B\text{K})$	$\kappa_{H,b}^{\text{HB}}$	μ/D
Lower bound	1.0	1.0	100	800	0.0001	1.8
Upper bound	2.5	4.0	600	2500 ^a	0.50	3.2

^aThis bound is increased to 2600 for the Pareto frontiers calculated assuming 2B and 3B models of water.

$$\delta_\rho(\Omega) = \frac{1}{N_p} \sum_{i=1}^{N_p} \left| \frac{\rho_{\text{liq}}^{\text{calc}}(T; \Omega) - \rho_{\text{liq}}^{\text{exp}}(T)}{\rho_{\text{liq}}^{\text{exp}}(T)} \right|, \quad (3)$$

and

$$\delta_p(\Omega) = \frac{1}{N_p} \sum_{i=1}^{N_p} \left| \frac{p_v^{\text{calc}}(T; \Omega) - p_v^{\text{exp}}(T)}{p_v^{\text{exp}}(T)} \right|, \quad (4)$$

where N_p is the number of experimental values of saturated liquid density and N_p of vapor pressure.

Analytical equations of state are known to fail reproducing the critical region due to the large-scale density fluctuations present there, which result in an overestimation of the predicted critical temperature and pressure. Non-analytical corrections to equations of state have been developed^{41–43} based on renormalization-group theory but such make the equation rather cumbersome and they are out of the scope of this work. We focus our efforts on determining models which are accurate for regions far enough from the critical region and to avoid any bias we restrict the calculation of deviations in Eqs. 3 and 4 to 95% of the experimental critical temperature. We choose to determine only models where the critical temperature is above the experimental value. For this purpose the constraint

$$T_c^{\text{exp}} - T_c^{\text{calc}}(\Omega) \leq 0, \quad (5)$$

is added to the optimization problem, where T_c^{exp} is the experimental critical temperature and T_c^{calc} is the calculated one.

An additional constraint is employed to restrict the maximum value of each objective function to 10%, i.e.,

$$\delta_\rho(\Omega) \leq 0.1, \quad (6)$$

and

$$\delta_p(\Omega) \leq 0.1, \quad (7)$$

as we are not interested in Pareto points with absurdly high deviations.

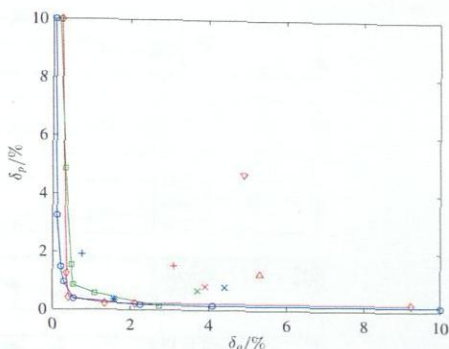


Figure 2. Deviations in saturated liquid density and vapor pressure for the Pareto frontiers calculated using 4C non-polar (blue circles), 2B non-polar (red diamonds), and 3B non-polar (green squares) water models.

The solid lines are a guide to the eye joining the Pareto points. The dispersed symbols are the corresponding values for the literature models following the same color code for the different schemes (triangle,⁵⁰ cross,⁵³ upside-down triangle,⁵² star,⁵¹ star⁵⁶). [Color figure can be viewed at wileyonlinelibrary.com]

Calculation details

The objective functions δ_ρ and δ_p (cf. Eqs. 3 and 4) for saturated liquid densities and vapor pressures, respectively, are in this work calculated through comparison with correlated data according to the IAPWS-IF97 formulation for water⁴⁴ in temperature intervals of 10 K in a temperature range from $T = 373$ to 613 K (i.e., ensuring temperatures below 95% the experimental critical temperature). The low temperature bound is chosen given the difficulty of physically-sound equations of state to reproduce with the standard state of the art developments the density anomaly of water.^{30,45–48} This approach is also employed to calculate the deviations in these properties for the literature models, for purposes of comparison (i.e., the same correlated data is used). As a second comparison, we also calculate deviations in the whole temperature range of vapor–liquid equilibrium, from $T = 273$ to 647 K, also in intervals of temperature of 10 K, and denote such

Table 2. PC-SAFT Literature Models for Water

Scheme	m	$\sigma/\text{\AA}$	$\varepsilon/(k_B\text{K})$	$\varepsilon_{H,b}^{\text{HB}}/(k_B\text{K})$	$\kappa_{H,b}^{\text{HB}}$	$\delta_\rho/\%$	$\delta_p/\%$	$\delta'_\rho/\%$	$\delta'_p/\%$	$\frac{T_c^{\text{exp}} - T_c^{\text{calc}}}{T_c^{\text{exp}}}/\%$	$\frac{p_c^{\text{exp}} - p_c^{\text{calc}}}{p_c^{\text{exp}}}/\%$	Reference
2B	1.0656	3.0007	366.51	2500.7	0.034868	5.31	1.26	8.93	1.69	7.77	65.97	50
2B	1.9599	2.362	279.42	2059.28	0.1750	3.10	1.52	5.64	1.20	6.79	53.76	53
2B	1.0953	2.8898	365.956	2515.67	0.034868	4.90	4.68	8.10	3.90	8.10	79.89	52
2B	1.3112	2.7613	372.37	2123.1	0.048987	3.91	0.82	7.59	0.98	8.35	66.82	51
4C	1.0656	3.0007	366.51	1800.0	0.01	2.92	45.79	5.35	39.12	2.32	84.28	57
4C	2.1945	2.229	141.66	1804.17	0.2039	0.75	1.91	3.04	2.04	5.16	42.70	53
4C	2.7500	2.0794	183.61	1354.1	0.3374	1.59	0.35	4.56	0.59	7.63	59.95	56
4C	1.5725	2.6270	291.13	1334.2	0.074347	4.40	0.80	8.59	0.90	10.20	87.06	51
3B	1.7960	2.4697	327.62	1558.4	0.068277	3.71	0.67	7.25	0.84	8.21	67.57	51
2B ^a	1.2255	2.7920	203.00	2406.7	0.07172	0.69	3.46	1.98	3.97	2.65	26.02	54
2B ^a	1.6963	2.5144	311.19	1469.1	0.0635	1.83	0.17	4.15	0.37	4.14	33.23	55

Their corresponding intermolecular model parameters are shown along with their deviations in saturated liquid density and vapor pressure, as well as their deviations in critical temperature and pressure. T_c^{exp} and p_c^{exp} are, respectively, the experimental critical temperature and pressure ($T_c^{\text{exp}} = 647.1$ K and $p_c^{\text{exp}} = 22.1$ MPa⁵⁰). k_B is Boltzmann's constant. Models are non-polar, unless specified otherwise.

^aPolar model obtained using the extension of Gross and Vrabec²⁵ with dipole moment $\mu = 1.85$ D.

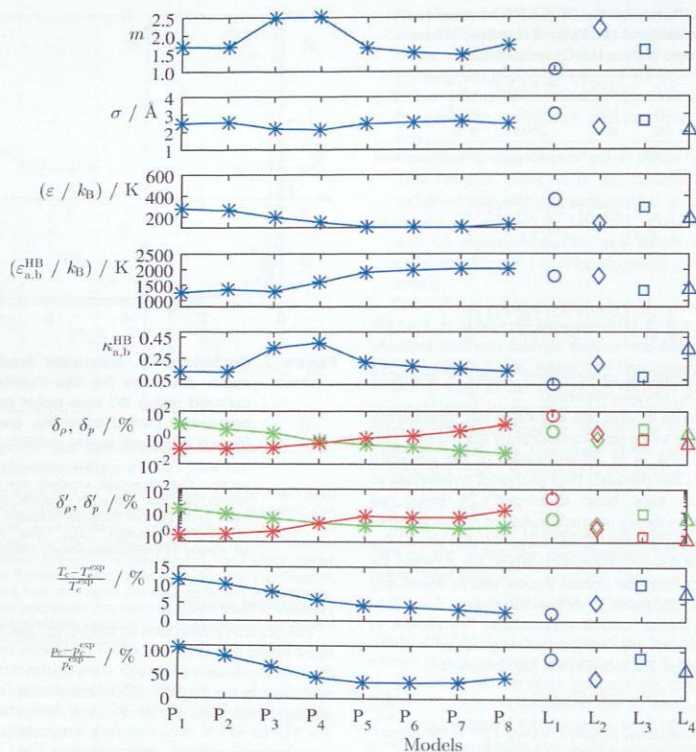


Figure 3. Intermolecular parameters, deviations in saturated liquid density and vapor pressure, as well as in the critical parameter values for 4C non-polar water models: P_i are the Pareto points calculated (star symbols connected by solid lines) and L_i are the literature models (circles,⁵⁷ diamonds,⁵³ squares,⁵¹ and triangles⁵⁶).

Deviations in vapor pressure are shown in red and in saturated liquid density in green. The solid lines are a guide to the eye joining the Pareto points. The parameter m is out of the bounds of the plot for the literature model⁵⁶ and therefore not represented. [Color figure can be viewed at wileyonlinelibrary.com]

deviations as δ'_ρ and δ'_p . The uncertainties of the IAPWS-IF97 formulation for water have been reported to be, in the region of interest, not higher than $\pm 0.05\%$ for both saturated liquid densities and pressures.⁴⁴

The bounds on the PC-SAFT parameters (and, where relevant, the dipole moment) employed during the optimizations carried out in this work are collected in Table 1.

The sandwiching and hyperboxing algorithm are carried out with an approximation quality of 1.01 and 1.09, respectively, for all the Pareto sets calculated. Other implementation details are found in the Supporting Information.

Application of MCO to Parameter Estimation

Review of literature models

An overview of the PC-SAFT models of water described in the literature is given in Table 2. It includes also the results of a comparison of the models with experimental data: deviations

are reported for saturated liquid densities and vapor pressures, calculated based on Eqs. 3 and 4 (cf. Section "Calculation details"), as well as for the predicted critical parameters. If the authors present more than one model, only that with the lowest deviation is discussed here. As a first observation, it can be seen water is in all studies modeled as a non-spherical core, i.e., m differs from 1.

Water associates through hydrogen-bonding interactions. This is accounted for in models of the SAFT family considering short-range association sites of two different types: one type mimics lone pairs of electrons (acceptor) and the other type mimics hydrogens (donor). Water has been typically modeled using two different association schemes. The first one is the so-called 4C association model, after the nomenclature of Huang and Radosz,⁴⁹ which assumes two association sites of each type; this model therefore enables that the molecule forms up to four hydrogen-bonds, as found in ice.²⁸ The second is the 2B association model (also after the same

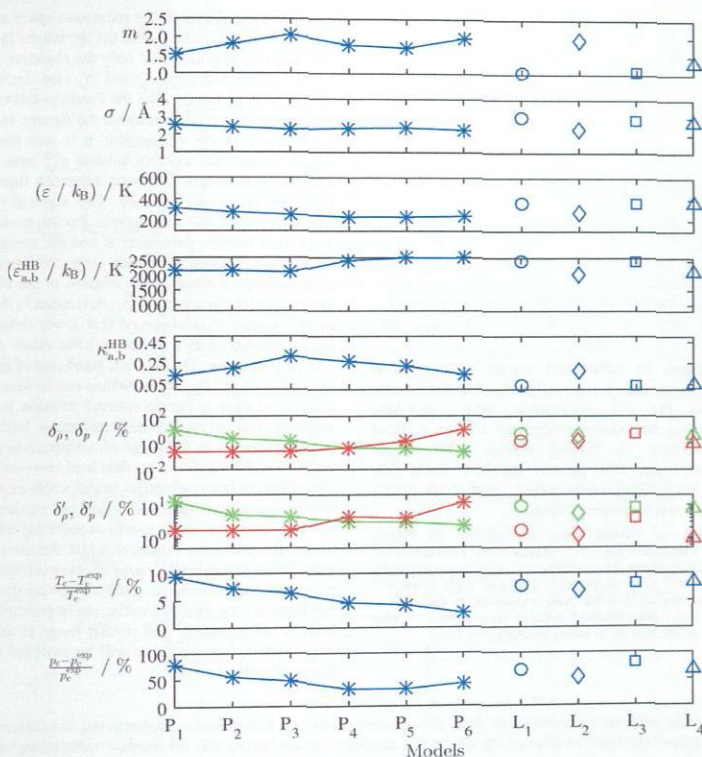


Figure 4. Intermolecular parameters, deviations in saturated liquid density and vapor pressure, as well as in the critical parameter values for 2B non-polar water models: P_i are the Pareto points calculated (star symbols connected by solid lines) and L_i are the literature models (circles,⁵⁰ diamonds,⁵³ squares,⁵² and triangles⁵¹). Deviations in vapor pressure are shown in red and in saturated liquid density in green. The solid lines are a guide to the eye joining the Pareto points. [Color figure can be viewed at wileyonlinelibrary.com]

classification scheme⁴⁹, which assumes one association site of each type. The PC-SAFT EoS has been applied to modeling water using either a 2B^{50–55} or a 4C^{51,53,56–58} association scheme. Although less frequent, a three-site model denoted as 3B⁴⁹ has also been used in the literature⁵¹ (see Table 2).

Water molecules possess a considerable dipole moment. The value of the dipole moment of water in the gas phase has been determined experimentally to be $\mu = 1.86$ D.^{59,60} It is known that the dipole moment is larger in condensed phases, for which values ranging from $\mu = 2.0$ D to $\mu = 3.0$ D are reported for water by different theoretical studies and extracted from X-ray data.^{61,62} There are two models in the literature^{54,55} that have also considered the dipolar nature of water through the extension of PC-SAFT of Gross and Vrabec.²⁵ In both studies, a 2B association site model and a dipole moment of $\mu = 1.85$ D are employed (cf. Table 2).

To obtain the parameters of their water models, all different authors followed a similar strategy. In general they employed saturated liquid densities and vapor pressures and one included also mole fractions of non-associated molecules.⁵⁶ In the work

of Niño-Amézquita et al.⁵⁷ the model obtained was a posteriori successfully tested against IR spectroscopy data on the mole fraction of non-associated molecules as well as surface tension data and second derivative properties.⁵⁸ In a number of works a temperature range from about 273 to 640 K^{50,53,54} was used in the parameter estimation. Smaller temperature ranges were used in the work of Aparicio and Hall,⁵¹ from 273 to 634 K, and Cameretti et al.,⁵² from 278 to 393 K. In the rest of studies^{55–57} the temperature range was not specified.

Models for water using other variants of the original PC-SAFT EoS, such as the simplified PC-SAFT^{63–65} the group-contribution polar GC-PPC-SAFT EoS,⁶⁶ or other polar versions⁶⁷ are not discussed here.

Results

Non-polar models using different association schemes

Pareto-optimal solutions have been calculated (see the Supporting Information for implementation details) for the three

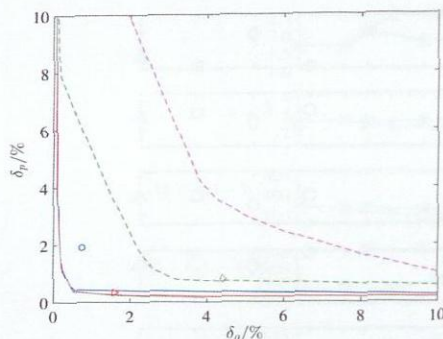


Figure 5. Deviations in saturated liquid density and vapor pressure for the Pareto frontiers calculated for 4C non-polar water models restricting the over-prediction of the critical temperature to values below 0.5% (pink dashed line), 2% (green dashed line), 5% (blue line), 7.5% (red line), and 10% (gray line) the experimental one.

