**Global optimization of catalyst recovery in a thermomorphic multiphase system using surrogate models**

Christian Kunde1,\*, Tobias Keßler1, Steffen Linke2, Kevin McBride2, Kai Sundmacher1,2, Achim Kienle1,2

*1 Otto von Guericke University Magdeburg, Universitätsplatz 2, 39106 Magdeburg, Germany
2 Max Planck Institute for Dynamics of Complex Technical Systems, Sandtorstraße 1, 39106 Magdeburg, Germany*

*\*Corresponding author: christian.kunde@ovgu.de*

**Highlights**

* Global optimization of catalyst recovery in an extraction cascade.
* Complex LLE and catalyst distribution models replaced by artificial neural network.
* Implicit model formulation reduces the input dimension of the surrogate model.
* Surrogate model quality is improved by optimization based bound tightening during preprocessing.

**1. Introduction**

The aim of using renewable resources for chemical processes and improving their energy efficiency calls for the exploration of novel and integrated process concepts. Thermomorphic multiphase systems (TMS) enable favorable reaction conditions as well as efficient catalyst recycling for homogeneously catalyzed reactions. A TMS is homogeneous at reaction conditions and a subsequent decrease in temperature results in biphasic behavior: a catalyst-lean product phase and a catalyst-rich phase that is recycled back to the reactor. If the separation of catalyst from the product phase in one step is not sufficient, the process can be extended by additional extraction stages to further increase recovery of valuable catalyst.

Mathematical optimization can be used to find the economically most viable realization of such a process. For nonlinear models with continuous decision variables this leads to nonlinear programs (NLP), which are typically hard to solve and may possess multiple local minima. Therefore, deterministic global optimization is required to avoid suboptimal design decisions based on poor local solutions. Thermodynamic models employed to predict the phase equilibrium of TMS and the catalyst distribution are often computationally difficult to handle within optimization problems, even in the case of local optimization. Replacing thermodynamic models with suitable surrogates provides the means to trade model accuracy for better computational tractability.

As an example, the hydroformylation of long-chain aldehydes with homogeneous catalysts using a TMS for catalyst recovery is considered in [1]. In that work, the thermodynamic models are replaced by a Kriging model to avoid convergence problems within the local optimization of the overall hydroformylation process. However, the resulting surrogate model comprises a large number of relatively complex nonlinear terms, which renders it computationally unfavorable for deterministic global optimization.

To overcome this problem, we present modifications to the surrogate construction aimed at reducing the number of nonlinear expressions and thus the computational complexity of the model. Globally optimal solutions of the resulting model are identified using BARON [2].

Figure 1. Flowsheet of the hydroformylation process considered in [1]. The highlighted area shows a multistage extraction cascade with solvent recycle.

The following methods are applicable for processes dealing with liquid-liquid-equilibria. However, we focus on a subprocess taken from [1], highlighted in Figure 1, as a case study. Catalyst is recovered from a product stream by an extraction solvent in a series of decanter units in a countercurrent setup. The extraction solvent is regenerated using a distillation column. As in [1], the reference data of the temperature dependent liquid-liquid equilibrium of a four-component mixture and distribution of catalyst between the separate phases is generated using a modified UNIFAC Dortmund model and COSMOtherm. The economic cost function comprises refrigeration, decanter units, catalyst loss, and costs for a short-cut distillation column.

**2. Methods and results**

A number of methods for data-driven surrogate modeling is available in the literature, see e.g. [3,4] for an overview. Based on testing with various Kriging formulations and artificial neural networks (ANN), an ANN with a single hidden layer and tangent hyperbolic activation function was selected to replace the thermodynamic reference models. The input dimension of the surrogate is reduced in comparison to [1] by choosing the position on the binodal curve as an input instead of the feed composition. This strategy, illustrated in Figure 2, results in an implicit model, but it simplifies the definition and modeling of valid input values.The quality of the ANN is further improved by reducing the range of input values with optimization based bound tightening in a preprocessing step. Error bounds for a least-squares fitted second order polynomial are chosen such that all available data points lie within the relaxed model. The polynomial surrogate model may have larger error bounds than an ANN, but computational effort is significantly lower. BARON is then utilized to calculate tighter bounds on the input variables based on the relaxed model.

Figure 2. Ternary phase diagram with a two-phase region. Input space highlighted for explicit (left) and implicit (right) model formulation.

These combined methods reduce the computation time and increase the accuracy of global optimization with surrogate models in the considered case study. The global optimization results also verify the findings presented in [1]. Application to other processes will be tested in the future.

**References**

1. K. McBride, N. M. Kaiser, K. Sundmacher, 2017. Computers & Chemical Engineering 105, 212–223.
2. M. R. Kılınç, N. V. Sahinidis, 2018. Optimization Methods and Software 33 (3), 540–562.
3. M. J. Asher, B. F. W. Croke, A. J. Jakeman, L. J. M. Peeters, 2015. Water Resour. Res. 51 (8), 5957–5973.
4. A. Bhosekar, M. Ierapetritou, 2018. Computers & Chemical Engineering 108, 250–267.