The solid (or dashed) lines are joining the Pareto points, which are here not represented. Literature 4C models are shown for comparison with open symbols: blue circle,⁵⁵ gray diamond,⁵¹ and red right triangle.⁵⁶ Following the same color code according to their proximity to the experimental critical temperature. [Color figure can be viewed at wileyonlinelibrary.com]

association schemes used for water in the literature (i.e., 4C, 2B, and 3B) using the objective functions defined in Section "Definition of the optimization problem." In Figure 2 the objective space of these Pareto frontiers is plotted along with the values for the literature models (note that one of the literature models, leading to high deviations in pressure, has been omitted from the graph for the purposes of plotting within a small scale). As seen the Pareto frontiers calculated present a sharp knee (the strong curvature near the origin) and relatively large almost linear parts in which one objective can be improved at practically no cost. It is seen that some of the 4C literature models lead to deviations that are close to the Pareto frontiers calculated, but in general none of the literature models appears to be in the Pareto-knee of the frontiers calculated. This may be due to a different definition of objective functions, which are often only vaguely specified. Comparing the three Pareto frontiers it is possible to see that the three types of models lead to similar deviations. The 3B association scheme yields, however, slightly poorer results than the other two models in the region of interest (i.e., the Pareto-knee). 4C models may lead to lower δ_{ρ} values if the description of vapor pressures is compromised. The optimal 4C and 2B models in the region of interest (the Pareto-knee) are however equivalent. From that perspective, it can be concluded that modeling water as either a four associating-site model or as a two associating-site model leads to practically no differences if the aim is to minimize the deviations of both saturated liquid density and vapor pressure.

The Pareto-optimal solutions for the 4C and 2B schemes are analyzed in more detail in Figures 3 and 4. In these figures, for

each Pareto point both the parameter space and the objective space are plotted, along with the deviations in the critical temperature and pressure. Not only the objective functions δ_{ρ} and δ_p are given but also δ'_{ρ} and δ'_p (see Section "Calculation details"). A comparison of the Pareto points to the existing literature models is also included in the figures. In Figure 3, which corresponds to the 4C scheme, it is seen that both the chain length m and the bonding volume $\kappa_{a,b}^{HB}$ peak in the region in which small values for both saturated liquid densities and vapor pressures are attained. The segment diameter σ stays rather constant for the various Pareto models, whereas the dispersion-energy parameter ϵ and the energy of association $\epsilon_{a,b}^{HB}$ present monotonic trends along the Pareto frontier which may indicate a more direct relation of the effect of those on the trade-offs observed for the deviations in the two properties. In this regard it is observed that lower deviations in density are accompanied by a decrease in the values of the dispersion-energy parameter. On the right-hand side of Figure 3a comparison with all 4C literature models can be seen, confirming that there is always a Pareto-optimal solution leading to a more accurate estimation of both saturated liquid densities and vapor pressures in the range of temperatures used for the estimation. Some literature models lead however to slightly lower deviations in both properties in the whole saturation range, but this is not surprising considering our models were not fitted for this purpose. It is worth wondering whether achieving lower deviations in saturated liquid densities and vapor pressures in the temperature range of interest leads to higher deviations in the estimated critical temperature. The models rendered by the Pareto frontier are in principle seen to present critical temperatures in a similar range as those of the literature models, but this topic will be analyzed in more detail in the next section.

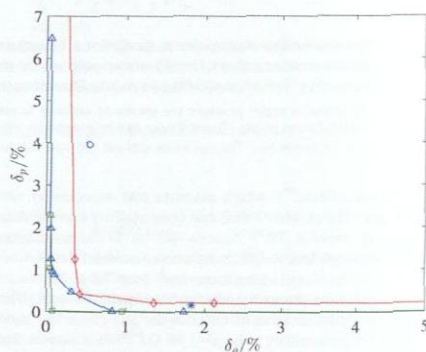


Figure 6. Deviations in saturated liquid density and vapor pressure for the Pareto frontiers calculated using 2B non-polar (red diamonds), 2B polar (blue triangles), and 2B polar fitting the dipole moment (green squares) water models.

The solid lines are a guide to the eye joining the Pareto points. The dispersed symbols are the corresponding values for the existing 2B polar literature models (circle,⁶⁴ star⁶⁵). [Color figure can be viewed at wileyonlinelibrary.com]

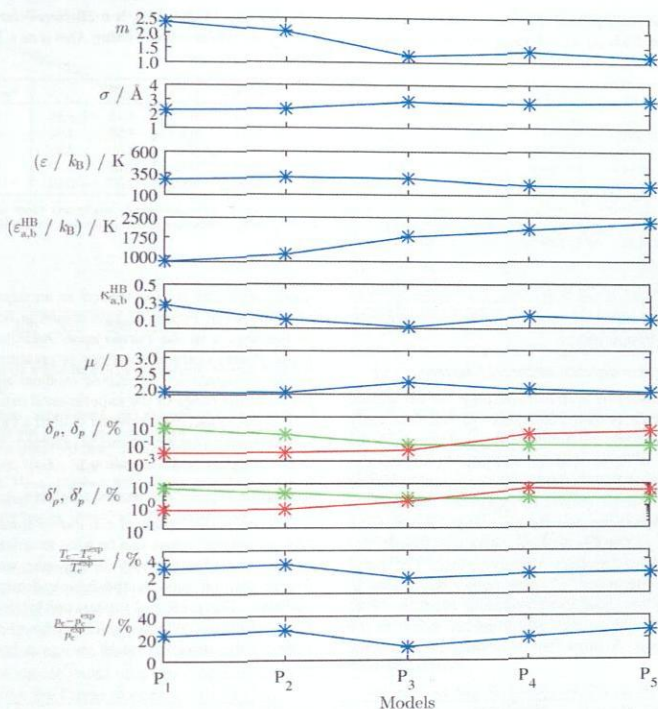


Figure 7. Intermolecular parameters, deviations in saturated liquid density and vapor pressure, as well as in the critical parameter values for 2B polar water models obtained fitting also the dipole moment: P_i are the Pareto points calculated (star symbols connected by solid lines).

Deviations in vapor pressure are shown in red and in saturated liquid density in green. The solid lines are a guide to the eye joining the Pareto points. [Color figure can be viewed at wileyonlinelibrary.com]

In Figure 4, which corresponds to the 2B scheme, it is seen that the trends in the parameters are similar to those shown in Figure 3 but the peaks in m and $\kappa_{a,b}^{HB}$ are smaller. The chain length and the bonding volume fluctuate less. The fact that in this case only two association sites are employed for water leads to models with higher energies of association compared to the 4C models. Pareto-optimal models are found which not only lead to lower deviations than the literature models in (δ_ρ, δ_p) , but also to lower deviations of the critical temperature and pressure and it is comforting to note that some of them further present lower deviations in the whole temperature range (i.e., δ'_ρ and δ'_p) than some of the literature models.

Similar trends are seen for the parameters of the 3B Models (cf. Supporting Information).

Optimization including the critical temperature

The definition of the objectives in Pareto optimization is flexible. Additional objectives, such as the deviation in the critical temperature, can always be added in a straightforward manner. An alternative to this approach is the consideration of requirements by introducing constraints. This is illustrated

here using the critical temperature calculated for 4C models as an example. The additional constraint included in the optimization problem is formulated as follows

$$\frac{T_c^{\text{calc}}(\Omega) - T_c^{\text{exp}}}{T_c^{\text{exp}}} \leq \epsilon. \quad (8)$$

Different values of ϵ are used, namely $\epsilon = 0.005, 0.02, 0.05, 0.075$, and 0.10 . The resulting Pareto frontiers are shown in Figure 5. The optimization of the critical temperature conflicts with the optimization of the original objectives (i.e., relaxing the constraint leads to Pareto frontiers with lower values for δ_ρ and δ_p) up to a certain limit, further than which the frontiers are seen to overlap. The constraint is active only up to that point. The Pareto frontiers calculated present a knee which is more or less beaked depending on the constraint. The literature models can be compared to the Pareto frontiers of the same color (corresponding to the same overestimation of the critical temperature). Among them that of von Solms et al.⁵⁶ is the one that approaches closer the corresponding Pareto frontier, but in general all the literature models are dominated by the corresponding Pareto frontiers (i.e., there are Pareto-optimal

Table 3. Selected Pareto-Optimal PC-SAFT Models: M_{4C} is a 4C Non-Polar Model, M_{2B} is a 2B Non-Polar Model, M_{P2B} is a 2B Polar Model, and M_{P2Bp} and M_{P4Cp} Are, Respectively, a 2B and a 4C Polar Model Using Also μ as a Parameter in the Optimization

Model	m	$\sigma/\text{\AA}$	$\varepsilon/(k_B K)$	$\varepsilon_{q,b}^{HB}/(k_B K)$	$\kappa_{q,b}^{HB}$	(μ/D)	$\delta_p/\%$	$\delta_p/\%$	$\delta'_p/\%$	$\delta'_p/\%$	$\frac{T_c - T_c^{calc}}{T_c^{exp}}/\%$	$\frac{p_c - p_c^{calc}}{p_c^{exp}}/\%$
M_{4C}	2.5000	2.1201	147.917	1581.945	0.3939	-	0.54	0.37	3.35	3.19	5.67	43.30
M_{2B}	1.7854	2.3609	233.787	2506.794	0.2637	-	0.41	0.43	3.10	4.36	4.60	32.12
M_{P2B}	2.2159	2.2396	214.485	1543.672	0.5000	1.8550	0.31	0.47	2.69	2.89	3.34	26.55
M_{P2Bp}	1.2256	2.8249	292.990	1760.237	0.0171	2.1870	0.07	0.02	2.20	1.57	1.76	12.26
M_{P4Cp}	1.1990	2.8792	285.368	1117.327	0.0144	2.2088	0.09	0.05	2.07	0.62	1.72	12.37

Their corresponding intermolecular model parameters are shown along with their deviations in saturated liquid density and vapor pressure, as well as their deviations in critical temperature and pressure. Note that these models have been obtained using a definition of the association contribution that is slightly different to the one used in typical PC-SAFT implementations (cf. Supporting Information).

solutions with lower values for both objective functions than those presented by the literature models for a given overestimation of the critical temperature).

Models considering the dipolar nature of water

A more detailed model of water accounting for the dipole moment of the molecule is now considered. In our first study the dipole moment is fixed to the experimental value in the gas phase ($\mu = 1.855 \text{ D}^{60}$), so that no additional parameter is introduced. The resulting Pareto frontier is compared to that of the corresponding non-polar model in Figure 6. The frontier for the polar model dominates that for the non-polar one, even though in the region of the Pareto knee, which is sharper for the non-polar case, both frontiers are very close. The polar models found in the literature^{54,55} show higher deviations in both properties than the best Pareto-optimal models. More details of the polar Pareto-optimal solutions are given in the Supporting Information. A third Pareto frontier in which the

dipole moment is also treated as an adjustable parameter is also shown in Figure 6. This results in further improvements in the region of the Pareto knee. Additional detail regarding those Pareto-optimal solutions is presented in Figure 7. The values obtained for the dipole moment along the frontier are found in the range of the experimental data for that property.

If a 4C association scheme is used a Pareto frontier rendering also very low deviations is obtained. The results are given in the Supporting Information.

Decision support in model selection

The objective space of the Pareto frontiers and the respective parameter values can be used to arrive at a more transparent choice of a model. Clearly one would focus only on Pareto-optimal models and ignore dominated models in the decision. The preferred models are located in the knee of the Pareto frontier. Which model to choose depends on the purpose of the model. One of the great benefits of the Pareto

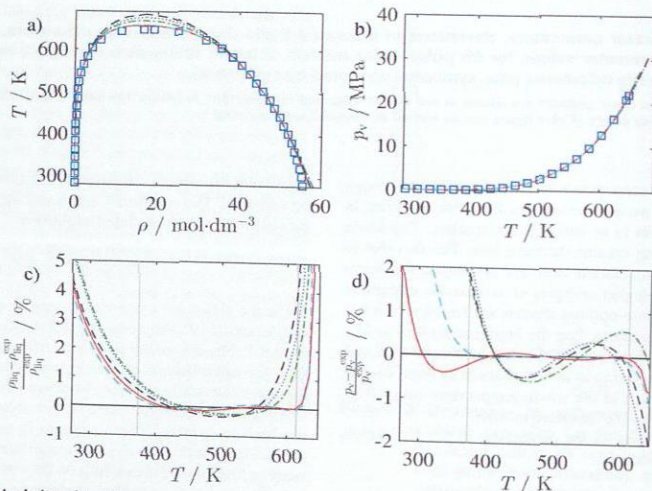


Figure 8. a) Saturated density, b) vapor pressure, c) deviation in saturated liquid density, and d) deviation in vapor pressure versus temperature for water.

The symbols correspond to correlated experimental data⁴⁴ while the curves correspond to the PC-SAFT (or its extended polar version) calculations for the models: M_{4C} (dashed black), M_{2B} (dotted blue), M_{P2B} (dash-dotted green), M_{P2Bp} (dashed light blue), and M_{P4Cp} (solid red) following the nomenclature specified in Table 3. The region between the gray lines in plots c) and d) indicates the temperature range used in the optimizations. [Color figure can be viewed at wileyonlinelibrary.com]

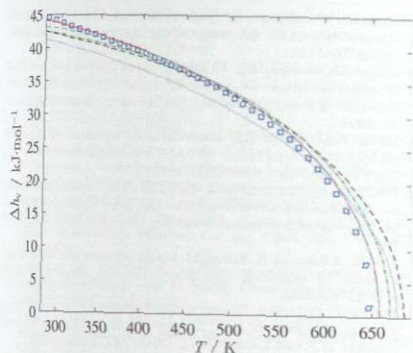


Figure 9. Enthalpy of vaporization of water versus temperature.

The symbols correspond to correlated experimental data⁴⁴ while the curves correspond to the PC-SAFT (or its extended polar version) calculations for the models: M_{4C} (dashed black), M_{2B} (dotted blue), M_{P2B} (dash-dot green), $M_{P2B\mu}$ (dashed light blue), and $M_{P4C\mu}$ (solid red) following the nomenclature specified in Table 3. [Color figure can be viewed at wileyonlinelibrary.com]

optimization is the knowledge of the trade-off one has to accept when using a certain model type. Knowing the Pareto frontier is also advantageous from the perspective that preferences and weights may change during the decision process when the decision maker sees all the available options. Eventually a model can be chosen based on a given scenario, but if the requirements change the Pareto frontier is still valid.

For the best Pareto frontiers obtained in this work, a Pareto-optimal model is selected and shown in Table 3 for comparison. Five models are presented: M_{4C} is a 4C non-polar model, M_{2B} is a 2B non-polar model, M_{P2B} is a 2B polar model, and $M_{P2B\mu}$ and $M_{P4C\mu}$ are, respectively, a 2B and a 4C polar model using also μ as a parameter in the optimization. The models have been selected based on visual inspection of the Pareto knees and with no preference given to minimizing one property over the second one. Overall it can be observed that the polar models obtained fitting also the dipole moment of water (i.e., $M_{P4C\mu}$ and $M_{P2B\mu}$) are the most spherical; the values for the dispersive energy are in a similar range for all models and higher differences are seen for the association energy, where the non-polar models are characterized by higher values (comparing within the same association scheme). It is also interesting to note that the polar models obtained using the dipole moment as an extra adjustable parameter present also rather lower values of the bonding volume, as is deemed consistent with the bonding constraints on which SAFT approaches are based.^{68,69} The agreement of these models with experimental data is depicted in Figure 8. On a first inspection of Figure 8a it is seen that most differences between the models are in the critical region, whereas at low temperature all models fail to reproduce the density anomaly of water. The latter is known to be a challenging feature not easily reproduced by models adjusted to capture the global behavior of this compound. The performance of the models to describe vapor pressure is not distinguished easily in Figure 8b. A closer look can be taken analyzing the deviations in Figures 8c, 8d; the region of

temperature used to adjust the parameters of the models is indicated by the vertical lines in these plots. The models $M_{P4C\mu}$ and $M_{P2B\mu}$ lead to low deviations in the whole temperature range considered in the estimation, and also to a lower over-prediction of the critical temperature (see Figure 8). The PC-SAFT EoS (and its polar extension) therefore demonstrates to be capable of providing a very good estimation of the VLE of water. Model $M_{P4C\mu}$ is also seen to outperform in the region of low temperatures, which was not included in the optimization problem, demonstrating good extrapolation capabilities of the equation. In particular, with the latter model it is remarkable that it is possible to achieve deviations lower than 0.1% for both liquid densities and vapor pressures (close to the uncertainties of the IAPWS-IF97 correlation) in the interval of temperatures from $T = 373$ to 613 K, and of about 2% for liquid densities and lower than 1% for vapor pressures from the triple point to the critical point (i.e., from $T = 273$ to 647 K).

As a final check the models are assessed in the prediction of the enthalpy of vaporization. This is shown in Figure 9. Overall all models are seen to provide a good description of this property, even though they were adjusted to reproduce saturated liquid densities and vapor pressures. Expressed in MCO terminology, the objective of minimizing the deviations in the enthalpy of vaporization is not conflicting with the two objectives used in the fit. On the other side, the good representation of this property could be expected given the fact that the models were also seen to provide a good description of saturated gas densities. The best description is again provided by model $M_{P4C\mu}$ over all the temperature range, confirming the enhanced performance of this model.

Conclusions

We present the first study on the application of MCO based on the determination of Pareto sets in the field of parameter estimation for equations of state. An adaptive hybrid algorithm combining a sandwiching and a hyperboxing technique is employed and the capabilities of the methodology are illustrated using PC-SAFT models of water as an example. Pareto-optimal solutions for PC-SAFT models with different level of detail in the description of the molecular characteristics of water are determined and compared to models that were published in the literature. New water models which lead to an improved agreement in the description of both saturated liquid densities and vapor pressures of water in comparison with existing ones are found. The overview which is obtained from inspection of the Pareto sets shows that PC-SAFT models with a four association-site scheme and those with a two association-site scheme lead to only minor differences in their capabilities to describe the present objectives. Accounting for the permanent dipole of the molecule through the incorporation of a polar contribution leads to a small improvement if the dipole moment is simply taken from literature and not adjusted. If however the dipole moment is included as an additional parameter in the optimization substantial improvements are achieved. In the latter case it is possible to obtain models which not only provide very low deviations for both equilibrium properties considered, but also lead to a reduced over-prediction of the critical temperature and an enhanced prediction of enthalpies of vaporization. In all studied cases Pareto-optimal models are found which are better than all previously published models of the same type in the range of temperatures of interest.

In future work it could be useful to extend the methodology to a three-dimensional (or larger) objective space, so that other properties could be included in the study, such as the degree of hydrogen-bonding considered by other authors.^{30,48,56}

In summary this work shows the usefulness of applying Pareto optimization in the field of parameterization of EoS and more generally in the development of thermodynamic models.

Acknowledgments

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Paper XI: Optimal Design of Laboratory and Pilot-Plant Experiments Using Multiobjective Optimization [Forte et al., 2017b]

Optimal Design of Laboratory and Pilot-Plant Experiments Using Multiobjective Optimization

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Supporting Information
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Performing an experimental design prior to the collection of data is in most circumstances important to ensure efficiency. The focus of this work is the combination of model-based and statistical approaches to optimal design of experiments. The knowledge encoded in the model is used to identify the most interesting range for the experiments via a Pareto optimization of the most important conflicting objectives. Analysis of the trade-offs found is in itself useful to design an experimental plan. This can be complemented using a factorial design in the most interesting part of the Pareto frontier.

Keywords: Design of experiments, Model discrimination, Multicriteria optimization, Parameter estimation, Pareto frontier

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1 Introduction

Reliable mathematical models are the key for the design, scale-up, and the optimization of processes. Even in the case of physically-sound high-fidelity models, assessing these against experimental measurements is an essential requirement for the model development. Models of practical engineering application invariably rely on a number of adjustable parameters which will require experimental data for their estimation and validation. Obtaining such experimental data is in most cases time-consuming and expensive. In this regard, the design of experiments (DOE) methodology plays a key role in planning the experiments in an efficient way, i.e., to achieve a maximum amount of information (information content) with the minimum number of experiments. An insight into the principles and strategies of experimental design can be found, e.g., in the review of Soravia and Orth [1] and in a historical review [2]. In particular, when a model is available, experimental design (known as model-based experimental design [3]) can provide a reliable and efficient tool to discriminate among different possible models and to minimize the uncertainty in the model-parameter estimates, i.e., to improve the statistical quality or parameter precision.

Optimal model-based experimental designs make use of the model equations and current parameter values to decide on the next experiment through evaluation of an objective function and application of an optimization technique. When the current estimate of model-parameters shall be improved, a typical objective function is the sensitivity of measured variables, such as conversion rates, concentration profiles, and temperatures, to the model parameter of inter-

est, e.g., stage efficiency, effective interfacial area, catalyst activity, activity coefficients at infinite dilution, and kinetic constants. In the case of model discrimination, the aim is to identify experimental conditions that maximize the divergence between the predictions of different models, e.g., an equilibrium-stage model vs a rate-based model or a plug-flow reactor model vs a model of a tubular reactor with nonideal flow behavior. A review on model discrimination techniques can be found in Schwaab et al. [4]. A different objective may also be finding experimental conditions that are not far from typical operation of the scaled-up plant or even reducing experimental uncertainties [5, 6].

In practical applications, there will be usually more than one quality measure or objective to be optimized in order to identify the most interesting range for experiments to be realized. Even when dealing with a parameter estimation problem, the most frequent scenario is that the sensitivity of one measured variable needs to be optimized to several parameters instead of only one single parameter. An example is a system exhibiting a complex reaction network; the determination of several kinetic constants in a laboratory

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experiment may be required. This problem is readily addressed by using a multiobjective optimization (MOO), also known as multicriteria optimization (MCO), and in a non-trivial case the objectives will be conflicting so that there will not be a single solution optimizing all.

The conventional approach to quantify the information content of an experiment in optimal experimental design is through information matrices, very often the Fisher information matrix (FIM) [7–9]. In principle, the elements of the information matrix constitute single objectives of what is in essence a MOO problem. The objective function that is typically maximized is, however, a scalar function of the information matrix, thus, the problem is ultimately approached using single-objective optimization. In the definition of the objective function, a certain optimality criterion is employed. Although attention has been paid to establishing different optimality criteria, differentiated by an alphabetic notation (the most common criteria are the A-, D-, and E-optimality criteria [9–11]), there is no best definition as in practice all of them show strengths and weaknesses [3], and they may also be conflicting with each other for nonlinear models [12]. For well-posed problems, this type of simplification to single-objective optimization by the use of the design criteria just mentioned may be useful to deal with a considerable number of parameters; for ill-posed problems, the direct application of these criteria can, however, lead to numerical instabilities and regularization techniques have to be applied [13].

Resorting to approach the optimal design of experiments (ODE) using a MOO technique enables the study of the trade-offs between conflicting objectives in a systematic way. The approach to find best compromises in a MOO problem dealing with conflicting objectives is known as Pareto optimization, after the Italian economist Pareto [14]. The solutions to these problems, called Pareto optimal or nondominated solutions, imply that the improvement of any of the objectives is not possible without worsening at least one other objective. The set comprising all these optimal solutions is the Pareto set, often referred to as the Pareto frontier of the MOO problem. Calculation of the Pareto frontier permits the user to have an overview of the design space, analyze trade-offs and make a judicious decision based on specific preferences.

In the field of chemical engineering, some studies focusing on model-based experimental design, i.e., design of experiments for improvement of parameter precision and/or model discrimination, using Pareto optimization started to appear in recent years [12, 15–24]. The trade-off between experimental effort and information gain is studied in [19] and [24]. Other investigations have focused on using MOO approaches to find trade-offs between maximizing the information content and minimizing parameter correlation [17, 18, 20]. Facing the simultaneous solution of model discrimination and improvement of model parameters through competing objective functions has also been the subject of some studies [21–23]. In spite of considering

MOO approaches, these investigations tackle parameter estimation through one (or more) of the traditional scalar functions of the FIM, and no effort has been made yet to use MOO in order to balance objectives resulting from practical applications and the information content. In summary, the application of MOO to ODE is still limited [3] and more effort is needed to exploit the potential of this technique to quantify different aspects of interest in further applications.

This work emphasizes the benefits of employing Pareto optimization in model-based experimental design of laboratory and pilot plant setups taken from the literature. Here, the different objectives of interest are not aggregated into one measure, but they are each individually considered. In particular, three case studies are discussed where the objectives of the ODE involve conflicting aims, such as reducing the uncertainty of estimated parameter values or of other estimated variables, operating close to typical process conditions, and discriminating between models. A key element in the strategy suggested in this work is the use of methodologies that allow a comprehensive analysis of the different trade-offs between the objectives involved. Based on this, a judicious decision on the DOE can be reached. It is important to emphasize that the strategy suggested is general and the objectives can be freely chosen by the user. Furthermore, this strategy supports including further constraints of, e.g., a pilot-plant setup (loading ranges, safety limits, etc.). This is advantageous compared to a pure statistical DOE which generally ignores any information contained in a model and therefore also suggests experiments that are probably less interesting. In the next section, the strategy followed is described and the different objective functions considered in this work are generically introduced. The application of the presented tools is then illustrated for three case studies with the intention not to determine strict designs but to give suggestions using straightforward and intuitive techniques for decision support in ODE.

2 Methodology

The strategy followed in this work to examine the different case studies consists of setting up the experiment design problem at hand as a MOO problem. In a first step, the multiple objectives are defined (see Sect. 2.1). In a second step, the set of Pareto-optimal solutions for the optimization problem are found with the MOO method described in Sect. 2.2. A sketch of a Pareto frontier for two objectives is represented in Fig. 1a. After analysis of the trade-offs found between the objectives of interest, the user can design an experimental plan which incorporates conditions spread out along the Pareto frontier. This selection is sketched along the Pareto frontier in Fig. 1a and in the optimization-parameter space in Fig. 1b. However, any model has admittedly certain uncertainty and the user can instead decide on sampling in the neighborhood of the conditions identified.

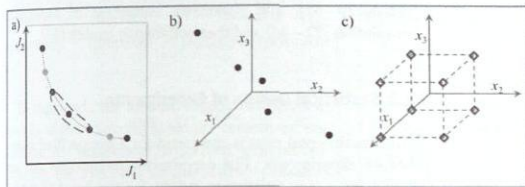


Figure 1. Sketch of a) a Pareto frontier computed for two objectives (J_1 and J_2), b) a suggestion for an experimental plan for three optimization parameters (x_1 , x_2 , and x_3) based on a selection of Pareto-optimal solutions, and c) an alternative experimental plan based on a factorial design. The dotted line represents the (unknown) Pareto frontier, the filled circles are Pareto-optimal solutions. The black circles represent a certain selection of Pareto-optimal solutions for a possible experimental plan. The dashed curve in (a) represents the region selected for a factorial design. The diamonds represent the corresponding experimental plan according to a full factorial design.

To this end, the user can alternatively compute an experimental plan with the statistical DOE approach described in Sect. 2.3 in a reduced range of experimental conditions which reflects such uncertainty. A sketch of the range chosen within the Pareto frontier is shown in Fig. 1a and the corresponding experimental design according to a statistical approach (a factorial design) in Fig. 1c. The latter is further explained in Sect. 2.3.

Simulations are carried out with the in-house process simulator CHEMASIM of BASF which provides functionalities for MOO, sensitivity studies, and ODE [25, 26].

2.1 Objective Functions

A number of different variables or parameters intervene in a given process model, as shown in Fig. 2. A set of experimental output variables y affected only by stochastic errors ε (these can include effects such as measurement errors on the output variable, the influence of other variables, and other sources of variation inherent in the process) which can be predicted by a nonlinear model $f(\theta, x)$ is assumed, so that

$$y = f(\theta, x) + \varepsilon \quad (1)$$

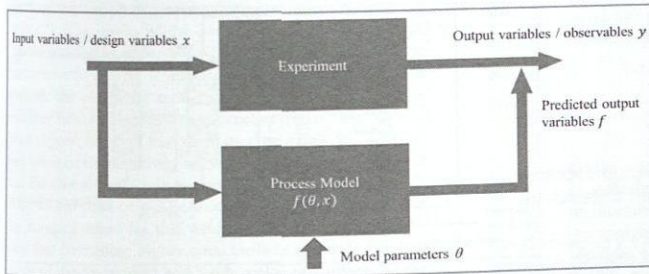


Figure 2. Variables and parameters intervening in a process model for the design of experiments.

dependent on a set of N_p model parameters θ and a set N_d of design or input variables x (a subset of which are used as optimization parameters). Different objective functions are considered in this work.

2.1.1 Sensitivity of the Output Variable y_i to a Model Parameter θ_j

The optimization problem for parameter estimation is based on maximizing the perturbation of the j th parameter on the prediction of the i th output. Usually, first derivatives are used in DOE to estimate local sensitivity. Here, averaged finite differences are used rather than derivatives to compute the sensitivity of the output variables with respect to the parameters. These are evaluated in this work using a factorial design analysis following [11]. Factorial design avoids correlation between parameters [27]. Other schemes to calculate so-called global sensitivities [26] are of course also possible.

In problems with a larger number of parameters, it is not meaningful to use each individual sensitivity as an objective. Therefore, a common practice when using first derivatives, i.e., the Jacobian matrix J , is to consider the FIM ($J^T J$) and to choose a scalar metric, e.g., A, D, E criteria, as objective. The present methodology allows also employing these conventionally used measures in model-based DOE [7–9], in this work evaluated for one design point. Another alternative extension of the applied approach for problems with many parameters is to consider a sensitivity matrix SM consisting of elements computed using global schemes. In that case, a similar approach is possible: the in general nonsquared matrix has to be converted into a squared information matrix (IM) by multiplication with its transpose, i.e.,

$$IM = SM^T SM \quad (2)$$

before applying the same scalar metrics as for the FIM, such as determinants or traces.

2.1.2 Closeness to Production Processes

In this case, the objective is minimizing the distance to the operation point characterizing the production process. For a chosen output variable y_i and a typical process value given by $\bar{y}_i$, an objective can be defined based on the squared difference, or for several variables the sum of the squared differences, as

$$J_1 = \sqrt{\sum_i (f_i(\theta, \mathbf{x}) - \bar{y}_i)^2} \quad (3)$$

The process value may in practice not be well specified, in which case this objective may be simply replaced by minimizing or maximizing a typical production objective, e.g., the costs or the profit of a plant.

2.1.3 Model Discrimination

The objective in this case consists of maximizing the difference in the predictions of the two models which, for N_m output variables y_i predicted by models I and II as f_i^I and f_i^{II} , can be expressed as

$$J_2 = \sqrt{\frac{1}{N_m} \sum_i (f_i^I(\theta, \mathbf{x}) - f_i^{II}(\theta, \mathbf{x}))^2} \quad (4)$$

2.1.4 Considering the Effect of the Uncertainty in Experimental Measurements on the Uncertainty of Estimated Values

Additional objective functions can be considered to find the operation conditions where the error propagation of experimental uncertainties to estimated variables is minimized. A variable g is assumed whose value is estimated out of a number N_e of experimental variables z_i which can be input or other output variables. Neglecting correlation or assuming the variables to be independent, the objective function has the form

$$J_3 = \sqrt{\sum_i \left(\frac{\partial g}{\partial z_i} \Delta z_i \right)^2} \quad (5)$$

where Δz_i is the experimental uncertainty of the measured variable z_i .

This list presents a variety of objective functions that are applicable for many ODE problems. The method presented in this work, however, is not limited to these objective functions. In principle, the user can define any objective function based on the given input variables, output variables, and/or model parameters.

2.2 Multiobjective Optimization

An adaptive method [25,28] based on a hybrid algorithm is employed here to calculate a minimal number of Pareto-optimal solutions to linearly approximate the complete Pareto frontier within a predefined tolerance. The methodology has previously been employed within product and process design and optimization

[25,26,29–31], and parameter estimation of molecular simulation [32–34] and thermodynamic models [35].

2.3 Statistical Design of Experiments

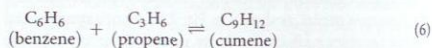
An experimental plan is computed for a prespecified number of experiments. The experimental conditions are set based on a factorial design matrix for the input variables chosen by the user. In the factorial design, the lower and upper limits of the input variables are identified by the user from the results of the MOO. A complete factorial design does not necessarily need to be set up, but the number of experiments is decided based on the estimated gain in relative variance that can be achieved (the accuracy in the estimated parameters can ideally, i.e., for linear models, be increased proportionally to the number of experiments [11,36]). The feasibility of the experimental plan can then be checked and an alternative feasible design can be suggested if necessary.

3 Case Studies

3.1 Cumene Process

The industrial process for the synthesis of cumene (isopropylbenzene) has been optimized by various research groups [37–39]. A simplified sketch with the main elements is shown in Fig. 3.

The production of cumene involves the reaction of benzene and propene in a gas-phase reactor at high temperature and pressure



and a sequential reaction between the unreacted propene and cumene to produce the by-product *p*-diisopropylbenzene

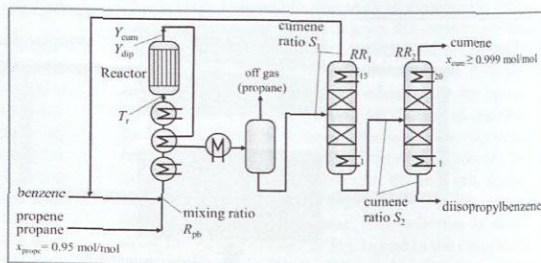
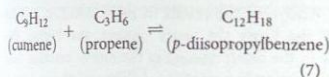


Figure 3. Simplified sketch of the process for the industrial production of cumene. The purities of the feed (x_{propene}) and product (x_{cumene}) are specified.



In this work, the forward kinetic constants k_1 and k_2 of these two reactions are considered uncertain. An experiment of interest aims at improving the precision of the kinetic constants while working close to typical process conditions and within the operating limits of the plant. Obviously, a production plant is not intended to be used for experimental investigations, but here it is used as an example for a mini- or pilot plant; the process might in principle be easily scaled down, which does not change the following principal findings. The task for improving the kinetic constants is therefore to maximize the sensitivity of appropriate measured variables to changes of the kinetic constants while not deviating far from realistic process conditions. The measured variables chosen to define the sensitivities are the yields of cumene (Y_{cum}) and p-diisopropylbenzene (Y_{dip}) in the reactor with regard to the amount of propane at the inlet, while typical process conditions are defined based on minimizing production costs, in particular operational expenditures divided by the amount of produced cumene. The forward kinetic constants (uncertain parameters) of the reactions described are varied by $\pm 10\%$ using a factorial design as sampling method. This uncertainty is chosen according to practical experience with kinetic models. The specific magnitude is only used here for demonstration purposes. Since the focus is not on partial derivatives as sensitivities, but finite differences or other global sensitivity measures are allowed [27], these rather large uncertainties can be handled. To reduce the complexity in the visualization of the results, the third objective (minimizing the production costs) is set as a constraint following an epsilon-constraint method [40]. The optimization parameters are the temperature of the reactor (T_r), the feed ratio (R_{pb}) of propene to benzene (both fed and recycled), the reflux ratios (RR_1 and RR_2), and the split ratios (S_1 and S_2 , see Fig. 3) in the distillation columns, and the load of the plant (capacity over a nominal value of 98 kt a^{-1}). The results of the MOO problem are shown in Fig. 4 for different upper-bound values of the constraint in the production costs (contour lines). For the conditions studied, the sensitivity measures are conflicting objectives and they further conflict with the cost objective (the calculations suggest however that there may be a limit in the conflict between the sensitivity measure for the yield of cumene and the cost objective). In general, the changes in the sensitivity of the yield of p-diisopropylbenzene are smaller, but the nominal values for this yield are also smaller. It can be seen that permitting higher costs leads in general to higher yields of the by-product and lower yields of cumene. These results are tabulated in the Supporting Information along with the parameter values. The MOO results obtained are

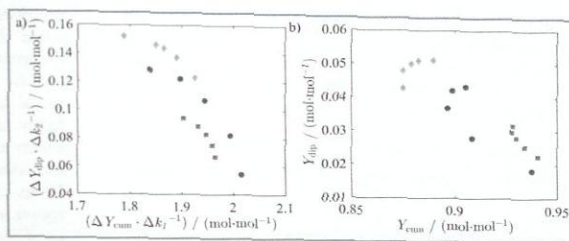


Figure 4. Pareto-optimal solutions for three values of the production costs (475 €t^{-1} as squares, 477 €t^{-1} as circles, and 479 €t^{-1} as diamonds) for the case study of the cumene process. Values of a) the two sensitivity measures chosen as objectives to be maximized (i.e., the sensitivity of the yield of cumene to changes in k_1 and that of the yield of diisopropylbenzene to changes in k_2) and b) the respective yields. The values are calculated using dimensionless kinetic constants.

in themselves an important result to design an efficient experimental plan. In fact, if the original ranges in which the parameters are allowed to vary during the optimizations and the final ranges where the Pareto-optimal solutions are located are compared (see Tab. 1), it can be seen that the range in the values of the parameter space has been considerably reduced. The range of possibilities where to conduct experiments is therefore reduced. Further reductions in the region of interest will depend on the user's preferences and an example as well as the proposed experimental design in that region is given in the Supporting Information, where the minimum number of experiments was chosen. As already mentioned, doubling the number of experiments can ideally, i.e., for linear models, halve the uncertainty of the measured variables.

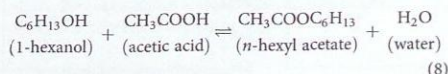
Table 1. Reduction in the original parameter space after Pareto optimization.

Parameter	Initially allowed range	Pareto-optimal range
T_r [K]	[340; 400]	[340.0; 341.1]
R_{pb} [mol mol ⁻¹]	[0.2; 0.9]	[0.44; 0.65]
RR_1 [-]	[0.1; 1]	[0.100; 0.201]
RR_2 [-]	[0.1; 1]	[0.285; 0.396]
$\ln(S_1)$ [-]	[-12; -1]	[-1.261; -2.480]
$\ln(S_2)$ [-]	[-12; -1]	[-9.277; -10.220]
Load [-]	[0.6; 1.2]	[0.600; 1.024]

3.2 Laboratory Reactor for Measuring the Kinetics for Reactive Distillation

The kinetics of a given reaction is often studied in the laboratory using standard procedures independently of the conditions at which the reaction occurs in the real process. Understanding the reaction kinetics at conditions close to

those used in the actual process may however be important for the reliable design and operation of the latter. In this example, the process of interest is a heterogeneously catalyzed reactive distillation (HCRD) where the reaction occurring is the esterification of *n*-hexyl acetate [41, 42]:



This type of reaction can be studied using standard laboratory reactors such as a batch reactor [43], a tubular reactor [44], or a continuous stirred tank reactor [41]. The drawback of all these reactors is, however, that the concentration of water is increasing when the reaction is progressing. In contrast, the concentration of water in the reaction zone of the HCRD column is typically very low because water, which is the lightest boiling component in this system, is continuously removed from the liquid phase. As the concentration of water has a significant impact on the catalyst [45, 46], a continuous stirred-tank reactor (CSTR) with partial evaporation of the liquid mixture is considered in this work that enables to measure the reaction kinetics while keeping the concentration of water in the liquid phase low, i.e., similar to that found in the reactive zone of the HCRD column. A sketch of this reactor setup is shown in Fig. 5. More details can be found in [41]. Compared to the standard CSTR without evaporation, the uncertainty in the determination of the reaction kinetics is larger with this reactor setup because of the propagation of the experimental error in the analysis of the composition and the mass flow rate in the vapor stream. Thus, important questions for the ODE are not only which experimental parameters should be chosen to maximize the sensitivity of a chosen observable (the mass fraction of hexyl acetate in the product) with respect to changes in the uncertain parameter (the forward kinetic constant of the reaction), but also which experimental parameters ensure a low concentration of water in the liquid phase (closeness to the process) and whether the gains in these two objectives justify the larger experimental complexity and the associated larger experimental error (details regarding experimental errors are given in [47]). The latter affect the uncertainty in the determination of the reaction kinetics, as mentioned, which is included as a third objective in the optimization task following Eq. (5). The optimization parameters are the feed mass flow rate (the composition is kept equimolar) and the heat duty. A constraint to limit the maximum flow rate of vapor is set. In Fig. 6, the results of the optimization with the three objectives of interest for the CSTR with partial evaporation are compared to the standard CSTR in which no vapor is produced, i.e., what would be a typical laboratory setup to measure the kinetics (see also the Supporting Information for the numerical values). It is clearly noticeable that with the CSTR with partial evaporation the sensitivity can be increased while at the same time the water content can be

decreased. Analyzing the results in more detail, it can be found that the lower the water content, the higher the uncertainty in the determination of the rate of reaction (see also the Supporting Information). In view of the results it would be advisable to work with evaporation and in a region of experimental conditions where an increase in sensitivity and a decrease in water content are achieved without excessively increasing the uncertainty of the reaction rate. Given the strong curvature of the Pareto frontier, this region where the sensitivity is maximized (indicated in Fig. 6 and also in the Supporting Information) may be a good suggestion for collecting experimental data. The proposed experimental design is given in the Supporting Information.

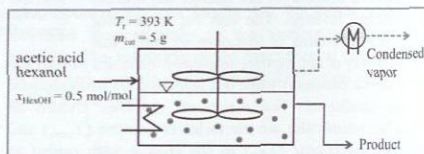


Figure 5. Simplified sketch of the CSTR with partial evaporation employed to measure the kinetics of the catalyzed esterification of *n*-hexyl acetate and values of the main design variables fixed during the optimizations.

3.3 Reactive Distillation Column

The conversion of the esterification reaction described in the previous case study is in principle limited by chemical equilibrium, but can be enhanced by integration of in situ separation. In such cases, the application of HCRD is beneficial. Recently, HCRD experiments were carried out with a laboratory setup that consists of a number of units combining a distillation tray and a catalyst-bed reaction section, so-called D+R trays [42]. The experimental setup is sketched in Fig. 7.

Two models are suggested [48, 49] to describe each of these D+R trays, as sketched in Fig. 8. The first one (Model A, shown in Fig. 8a) consists of a vapor-liquid equilibrium (VLE) stage with a superimposed CSTR, i.e., the reaction is kinetically controlled; in the second (Model B, shown in Fig. 8b) the arrangement of these two elements is sequential and the catalyst bed is modeled as a series of CSTRs to mimic the characteristics of a plug-flow reactor [49]. Discriminating between these two models is the motivation for an experimental design discussed in the following. With this aim, a first objective is built based on the sum of the differences in the predictions by the two models regarding the product composition at various measuring points along the column, which is set to be maximized so as to discriminate between the models. This objective, $\Delta x_{m, \text{HexAc}_i}^{A,B}$, is calculated considering a total of eight sampling points (one after each D+R tray the experimental setup consists of), following the

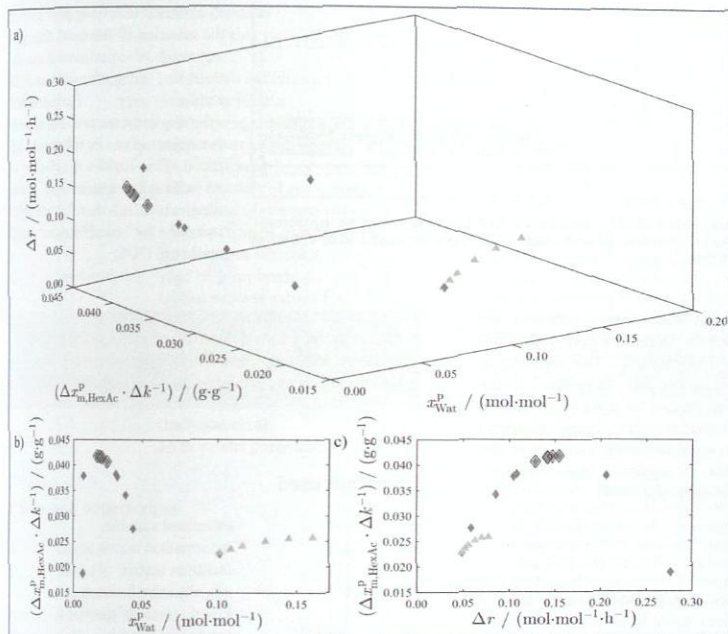


Figure 6. Pareto-optimal solutions for the case study of the laboratory reactor. Note that the sensitivity measured is maximized whereas the water content and the uncertainty of the reaction rate are minimized. The three objective functions are shown a) in a three-dimensional diagram, b) as a projection of the sensitivity measure versus the concentration of water, and c) as a projection of the sensitivity measure versus the uncertainty of the reaction rate. In all cases, results for the CSTR with partial evaporation are presented as diamonds and for the CSTR without evaporation as triangles. The region chosen for experimental design is indicated with black marker-edge colors. The values are calculated using a dimensionless kinetic constant.

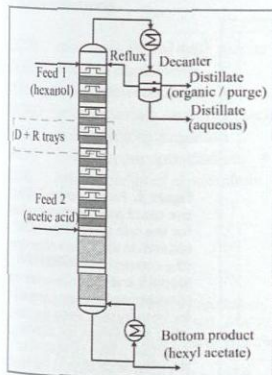


Figure 7. Sketch of the HCRD experimental setup.

real setup [42]; the difference in the compositions are summed as shown in Eq. (4) for the eight liquid streams. To be close to the real process conditions, the conversion X_{HexOH}^p in the benchmark model (Model B, developed by [49]) is set to be maximized as a second objective. The optimization parameters are the feed flow rate, the amount of catalyst, and the ratio of the reboiler duty to the feed flow. In Fig. 9a it can be seen that both objectives are conflicting and the Pareto frontier is nonconvex. If the aim is increasing the conversion, higher values for the mass of catalyst (Fig. 9b), the feed rate (Fig. 9c), and the heat to feed ratio (Fig. 9d) are favorable. By means of this ODE approach, experimental parameters can be identified for which the two models predict significant differences in the concentration profiles but where the closeness to the production process, i.e., the conversion of hexanol, is still high. The results are also tabulated in the Supporting Information. It has been noted that the conversion calculated with Model A follows the same trend and is in all cases higher than with

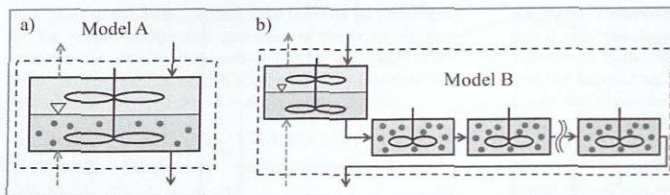


Figure 8. Schematic of the two models used to describe the D+R trays (delimited by the discontinuous lines) in the HCRD column: a) VLE stage with single CSTR superimposed and b) VLE stage with a number of sequential CSTRs.

Model B; on the other side, the purities achieved are throughout higher than 0.9 in mass fraction with both models (see the Supporting Information). The variation of the experimental input parameters that correspond to the Pareto frontier shown in Fig. 9a can be used as an experimental plan by itself; alternatively, as described above depending on the preferences of the user, a region of the Pareto frontier can be chosen, as suggested in the Supporting Information to carry out statistical DOE.

4 Conclusions

In this work, the capabilities of using MOO in the field of ODE for model development have been illustrated using three case studies as examples. Different types of conflicting objectives have been considered involving aims such as improving parameter precision, working at conditions close to the process, and discriminating between alternative models. It has been demonstrated that the usage of reliable tools to compute Pareto sets can provide the user with useful information to study the trade-offs between the pertinent objec-

tive functions and support him in the selection of the most interesting range of experimental conditions in a straightforward and intuitive way. Furthermore, arbitrary constraints of the experimental setup can be taken into account. This enables the design of an efficient experimental planning, which can then be complemented by combination with statistical DOE.

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Symbols used

g	[-]	estimated variable
$\mathbf{IM}$	[-]	information matrix
J	[-]	Jacobian matrix
f_n	[-]	n th objective function
k_i	[-]	kinetic factor of reaction i
$\dot{m}$	[kg h ⁻¹]	total mass flow
m_i	[kg]	mass of component i
N_d	[-]	number of design or input variables
N_e	[-]	number of experimental variables
N_m	[-]	number of output
N_p	[-]	number of model parameters
Q	[kW]	heat duty

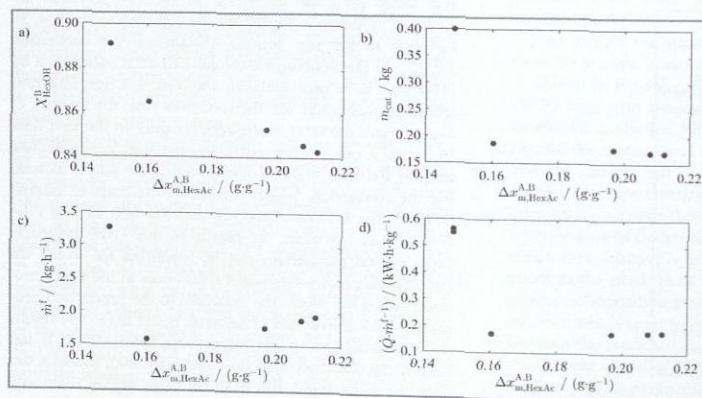


Figure 9. Pareto-optimal objective space and parameter values for the case study of the HCRD column. In a) the two objectives (the conversion obtained in Model B and the differences in concentration of hexyl acetate for both models along the column) are plotted; the second objective is plotted against b) the mass of catalyst, c) the feed flow rate, and d) the ratio of heat duty to feed flow.

r	[mol mol ⁻¹ h ⁻¹]	rate of reaction
$R_{p,b}$	[mol mol ⁻¹]	molar mixing ratio propene to benzene
RR_i	[-]	reflux ratio in column i
SM	[-]	sensitivity matrix
S_i	[-]	split ratio in column i
T_r	[K]	temperature of the reactor
x	[-]	set of design or input variables
x_i	[mol mol ⁻¹]	molar fraction of component i
X_i	[-]	conversion of component i
$x_{m,i}$	[g g ⁻¹]	mass fraction of component i
y	[-]	set of output variables
Y_i	[mol mol ⁻¹]	yield of component i
y_i	[-]	typical process value of y_i
z_i	[-]	input/output variable

Greek symbols

ε	[-]	stochastic error
θ	[-]	set of model parameters

Sub- and superscripts

A	Model A
B	Model B
cat	catalyst
cum	n -cumene
dip	p -diisopropylbenzene
f	feed stream
HexAc	n -hexyl acetate
HexOH	1-hexanol
p	product stream
prope	propene
Wat	water

Abbreviations

CSTR	continuous stirred-tank reactor
DOE	design of experiments
FIM	Fisher information matrix
HCRD	heterogeneously catalyzed reactive distillation
MCO	multicriteria optimization
MOO	multiobjective optimization
ODE	optimal design of experiments

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Paper XII: Decision Support for the Design and Operation of Water Supply Systems [Nowak et al., 2015]

Optimal Design of Laboratory and Pilot-Plant Experiments Using Multiobjective Optimization

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Supporting Information
available online

Performing an experimental design prior to the collection of data is in most circumstances important to ensure efficiency. The focus of this work is the combination of model-based and statistical approaches to optimal design of experiments. The knowledge encoded in the model is used to identify the most interesting range for the experiments via a Pareto optimization of the most important conflicting objectives. Analysis of the trade-offs found is in itself useful to design an experimental plan. This can be complemented using a factorial design in the most interesting part of the Pareto frontier.

Keywords: Design of experiments, Model discrimination, Multicriteria optimization, Parameter estimation, Pareto frontier

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1 Introduction

Reliable mathematical models are the key for the design, scale-up, and the optimization of processes. Even in the case of physically-sound high-fidelity models, assessing these against experimental measurements is an essential requirement for the model development. Models of practical engineering application invariably rely on a number of adjustable parameters which will require experimental data for their estimation and validation. Obtaining such experimental data is in most cases time-consuming and expensive. In this regard, the design of experiments (DOE) methodology plays a key role in planning the experiments in an efficient way, i.e., to achieve a maximum amount of information (information content) with the minimum number of experiments. An insight into the principles and strategies of experimental design can be found, e.g., in the review of Soravia and Orth [1] and in a historical review [2]. In particular, when a model is available, experimental design (known as model-based experimental design [3]) can provide a reliable and efficient tool to discriminate among different possible models and to minimize the uncertainty in the model-parameter estimates, i.e., to improve the statistical quality or parameter precision.

Optimal model-based experimental designs make use of the model equations and current parameter values to decide on the next experiment through evaluation of an objective function and application of an optimization technique. When the current estimate of model-parameters shall be improved, a typical objective function is the sensitivity of measured variables, such as conversion rates, concentration profiles, and temperatures, to the model parameter of inter-

est, e.g., stage efficiency, effective interfacial area, catalyst activity, activity coefficients at infinite dilution, and kinetic constants. In the case of model discrimination, the aim is to identify experimental conditions that maximize the divergence between the predictions of different models, e.g., an equilibrium-stage model vs a rate-based model or a plug-flow reactor model vs a model of a tubular reactor with nonideal flow behavior. A review on model discrimination techniques can be found in Schwaab et al. [4]. A different objective may also be finding experimental conditions that are not far from typical operation of the scaled-up plant or even reducing experimental uncertainties [5, 6].

In practical applications, there will be usually more than one quality measure or objective to be optimized in order to identify the most interesting range for experiments to be realized. Even when dealing with a parameter estimation problem, the most frequent scenario is that the sensitivity of one measured variable needs to be optimized to several parameters instead of only one single parameter. An example is a system exhibiting a complex reaction network; the determination of several kinetic constants in a laboratory

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experiment may be required. This problem is readily addressed by using a multiobjective optimization (MOO), also known as multicriteria optimization (MCO), and in a non-trivial case the objectives will be conflicting so that there will not be a single solution optimizing all.

The conventional approach to quantify the information content of an experiment in optimal experimental design is through information matrices, very often the Fisher information matrix (FIM) [7–9]. In principle, the elements of the information matrix constitute single objectives of what is in essence a MOO problem. The objective function that is typically maximized is, however, a scalar function of the information matrix, thus, the problem is ultimately approached using single-objective optimization. In the definition of the objective function, a certain optimality criterion is employed. Although attention has been paid to establishing different optimality criteria, differentiated by an alphabetic notation (the most common criteria are the A-, D-, and E-optimality criteria [9–11]), there is no best definition as in practice all of them show strengths and weaknesses [3], and they may also be conflicting with each other for nonlinear models [12]. For well-posed problems, this type of simplification to single-objective optimization by the use of the design criteria just mentioned may be useful to deal with a considerable number of parameters; for ill-posed problems, the direct application of these criteria can, however, lead to numerical instabilities and regularization techniques have to be applied [13].

Resorting to approach the optimal design of experiments (ODE) using a MOO technique enables the study of the trade-offs between conflicting objectives in a systematic way. The approach to find best compromises in a MOO problem dealing with conflicting objectives is known as Pareto optimization, after the Italian economist Pareto [14]. The solutions to these problems, called Pareto optimal or nondominated solutions, imply that the improvement of any of the objectives is not possible without worsening at least one other objective. The set comprising all these optimal solutions is the Pareto set, often referred to as the Pareto frontier of the MOO problem. Calculation of the Pareto frontier permits the user to have an overview of the design space, analyze trade-offs and make a judicious decision based on specific preferences.

In the field of chemical engineering, some studies focusing on model-based experimental design, i.e., design of experiments for improvement of parameter precision and/or model discrimination, using Pareto optimization started to appear in recent years [12, 15–24]. The trade-off between experimental effort and information gain is studied in [19] and [24]. Other investigations have focused on using MOO approaches to find trade-offs between maximizing the information content and minimizing parameter correlation [17, 18, 20]. Facing the simultaneous solution of model discrimination and improvement of model parameters through competing objective functions has also been the subject of some studies [21–23]. In spite of considering

MOO approaches, these investigations tackle parameter estimation through one (or more) of the traditional scalar functions of the FIM, and no effort has been made yet to use MOO in order to balance objectives resulting from practical applications and the information content. In summary, the application of MOO to ODE is still limited [3] and more effort is needed to exploit the potential of this technique to quantify different aspects of interest in further applications.

This work emphasizes the benefits of employing Pareto optimization in model-based experimental design of laboratory and pilot plant setups taken from the literature. Here, the different objectives of interest are not aggregated into one measure, but they are each individually considered. In particular, three case studies are discussed where the objectives of the ODE involve conflicting aims, such as reducing the uncertainty of estimated parameter values or of other estimated variables, operating close to typical process conditions, and discriminating between models. A key element in the strategy suggested in this work is the use of methodologies that allow a comprehensive analysis of the different trade-offs between the objectives involved. Based on this, a judicious decision on the DOE can be reached. It is important to emphasize that the strategy suggested is general and the objectives can be freely chosen by the user. Furthermore, this strategy supports including further constraints of, e.g., a pilot-plant setup (loading ranges, safety limits, etc.). This is advantageous compared to a pure statistical DOE which generally ignores any information contained in a model and therefore also suggests experiments that are probably less interesting. In the next section, the strategy followed is described and the different objective functions considered in this work are generically introduced. The application of the presented tools is then illustrated for three case studies with the intention not to determine strict designs but to give suggestions using straightforward and intuitive techniques for decision support in ODE.

2 Methodology

The strategy followed in this work to examine the different case studies consists of setting up the experiment design problem at hand as a MOO problem. In a first step, the multiple objectives are defined (see Sect. 2.1). In a second step, the set of Pareto-optimal solutions for the optimization problem are found with the MOO method described in Sect. 2.2. A sketch of a Pareto frontier for two objectives is represented in Fig. 1a. After analysis of the trade-offs found between the objectives of interest, the user can design an experimental plan which incorporates conditions spread out along the Pareto frontier. This selection is sketched along the Pareto frontier in Fig. 1a and in the optimization-parameter space in Fig. 1b. However, any model has admittedly certain uncertainty and the user can instead decide on sampling in the neighborhood of the conditions identified.

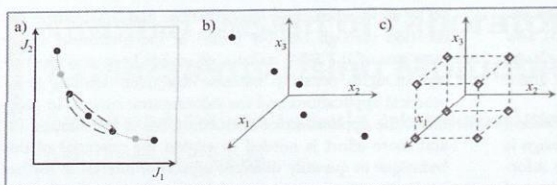


Figure 1. Sketch of a) a Pareto frontier computed for two objectives (J_1 and J_2), b) a suggestion for an experimental plan for three optimization parameters (x_1 , x_2 , and x_3) based on a selection of Pareto-optimal solutions, and c) an alternative experimental plan based on a factorial design. The dotted line represents the (unknown) Pareto frontier, the filled circles are Pareto-optimal solutions. The black circles represent a certain selection of Pareto-optimal solutions for a possible experimental plan. The dashed curve in (a) represents the region selected for a factorial design. The diamonds represent the corresponding experimental plan according to a full factorial design.

To this end, the user can alternatively compute an experimental plan with the statistical DOE approach described in Sect. 2.3 in a reduced range of experimental conditions which reflects such uncertainty. A sketch of the range chosen within the Pareto frontier is shown in Fig. 1a and the corresponding experimental design according to a statistical approach (a factorial design) in Fig. 1c. The latter is further explained in Sect. 2.3.

Simulations are carried out with the in-house process simulator CHEMASIM of BASF which provides functionalities for MOO, sensitivity studies, and ODE [25, 26].

2.1 Objective Functions

A number of different variables or parameters intervene in a given process model, as shown in Fig. 2. A set of experimental output variables y affected only by stochastic errors ε (these can include effects such as measurement errors on the output variable, the influence of other variables, and other sources of variation inherent in the process) which can be predicted by a nonlinear model $f(\theta, x)$ is assumed, so that

$$y = f(\theta, x) + \varepsilon \quad (1)$$

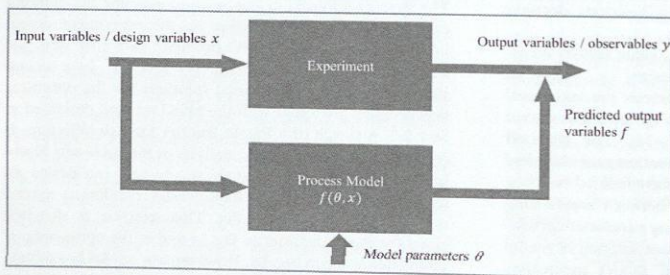


Figure 2. Variables and parameters intervening in a process model for the design of experiments.

dependent on a set of N_p model parameters θ and a set N_d of design or input variables x (a subset of which are used as optimization parameters). Different objective functions are considered in this work.

2.1.1 Sensitivity of the Output Variable y_i to a Model Parameter θ_j

The optimization problem for parameter estimation is based on maximizing the perturbation of the j th parameter on the prediction of the i th output. Usually, first derivatives are used in DOE to estimate local sensitivity. Here, averaged finite differences are used rather than derivatives to compute the sensitivity of the output variables with respect to the parameters. These are evaluated in this work using a factorial design analysis following [11]. Factorial design avoids correlation between parameters [27]. Other schemes to calculate so-called global sensitivities [26] are of course also possible.

In problems with a larger number of parameters, it is not meaningful to use each individual sensitivity as an objective. Therefore, a common practice when using first derivatives, i.e., the Jacobian matrix J , is to consider the FIM ($J^T J$) and to choose a scalar metric, e.g., A, D, E criteria, as objective. The present methodology allows also employing these conventionally used measures in model-based DOE [7–9], in this work evaluated for one design point. Another alternative extension of the applied approach for problems with many parameters is to consider a sensitivity matrix SM consisting of elements computed using global schemes. In that case, a similar approach is possible: the in general nonsquared matrix has to be converted into a squared information matrix (IM) by multiplication with its transpose, i.e.,

$$IM = SM^T SM \quad (2)$$

before applying the same scalar metrics as for the FIM, such as determinants or traces.

2.1.2 Closeness to Production Processes

In this case, the objective is minimizing the distance to the operation point characterizing the production process. For a chosen output variable y_i and a typical process value given by $\bar{y}_i$, an objective can be defined based on the squared difference, or for several variables the sum of the squared differences, as

$$J_1 = \sqrt{\sum_i (f_i(\theta, \mathbf{x}) - \bar{y}_i)^2} \quad (3)$$

The process value may in practice not be well specified, in which case this objective may be simply replaced by minimizing or maximizing a typical production objective, e.g., the costs or the profit of a plant.

2.1.3 Model Discrimination

The objective in this case consists of maximizing the difference in the predictions of the two models which, for N_m output variables y_i predicted by models I and II as f_i^I and f_i^{II} , can be expressed as

$$J_2 = \sqrt{\frac{1}{N_m} \sum_i (f_i^I(\theta, \mathbf{x}) - f_i^{II}(\theta, \mathbf{x}))^2} \quad (4)$$

2.1.4 Considering the Effect of the Uncertainty in Experimental Measurements on the Uncertainty of Estimated Values

Additional objective functions can be considered to find the operation conditions where the error propagation of experimental uncertainties to estimated variables is minimized. A variable g is assumed whose value is estimated out of a number N_e of experimental variables z_i which can be input or other output variables. Neglecting correlation or assuming the variables to be independent, the objective function has the form

$$J_3 = \sqrt{\sum_i \left(\frac{\partial g}{\partial z_i} \Delta z_i \right)^2} \quad (5)$$

where Δz_i is the experimental uncertainty of the measured variable z_i .

This list presents a variety of objective functions that are applicable for many ODE problems. The method presented in this work, however, is not limited to these objective functions. In principle, the user can define any objective function based on the given input variables, output variables, and/or model parameters.

2.2 Multiobjective Optimization

An adaptive method [25,28] based on a hybrid algorithm is employed here to calculate a minimal number of Pareto-optimal solutions to linearly approximate the complete Pareto frontier within a predefined tolerance. The methodology has previously been employed within product and process design and optimization

[25,26,29–31], and parameter estimation of molecular simulation [32–34] and thermodynamic models [35].

2.3 Statistical Design of Experiments

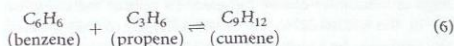
An experimental plan is computed for a prespecified number of experiments. The experimental conditions are set based on a factorial design matrix for the input variables chosen by the user. In the factorial design, the lower and upper limits of the input variables are identified by the user from the results of the MOO. A complete factorial design does not necessarily need to be set up, but the number of experiments is decided based on the estimated gain in relative variance that can be achieved (the accuracy in the estimated parameters can ideally, i.e., for linear models, be increased proportionally to the number of experiments [11,36]). The feasibility of the experimental plan can then be checked and an alternative feasible design can be suggested if necessary.

3 Case Studies

3.1 Cumene Process

The industrial process for the synthesis of cumene (isopropylbenzene) has been optimized by various research groups [37–39]. A simplified sketch with the main elements is shown in Fig. 3.

The production of cumene involves the reaction of benzene and propene in a gas-phase reactor at high temperature and pressure



and a sequential reaction between the unreacted propene and cumene to produce the by-product *p*-diisopropylbenzene

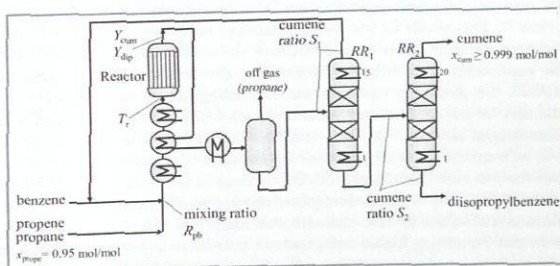
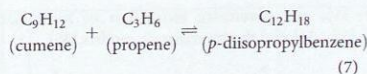


Figure 3. Simplified sketch of the process for the industrial production of cumene. The purities of the feed (x_{propene}) and product (x_{cum}) are specified.



In this work, the forward kinetic constants k_1 and k_2 of these two reactions are considered uncertain. An experiment of interest aims at improving the precision of the kinetic constants while working close to typical process conditions and within the operating limits of the plant. Obviously, a production plant is not intended to be used for experimental investigations, but here it is used as an example for a mini- or pilot plant; the process might in principle be easily scaled down, which does not change the following principal findings. The task for improving the kinetic constants is therefore to maximize the sensitivity of appropriate measured variables to changes of the kinetic constants while not deviating far from realistic process conditions. The measured variables chosen to define the sensitivities are the yields of cumene (Y_{cum}) and *p*-diisopropylbenzene (Y_{dip}) in the reactor with regard to the amount of propane at the inlet, while typical process conditions are defined based on minimizing production costs, in particular operational expenditures divided by the amount of produced cumene. The forward kinetic constants (uncertain parameters) of the reactions described are varied by $\pm 10\%$ using a factorial design as sampling method. This uncertainty is chosen according to practical experience with kinetic models. The specific magnitude is only used here for demonstration purposes. Since the focus is not on partial derivatives as sensitivities, but finite differences or other global sensitivity measures are allowed [27], these rather large uncertainties can be handled. To reduce the complexity in the visualization of the results, the third objective (minimizing the production costs) is set as a constraint following an epsilon-constraint method [40]. The optimization parameters are the temperature of the reactor (T_r), the feed ratio (R_{pb}) of propene to benzene (both fed and recycled), the reflux ratios (RR_1 and RR_2), and the split ratios (S_1 and S_2 , see Fig. 3) in the distillation columns, and the load of the plant (capacity over a nominal value of 98 kt a^{-1}). The results of the MOO problem are shown in Fig. 4 for different upper-bound values of the constraint in the production costs (contour lines). For the conditions studied, the sensitivity measures are conflicting objectives and they further conflict with the cost objective (the calculations suggest however that there may be a limit in the conflict between the sensitivity measure for the yield of cumene and the cost objective). In general, the changes in the sensitivity of the yield of *p*-diisopropylbenzene are smaller, but the nominal values for this yield are also smaller. It can be seen that permitting higher costs leads in general to higher yields of the by-product and lower yields of cumene. These results are tabulated in the Supporting Information along with the parameter values. The MOO results obtained are

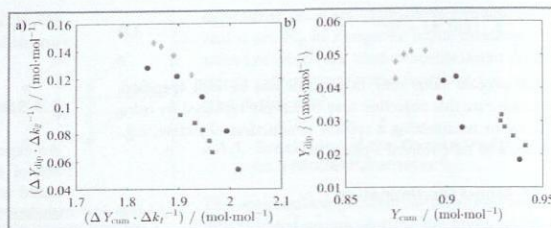


Figure 4. Pareto-optimal solutions for three values of the production costs (475 €t^{-1} as squares, 477 €t^{-1} as circles, and 479 €t^{-1} as diamonds) for the case study of the cumene process. Values of a) the two sensitivity measures chosen as objectives to be maximized (i.e., the sensitivity of the yield of cumene to changes in k_1 and that of the yield of diisopropylbenzene to changes in k_2) and b) the respective yields. The values are calculated using dimensionless kinetic constants.

in themselves an important result to design an efficient experimental plan. In fact, if the original ranges in which the parameters are allowed to vary during the optimizations and the final ranges where the Pareto-optimal solutions are located are compared (see Tab. 1), it can be seen that the range in the values of the parameter space has been considerably reduced. The range of possibilities where to conduct experiments is therefore reduced. Further reductions in the region of interest will depend on the user's preferences and an example as well as the proposed experimental design in that region is given in the Supporting Information, where the minimum number of experiments was chosen. As already mentioned, doubling the number of experiments can ideally, i.e., for linear models, halve the uncertainty of the measured variables.

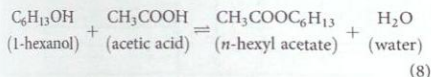
Table 1. Reduction in the original parameter space after Pareto optimization.

Parameter	Initially allowed range	Pareto-optimal range
T_r [K]	[340; 400]	[340.0; 341.1]
R_{pb} [mol mol $^{-1}$]	[0.2; 0.9]	[0.44; 0.65]
RR_1 [–]	[0.1; 1]	[0.100; 0.201]
RR_2 [–]	[0.1; 1]	[0.285; 0.396]
$\ln(S_1)$ [–]	[–12; –1]	[–1.261; –2.480]
$\ln(S_2)$ [–]	[–12; –1]	[–9.277; –10.220]
Load [–]	[0.6; 1.2]	[0.600; 1.024]

3.2 Laboratory Reactor for Measuring the Kinetics for Reactive Distillation

The kinetics of a given reaction is often studied in the laboratory using standard procedures independently of the conditions at which the reaction occurs in the real process. Understanding the reaction kinetics at conditions close to

those used in the actual process may however be important for the reliable design and operation of the latter. In this example, the process of interest is a heterogeneously catalyzed reactive distillation (HCRD) where the reaction occurring is the esterification of *n*-hexyl acetate [41, 42]:



This type of reaction can be studied using standard laboratory reactors such as a batch reactor [43], a tubular reactor [44], or a continuous stirred tank reactor [41]. The drawback of all these reactors is, however, that the concentration of water is increasing when the reaction is progressing. In contrast, the concentration of water in the reaction zone of the HCRD column is typically very low because water, which is the lightest boiling component in this system, is continuously removed from the liquid phase. As the concentration of water has a significant impact on the catalyst [45, 46], a continuous stirred-tank reactor (CSTR) with partial evaporation of the liquid mixture is considered in this work that enables to measure the reaction kinetics while keeping the concentration of water in the liquid phase low, i.e., similar to that found in the reactive zone of the HCRD column. A sketch of this reactor setup is shown in Fig. 5. More details can be found in [41]. Compared to the standard CSTR without evaporation, the uncertainty in the determination of the reaction kinetics is larger with this reactor setup because of the propagation of the experimental error in the analysis of the composition and the mass flow rate in the vapor stream. Thus, important questions for the ODE are not only which experimental parameters should be chosen to maximize the sensitivity of a chosen observable (the mass fraction of hexyl acetate in the product) with respect to changes in the uncertain parameter (the forward kinetic constant of the reaction), but also which experimental parameters ensure a low concentration of water in the liquid phase (closeness to the process) and whether the gains in these two objectives justify the larger experimental complexity and the associated larger experimental error (details regarding experimental errors are given in [47]). The latter affect the uncertainty in the determination of the reaction kinetics, as mentioned, which is included as a third objective in the optimization task following Eq. (5). The optimization parameters are the feed mass flow rate (the composition is kept equimolar) and the heat duty. A constraint to limit the maximum flow rate of vapor is set. In Fig. 6, the results of the optimization with the three objectives of interest for the CSTR with partial evaporation are compared to the standard CSTR in which no vapor is produced, i.e., what would be a typical laboratory setup to measure the kinetics (see also the Supporting Information for the numerical values). It is clearly noticeable that with the CSTR with partial evaporation the sensitivity can be increased while at the same time the water content can be

decreased. Analyzing the results in more detail, it can be found that the lower the water content, the higher the uncertainty in the determination of the rate of reaction (see also the Supporting Information). In view of the results it would be advisable to work with evaporation and in a region of experimental conditions where an increase in sensitivity and a decrease in water content are achieved without excessively increasing the uncertainty of the reaction rate. Given the strong curvature of the Pareto frontier, this region where the sensitivity is maximized (indicated in Fig. 6 and also in the Supporting Information) may be a good suggestion for collecting experimental data. The proposed experimental design is given in the Supporting Information.

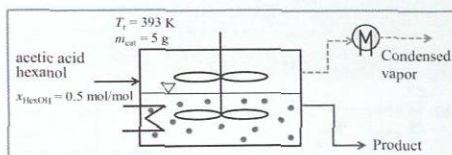


Figure 5. Simplified sketch of the CSTR with partial evaporation employed to measure the kinetics of the catalyzed esterification of *n*-hexyl acetate and values of the main design variables fixed during the optimizations.

3.3 Reactive Distillation Column

The conversion of the esterification reaction described in the previous case study is in principle limited by chemical equilibrium, but can be enhanced by integration of in situ separation. In such cases, the application of HCRD is beneficial. Recently, HCRD experiments were carried out with a laboratory setup that consists of a number of units combining a distillation tray and a catalyst-bed reaction section, so-called D+R trays [42]. The experimental setup is sketched in Fig. 7.

Two models are suggested [48, 49] to describe each of these D+R trays, as sketched in Fig. 8. The first one (Model A, shown in Fig. 8a) consists of a vapor-liquid equilibrium (VLE) stage with a superimposed CSTR, i.e., the reaction is kinetically controlled; in the second (Model B, shown in Fig. 8b) the arrangement of these two elements is sequential and the catalyst bed is modeled as a series of CSTRs to mimic the characteristics of a plug-flow reactor [49]. Discriminating between these two models is the motivation for an experimental design discussed in the following. With this aim, a first objective is built based on the sum of the differences in the predictions by the two models regarding the product composition at various measuring points along the column, which is set to be maximized so as to discriminate between the models. This objective, $\Delta_{m, \text{HexAc}}^{A,B}$, is calculated considering a total of eight sampling points (one after each D+R tray the experimental setup consists of), following the

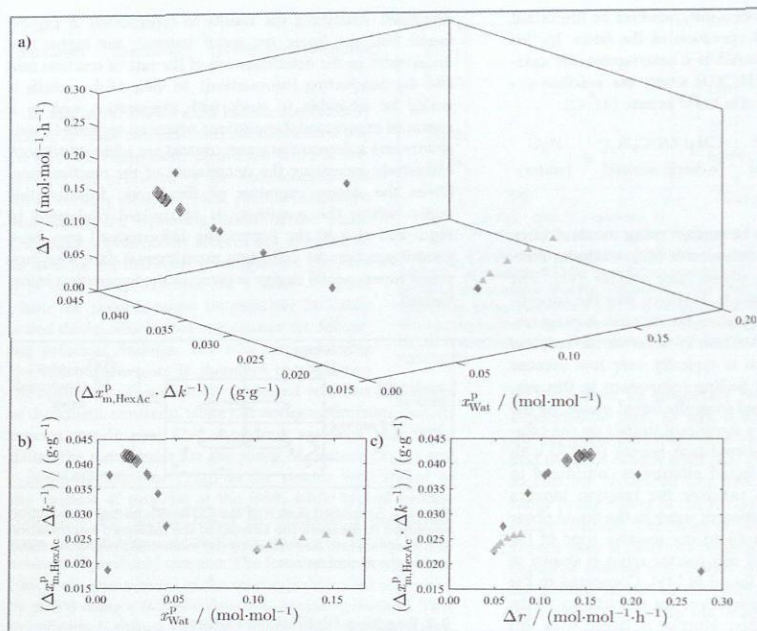


Figure 6. Pareto-optimal solutions for the case study of the laboratory reactor. Note that the sensitivity measured is maximized whereas the water content and the uncertainty of the reaction rate are minimized. The three objective functions are shown a) in a three-dimensional diagram, b) as a projection of the sensitivity measure versus the concentration of water, and c) as a projection of the sensitivity measure versus the uncertainty of the reaction rate. In all cases, results for the CSTR with partial evaporation are presented as diamonds and for the CSTR without evaporation as triangles. The region chosen for experimental design is indicated with black marker-edge colors. The values are calculated using a dimensionless kinetic constant.

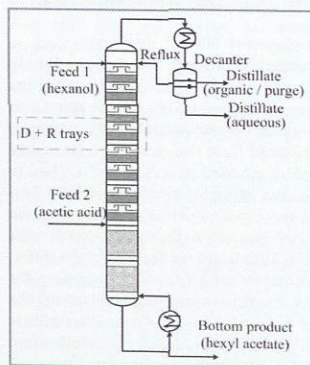


Figure 7. Sketch of the HCRD experimental setup.

real setup [42]; the difference in the compositions are summed as shown in Eq. (4) for the eight liquid streams. To be close to the real process conditions, the conversion X_{HexOH}^B in the benchmark model (Model B, developed by [49]) is set to be maximized as a second objective. The optimization parameters are the feed flow rate, the amount of catalyst, and the ratio of the reboiler duty to the feed flow. In Fig. 9a it can be seen that both objectives are conflicting and the Pareto frontier is nonconvex. If the aim is increasing the conversion, higher values for the mass of catalyst (Fig. 9b), the feed rate (Fig. 9c), and the heat to feed ratio (Fig. 9d) are favorable. By means of this ODE approach, experimental parameters can be identified for which the two models predict significant differences in the concentration profiles but where the closeness to the production process, i.e., the conversion of hexanol, is still high. The results are also tabulated in the Supporting Information. It has been noted that the conversion calculated with Model A follows the same trend and is in all cases higher than with

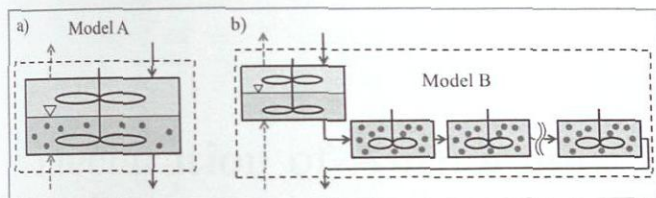


Figure 8. Schematic of the two models used to describe the D+R trays (delimited by the discontinuous lines) in the HCRD column: a) VLE stage with single CSTR superimposed and b) VLE stage with a number of sequential CSTRs.

Model B; on the other side, the purities achieved are throughout higher than 0.9 in mass fraction with both models (see the Supporting Information). The variation of the experimental input parameters that correspond to the Pareto frontier shown in Fig. 9a can be used as an experimental plan by itself; alternatively, as described above depending on the preferences of the user, a region of the Pareto frontier can be chosen, as suggested in the Supporting Information to carry out statistical DOE.

4 Conclusions

In this work, the capabilities of using MOO in the field of ODE for model development have been illustrated using three case studies as examples. Different types of conflicting objectives have been considered involving aims such as improving parameter precision, working at conditions close to the process, and discriminating between alternative models. It has been demonstrated that the usage of reliable tools to compute Pareto sets can provide the user with useful information to study the trade-offs between the pertinent objec-

tive functions and support him in the selection of the most interesting range of experimental conditions in a straightforward and intuitive way. Furthermore, arbitrary constraints of the experimental setup can be taken into account. This enables the design of an efficient experimental planning, which can then be complemented by combination with statistical DOE.

We are grateful for valuable contributions in the project by Roger Böttcher, Oliver Hirth, Regina Benfer, Tobias Keller (BASF) and Jan Schwientek (Fraunhofer ITWM).

Symbols used

g	[-]	estimated variable
$\mathbf{IM}$	[-]	information matrix
$\mathbf{J}$	[-]	Jacobian matrix
J_n	[-]	n th objective function
k_i	[-]	kinetic factor of reaction i
$\dot{m}$	[kg h ⁻¹]	total mass flow
m_i	[kg]	mass of component i
N_d	[-]	number of design or input variables
N_e	[-]	number of experimental variables
N_m	[-]	number of output
N_p	[-]	number of model parameters
$\dot{Q}$	[kW]	heat duty

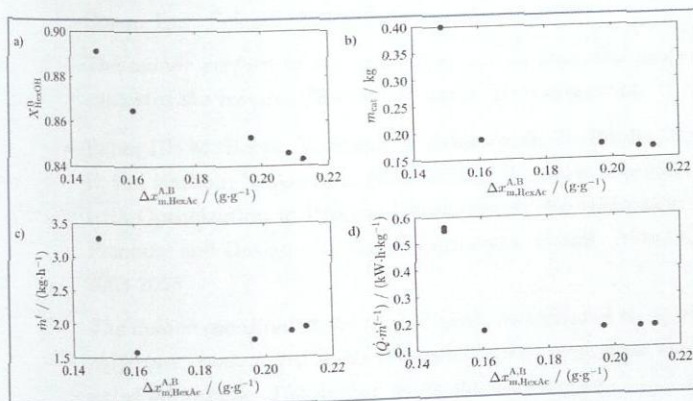


Figure 9. Pareto-optimal objective space and parameter values for the case study of the HCRD column. In a) the two objectives (the conversion obtained in Model B and the differences in concentration of hexyl acetate for both models along the column) are plotted; against b) the mass of catalyst, c) the feed flow rate, and d) the ratio of heat duty to feed flow.

Declaration of Authorship

This habilitation thesis contains material that has been published previously or that is included in submitted publications. In the following, these publications are listed together with a statement on the contributions of the author of the present habilitation thesis.

- Paper I: M. Bortz, J. Burger, N. Asprion, S. Blagov, R. Böttcher, U. Nowak, A. Scheithauer, R. Welke, K.-H. Küfer: Multi-Criteria Optimization in Chemical Process Design and Decision Support by Navigation on Pareto Sets. *Comp. Chem. Eng.* 60 (2014) 354-363

The author coordinated the project work, contributed to setting up the software architecture, designed algorithms, contributed to their implementation, performed the simulations and evaluated the results. The author wrote the manuscript.

- Paper II: M. Bortz, J. Burger, N. Asprion, S. Blagov, K.-H. Küfer, H. Hasse: On the Effort of Approaching Pure Components and Azeotropes in Distillation. *Chem. Eng. Science*, 127 (2015) 253-259

The author performed the analytical calculations and numerical simulations and evaluated the results. The author wrote the manuscript.

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

The author coordinated the project work, contributed to setting up the software architecture, contributed to its implementation, performed the simulations and evaluated the results. The author wrote the manuscript.

- Paper IV: N. Asprion, R. Benfer, S. Blagov, R. Böttcher, M. Bortz, M. Berezhnyi, J. Burger, E. von Harbou, K.-H. Küfer, H. Hasse: INES - An Interface between Experiments and Simulation to Support the Development of Robust Process Design. *Chemie Ingenieur Technik* 87 (2015) 1810-1825

The author coordinated the project work, contributed to setting up the software architecture, designed algorithms, contributed to their implementation, partly performed the simulations and evaluated the results. The author contributed to the writing of the chapters related to these issues of the manuscript.

- Paper V: D. Nowak, M. Bortz, H. Roclawski: Decision Support for the Design and Operation of Water Supply Systems, in : 13th Computer Control for Water Industry Conference, CCWI 2015, volume 119, pp. 442-449

The author coordinated the project work, contributed to setting up the software architecture, partly performed the simulations and evaluated the results. The author contributed to the writing of the chapter related to the practical applications of the manuscript.

- Paper VI: M. von Kurnatowski, M. Bortz, A. Scherrer, A. Hoffmann, H.-M. Lorenz, M. Caraucan, T. Grützner, N. Künzle, K.-H. Küfer: Multi-Criteria Optimization of an Industrial World-Scale Process

The author coordinated the project work, contributed to setting up the software architecture, designed algorithms, and partly evaluated simulation results. The author contributed to the writing of the chapters related to these issues of the manuscript.

- Paper VII: M. Bortz, J. Burger, E. von Harbou, M. Klein, J. Schwientek, N. Asprion, R. Böttcher, K.-H. Küfer, H. Hasse: Efficient Approach for Calculating Pareto Boundaries under Uncertainties in Chemical Process Design. *Industrial & Engineering Chemistry Research* 56 (2017) 12672 - 12682

The author coordinated the project work, contributed to setting up the software architecture, designed algorithms, contributed to their implementation, partly performed the simulations and evaluated the results. The author wrote the manuscript.

- Paper VIII: N. Asprion, S. Blagov, R. Böttcher, J. Schwientek, J. Burger, E. von Harbou, M. Bortz: Simulation and Multi-Criteria Optimization under Uncertain Model Parameters of a Cumene Process, *Chemie Ingenieur Technik* 89 (2017) 665-674

The author coordinated the project work, contributed to setting up the software architecture, designed algorithms, contributed to their implementation, partly performed the simulations and evaluated the results. The author contributed to the writing of the chapters related to these issues of the manuscript.

- Paper IX: A. Hoffmann, M. Bortz, R. Welke, J. Burger, K.-H. Küfer, H. Hasse: Stage-to-Stage Calculations of Distillation Columns by Fixed-Point Iteration and Application of the Banach Fixed-Point Theorem. *Chem. Eng. Science* 164 (2017) 188-201

The author provided the key idea of the fixed-point iteration, contributed to the simulations and their evaluation and contributed to the writing of the manuscript.

- Paper X: N. Asprion, R. Böttcher, R. Pack, M.E. Stavrou, J. Höller, J. Schwientek, M. Bortz: Graybox Models - New Opportunities for the Optimization of Entire Processes, in: 27th European Symposium on Computer Aided Process Engineering, volume 40 (2017) pp. 97-102

The author coordinated the project work, contributed to setting up the software architecture, designed algorithms, partly performed the simulations and evaluated the results. The author contributed to the writing of the chapters related to these issues of the manuscript.

- Paper XI: E. Forte, E. Harbou, J. Burger, N. Asprion, M. Bortz: Optimal Design of Laboratory and Pilot-Plant Experiments Using Multiobjective Optimization, *Chem. Ing. Tech.* 89 (2017) 645

The author provided the key idea of treating optimale experimental design in a multicriteria setting together with process-related objectives and contributed to the writing of the manuscript.

- Paper XII: E. Forte, J. Burger, K. Langenbach, H. Hasse, M. Bortz: Multi-Criteria Optimization for Parametrization of SAFT-Type Equations of State for Water, Thermodynamics and Molecular-Scale Phenomena 89 (2017) 226

The author supervised the implementation of adaptive scalarization schemes, was involved in the evaluation of the results and contributed to the writing of the manuscript.

Curriculum Vitae

Michael Bortz



Date of Birth 21.03.1976

Academic Education

- 10/1996 - 07/1998 Basic Studies of Physics, University Dortmund
- 09/1998 - 06/1999 Maîtrise de Physique, Université Joseph Fourier, Grenoble (France)
- 10/1999 - 12/2001 Advanced Study Period of Physics, University Dortmund
- 12/2001 Diploma Thesis in Theoretical Many-Body Physics,
Supervised by Prof. A. Klümper
(University Dortmund, Final Grade "sehr gut")
- 12/2003 Dissertaion Thesis in Theoretical Many-Body Physics,
supervised by Prof. A. Klümper (Universita Dortmund)
"A lattice path integral approach to the Kondo problem",
Final Grade "summa cum laude".

Scientific Career

- 01/2002-12/2003 Research Assistant at the Institute for Physics, University Dortmund, including Teaching (Tutorials) in Classical Mechanics, Quantum Mechanics, Statistical Mechanics, Solid State Physics and General Relativity.
- 01/2004-04/2005 Postdoctoral Research Fellow in the Group of Physics, University Wuppertal, with teaching as above.
- 05/2005-04/2007 Postdoctoral Research Fellow at the Research School of Physical Sciences and Engineering, Australian National University, Canberra
- 07/2007-09/2009 Postdoctoral Research Fellow at the Department for Physics, Technical University Kaiserslautern, with teaching activities as above.
- since 09/2009 Scientist in the Department for Optimization, Fraunhofer Institute for Industrial Mathematics (ITWM)

Awards

- 10/1996-12/2001 Scholarship of the Studienstiftung des deutschen Volkes
- 06/2002-12/2003 Dissertation Scholarship of the Studienstiftung des deutschen Volkes
- 01/2005 Dissertation Award of the University Dortmund
- 05/2005-04/2007 Research Scholarship of the German Research Foundation (DFG) for a research project at the Australian National University in Canberra, Australien, in the group of Prof. M.T. Batchelor.
- 01/2009-02/2009 Research Scholarship of the European Science Foundation for a research project at the University of Oxford in the group of Prof. F.H.L. Essler.
- 05/2016 Stifterverband Science Prize for Tailor-Made Radiation Therapy, shared with K.-H. Küfer, A. Scherrer, P. Süss, K. Teichert.

Annual Report of the Board of Directors

For the year ending December 31, 1910

Presented to the Shareholders at the Annual Meeting held on January 10, 1911

By the Board of Directors

The Board of Directors has the honor to acknowledge the interest and cooperation of the Shareholders in the management of the Company during the year 1910.

The year 1910 has been a year of unusual activity and progress for the Company. The Board of Directors has endeavored to conduct the business of the Company in a manner consistent with the best interests of the Shareholders.

The financial results of the year 1910 are shown in the accompanying statement of the Board of Directors. The Company has realized a net profit of \$100,000, which is a record for the Company.

The Board of Directors has recommended that the net profit of \$100,000 be distributed to the Shareholders in the form of a dividend of \$1.00 per share.

The Board of Directors has also recommended that the Company purchase 10,000 shares of its own stock at a price of \$10.00 per share.

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Publication List Michael Bortz

Refereed Publications in Journals

- [1] M. Bortz; Lattice path integral approach to the Kondo model;
Doktorarbeit (Universität Dortmund 2003), <http://hdl.handle.net/2003/2384>
- [2] M. Bortz and A. Klümper; Lattice path integral approach to the one-dimensional Kondo model; J. Phys. A **37** (2004) 6413
- [3] M. Bortz and A. Klümper; The anisotropic multichannel spin- S Kondo model: Calculation of scales from a novel exact solution; Eur. Phys. J. B **40** (2004) 25
- [4] M. Bortz, A. Klümper und C. Scheeren; Crossover from Anderson- to Kondo-like behavior: Universality induced by spin-charge separation; Phys. Rev. B **71** (2005) 144421
- [5] M. Bortz and J. Sirker; Boundary susceptibility in the open XXZ-chain; J. Phys. A **38** (2005) 5957
- [6] M. Bortz and F. Göhmann; Exact thermodynamic limit of short-range correlation functions of the antiferromagnetic XXZ-chain at finite temperatures; Eur. Phys. J. B **46** (2005) 399
- [7] M.T. Batchelor, M. Bortz, X.W. Guan and N. Oelkers; Exact results for the 1D interacting Fermi gas with arbitrary polarization; J. Phys.: Conf. Ser. **42** (2006) 5-10
- [8] M.T. Batchelor, M. Bortz, X.W. Guan and N. Oelkers; Exact results for the 1D mixed Bose-Fermi interacting gas; Phys. Rev. A **72** (2005) 061603(R)

- [9] F. Göhmann, M. Bortz and H. Frahm; Surface free energy for systems with integrable boundary conditions; *J. Phys. A* **38** (2005) 10879
- [10] J. Sirker and M. Bortz; Quantum versus classical behavior in the boundary susceptibility of the ferromagnetic Heisenberg chain; *Phys. Rev. B* **73** (2006) 014424
- [11] M.T. Batchelor, M. Bortz, X.W. Guan and N. Oelkers; Evidence for the super Tonks-Girardeau gas; *J. Stat. Mech.* (2005) L10001
- [12] J. Sirker and M. Bortz; The open XXZ-chain: Bosonisation, Bethe ansatz and logarithmic corrections; *J. Stat. Mech.* (2006) P01007
- [13] N. Oelkers, M.T. Batchelor, M. Bortz, and X.W. Guan; Bethe Ansatz study of one-dimensional Bose and Fermi gases with periodic and hard wall boundary conditions; *J. Phys. A* **39** (2006) 1073
- [14] M.T. Batchelor, M. Bortz, X.W. Guan and N. Oelkers; Collective dispersion relations for the 1D interacting two-component Bose and Fermi gases; *J. Stat. Mech.* (2006) P03016
- [15] M. Bortz and J. Sirker; The one-dimensional Hubbard model with open ends: Universal divergent contributions to the magnetic susceptibility; *J. Phys. A* **39** (2006) 7187
- [16] M. Bortz and S. Sergeev; The q -deformed Bose gas: Integrability and thermodynamics; *Eur. Phys. J. B* **51** (2006) 395
- [17] M. Bortz; Finite temperature Drude weight of an integrable Bose chain; *J. Stat. Mech.* (2006) P08016
- [18] M. Bortz; Low-temperature asymptotics of integrable systems in an external field; *J. Phys. A* **40** (2007) 1

- [19] M. Bortz and J. Stolze; Spin- and entanglement-dynamics in the central spin model with homogeneous couplings; *J. Stat. Mech.* (2007) P06018
- [20] M. Bortz, J. Sato and M. Shiroishi; String correlation functions of the spin-1/2 Heisenberg XXZ chain; *J. Phys. A* **40** (2007) 4253
- [21] M. Bortz and J. Stolze; Exact dynamics in the inhomogeneous central-spin model; *Phys. Rev. B* **76** (2007) 014304
- [22] X.-W. Guan, M. T. Batchelor, C. Lee and M. Bortz; Phase Transitions and Pairing Signature in Strongly Attractive Fermi Atomic Gases; *Phys. Rev. B* **76** (2007) 085120
- [23] I. Schneider, A. Struck, M. Bortz and S. Eggert; Local Density of States for Individual Energy Levels in Finite Quantum Wires; *Phys Rev. Lett.* **101** (2008) 206401
- [24] S. Söffing, M. Bortz and S. Eggert; Wigner crystal vs. Friedel oscillations in the one-dimensional Hubbard model; *Phys. Rev. B* **79** (2009) 195114
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- [26] M. Bortz, M. Karbach, I. Schneider and S. Eggert; Lattice vs. continuum theory of the periodic Heisenberg chain; *Phys. Rev. B* **79** (2009) 245414
- [27] M. Bortz, S. Eggert, J. Stolze; Spectrum and Screening cloud in the central spin model; *Phys. Rev. B* **81** (2010) 035315
- [28] M. Bortz, S. Eggert, C. Schneider, R. Stübner, J. Stolze; Dynamics and decoherence in the central spin model using exact methods; *Phys. Rev. B.* **82** (2010) 161308

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- [30] A. Scherrer, P. Süß, T. Grebe, I. Serna, M. Bortz, K.-H. Küfer, B. Rhein, N. Nikolay, J. Debus;
A new planning tool for fast online dose optimization of IMRT plans;
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- [33] J. Burger, N. Asprion, S. Blagov, R. Böttcher, U. Nowak, M. Bortz, R. Welke, K.-H.K. Küfer, H. Hasse; Multi-Objective Optimization and Decision Support in Process Engineering – Implementation and Application;
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On the Effort of Approaching Pure Components and Azeotropes in Distillati
Chem. Eng. Science, **127** (2015) 253-259
- [35] N. Asprion, J. Burger, M. Bortz; Nachhaltiges Prozessdesign – Integration von Ökobilanz und Toxizitätsbewertung in Prozesssimulation optimiert chemische Prozesse; *CHEManager* **20** (2015) 11.

- [36] N. Asprion, R. Benfer, S. Blagov, R. Böttcher, M. Bortz, M. Berezhnyi, J. Burger, E. von Harbou, K.-H. Küfer, H. Hasse; INES - An Interface between Experiments and Simulation to Support the Development of Robust Process Design.
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- [37] M. Bortz, J. Burger, E. Forte, E. von Harbou, N. Asprion, H. Hasse;
A Pareto- Based Approach to Optimal Design of Experiments,
Chem. Ing. Tech. **88** (2016) 1377
- [38] H. Krieg, D. Nowak, A. Knapp, C. Geil, H. Roclawski, M. Böhle:
Entscheidungsunterstützung für Planung und Betrieb von Trinkwasser-
versorgungsanlagen – Decision support for planing and operation of drinking water
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to Consider Uncertainty in Equations of State for the Use in Process Simulation
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- [40] M. von Kurnatowski, M. Bortz, A. Scherrer, A. Hoffmann, H.-M. Lorenz,
M. Caraucan, T. Grützner, N. Künzle, K.-H. Küfer;
Multi-Criteria Optimization of an Industrial World-Scale Process
Chem. Ing. Techn. **89** (2017) 1471
- [41] M. Bortz, J. Burger, E. von Harbou, M. Klein, J. Schwientek, N. Asprion,
R. Böttcher, K.-H. Küfer, H. Hasse; Efficient Approach for Calculating Pareto
Boundaries under Uncertainities in Chemical Process Design.
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- [42] N. Asprion, S. Blagov, R. Böttcher, J. Schwientek, J. Burger, E. von Harbou,
M. Bortz; Simulation and Multic-Criteria Optimization under Uncertain Model
Parameters of a Cumene Process, Chemie Ingenieur Technik **89** (2017) 665

- [43] A. Hoffmann, M. Bortz, R. Welke, J. Burger, K.-H. Küfer, H. Hasse;
Stage-to-Stage Calculations of Distillation Columns by Fixed-Point Iteration
and Application of the Banach Fixed-Point Theorem.
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- [44] E. Forte, E. Harbou, J. Burger, N. Asprion, M. Bortz; Optimal Design of
Laboratory and Pilot-Plant Experiments Using Multiobjective Optimization;
Chem. Ing. Tech. **89** (2017) 645.
- [45] E. Forte, J. Burger, K. Langenbach, H. Hasse, M. Bortz;
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- [46] N. Yakut, K. Krüning, G. Foltin, J. Burger, M. Krauss, N. Asprion, M. Bortz,
M. Roth; Modelldurchgängigkeit in der Prozessindustrie am Beispiel
virtueller Inbetriebnahme; *Chem. Ing. Tech.* **89** (2017) 1444
- [47] E. von Harbou, O. Ryll, M. Schrabback, M. Bortz, H. Hasse;
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Simulation, and Error Analysis; *Chem. Ing. Techn.* **89** (2017) 1315
- [48] M. von Kurnatowski, M. Bortz, P. Klein, B. Kintzel, C. Cremers;
Quantitative Kinetic Analysis of a PdAu 3 Alloy Catalyst for Oxygen
Electro-Reduction; *J. Electrochem. Soc.* **164** (2017) H1072

Conference Proceedings

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- [2] N. Asprion, S. Blagov, O. Ryll, R. Welke, A. Winterfeld, A. Dittel, M. Bortz, K.-H. Küfer, J. Burger, A. Scheithauer, H. Hasse; Pareto-Navigation in Chemical Engineering; *Computer Aided Chemical Engineering* **29 A** (2011) 422
- [3] N. Asprion, S. Blagov, O. Ryll, R. Welke, A. Winterfeld, A. Dittel, M. Bortz, K.-H. Küfer, J. Burger, A. Scheithauer, H. Hasse; Decision support for process development in the chemical industry; *Chemical Engineering Transactions* **24** (2011) 301
- [4] N. Asprion, O. Ryll, S. Blagov, R. Böttcher, J. Burger, A. Scheithauer, H. Hasse, R. Welke, A. Dittel, M. Bortz; Pareto-Optimierung in der Verfahrenstechnik; *Chemie Ingenieur Technik* **84** (2012) 1410
- [5] M. Bortz, R. Welke, J. Burger, A. Scheithauer, S. Blagov, A. Dittel, N. Asprion, K.-H. Küfer, H. Hasse; Hierarchische Modellierung, Simulation und Optimierung von Destillationsprozessen; *Chemie Ingenieur Technik* **85** (2013) 1407
- [6] M. Bortz, J. Schwientek, K.-H. Küfer, J. Burger, E. von Harbou, H. Hasse, O. Hirth, N. Asprion, S. Blagov; Minimizing the Impact of Uncertain Model Parameters on Process Design; *Chem. Ing. Techn.* **87** (2015) 1061
- [7] A. Hoffmann, M. Bortz, J. Burger, K.-H. Küfer, H. Hasse; Robuste Simulation und gleichzeitige Optimierung von Fließbildern mittels Schießverfahren; *Chem. Ing. Techn.* **87** (2015) 1059

- [8] J. Burger, H. Hasse, M. Kaul, S. Deublein, F. Ruether, S. Blagov, G. Foltin, M. Bortz, K.-H. Küfer: Short-Cut-Modelle für den konzeptionellen Entwurf von Trennverfahren – Von den Grundlagen in die industrielle Praxis; Chem. Ing. Techn. **87** (2015) 1062
- [9] D. Nowak, M. Bortz, H. Roelawski; Decision Support for the Design and Operation of Water Supply Systems, in: 13th Computer Control for Water Industry Conference, CCWI 2015, **119**, 442
- [10] M. Bortz, V. Maag, J. Schwientek, R. Benfer, R. Böttcher, J. Burger, E. von Harbou, N. Asprion, K.-H. Küfer, H. Hasse; Decision Support by Multicriteria Optimization in Process Development: An Integrated Approach for Robust Planning and Design of Plant Experiments. Comp. Aided Chem. Eng. **37** (2015) 2063-2068
- [11] N. Asprion, R. Böttcher, R. Pack, M. Bortz, J. Schwientek, J. Höller; Graybox-Modelle – Neue Möglichkeiten für die Optimierung von Gesamtverfahren; Chem. Ing. Tech. **88** (2016) 1312
- [12] E. Forte, J. Burger, K. Langenbach, M. Bortz, H. Hasse; Multi-Criteria Optimization of Equations-of-State Models Using Water and PCP-SAFT as an Example Chem. Ing. Tech. **88** (2016) 1285
- [13] A. Hoffmann, M. Bortz, J. Burger, K.-H. Küfer, M. Bortz, H. Hasse; A new Scheme for Process Simulation by Optimization: Distillation as an Exam Computer Aided Chemical Engineering **38** (2016) 205
- [14] N. Asprion, R. Böttcher, R. Pack, M.E. Stavrou, J. Höller, J. Schwientek, M. Bortz; Graybox Models - New Opportunities for the Optimization of Entire Processes, in: 27th European Symposium on Computer Aided Process Engineering, **40** (2017) 97

- [15] M. Bortz, J. Höller, J. Schwientek, R. Böttcher, O. Hirth, N. Asprion; Experimental Design in a Multicriteria Optimization Context: An Adaptive Scheme; IFAC PapersOnLine **51** (2018)

Book Contributions

- [1] K.-H. Küfer, M. Bortz; Section "Optimization" in chapter "Mathematics in Chemical Engineering"; Ullmann's Encyclopedia of Industrial Chemistry

Patents

- [1a] K.-H. Küfer, A. Scherrer, M. Monz, P. Süss, M. Bortz; Anpassen einer Dosisverteilungs-Einstellung für ein technisches Gerät der Tumorthherapie
Amtsaktenzeichen: 102010060847.5
- [1b] K.-H. Küfer, A. Scherrer, M. Monz, P. Süss, M. Bortz; Customization of a Dose Distribution Setting for a Technical Appliance for Tumour Therapy;
Publication number: US20130304503
- [2a] A. Scherrer, K.-H. Küfer, P. Süss, M. Bortz; Navigierbare Darstellung einer Lösungsvielfalt von Therapieplänen; Patent-Nr. 1951/2795496
- [2b] A. Scherrer, K.-H. Küfer, P. Süss, M. Bortz; Navigable Presentation of a Variety of Solutions for Therapy Plans; Patent number: US9824187

Supervised Student Theses

Michael Bortz

- Xenia Reit, Positioning and Thermal Effect of the Ultrasonic Field in the Extracorporeal Focused Ultrasound Therapy. Diploma thesis, 2009

The author supervised the thesis.

- Richard Welke, Multicriteria Optimization in Chemical Engineering. PhD thesis, 2012

The author co-supervised the thesis.

- Dominik Dürig, Greybox Approach for Chemical Production Plants - Integration of Process Data and Simulation. Master thesis, 2016

The author supervised the thesis.

- Anna Hoffmann, Integrated Simulation and Optimization of Distillation-based Flowsheets. PhD thesis, 2016

The author co-supervised the thesis.

- Philipp Pelz, Verlässlichkeit von Regressionsgewichten bei der Modellanpassung von Fließbildsimulationen an Betriebsdaten (Reliability of regression weights for the model adjustment of flowsheet simulations to process data). Master thesis 2018

The author supervised the thesis.

Process engineering faces the challenge of finding good compromises in the trade-offs between cost and quality measures. Therefore, reliable models of the processes are needed, which are suited for model-based optimization. In this work, the complete workflow of process data preprocessing, hybrid modelling and mathematical multicriteria optimization including model uncertainties is addressed. The emphasis is always on the development of methods to support decisions and to make them transparent by comparisons between alternatives. The application domains stem from chemical production and public water supply.

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