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Simultaneous design of the optimal reaction and process concept for multiphase systems



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AUTHOR - HIGHLIGHTS

- Model-based method to determine best reaction concept within the overall process for multiphase systems.
- Apparatus independent model of reaction system yields optimal reaction route as basis for reactor design.
- Detailed process model for the hydroformylation of 1-dodecene in a thermomorphic solvent system.
- Minimization of production costs considering costs for raw material, utilities, and depreciation.

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ABSTRACT

In complex chemical processes optimizing the reactor with respect to a stand-alone reactor performance criterium such as product selectivity does not necessarily yield the best process-wide reaction concept. Especially in case of multiphase reaction systems, which often involve complex reaction networks, nonideal phase behavior and multiple recycles, reactor and process have to be optimized simultaneously since the reactor affects the separation units and vice versa. In order to derive the process-wide optimal reaction concept in combination with optimal process parameters, a systematic optimization procedure based on a large scale optimization problem constrained by a system of differential algebraic equations (DAE) is presented. The optimization problem contains a detailed model of the reaction section, a process model describing the other units of the process, and models for operational and fixed costs. The solution of the optimization is a set of process parameters and optimal profiles of heat and material fluxes over the reaction coordinate which minimize the production costs. The method is exemplified on the rhodium catalyzed hydroformylation of 1-dodecene in a thermomorphic solvent system.

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1. Introduction

As core of the chemical process the reactor decisively affects the economics of the entire chemical production process. In order to reduce the losses of solvents and unconverted products in the chemical process, the system of reactor and separation units is normally connected via recycle streams constituting a feed-back system. Hence, changing the conditions in any unit will affect the performance of the whole process. As a consequence, to identify an optimal reactor concept for any chemical process it is necessary to consider the entire process and to perform the reactor and process design simultaneously. While this conclusion is rather

obvious, as of now there is still no general applicable method available to perform this task.

Common reactor design methods such as heuristics or attainable region approaches (Horn, 1964; Glasser et al., 1987; Hildebrandt and Glasser, 1990; Hildebrandt et al., 1990; Feinberg and Hildebrandt, 1997) yield only solutions which are limited by the set of predefined reactors, and do not consider the requirements for complex reaction networks and solvent recycles. The hybrid attainable region approach developed in the research group of Biegler (Balakrishna and Biegler, 1992a, 1992b, 1993; Lakshmanan and Biegler, 1996) enables the consideration of the process flowsheet, however, it does not allow for the derivation of new reactor concepts.

Since the rise of efficient MINLP solvers, superstructures have become an option which allows one to find the optimal set and interconnection of flowsheet units (Achenie and Biegler, 1986, 1990; Kokossis and Floudas, 1991, 1994; Hillestad, 2005). These

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methods are used to identify the optimal process structure and process parameters by solving large scale MINLPs which, however, are not easy to solve and often yield local optima. The effect of recycles can be included, but again the reactor has to be pre-defined and only the optimal candidate amongst the implemented reactors will be identified. Hence, it is still uncertain if the identified reactor is really optimal for the specific reaction system.

In order to account for the full complexity of the reaction system, the concept of elementary process functions (EPF) of Freund and Sundmacher (2008) will be applied in this work. The basic idea is to track a fluid element over time, and due to the progress of the reaction the composition of the fluid element, which is traveling through the reactor, experiences a continuous change. This leads to a subsequent change of the optimal reaction conditions which can be adjusted via mass and energy fluxes. These fluxes are the solution of an optimal control problem which is constrained by the balance equations of the fluid element, constitutive equations to describe the phase properties, reaction kinetics, and physical boundaries. Several examples for the application of the EPF concept toward the design of optimal reactors have recently been presented by our group (Peschel et al., 2010, 2011a, 2011b, 2012a, 2012b; Freund et al., 2011).

In the light of the above-mentioned interaction of reactor and process, the EPF concept was applied for the plant-wide optimal reactor design on the example of the ethylene oxide process (Peschel et al., 2012b) and it was shown that the production costs of the process could be significantly decreased. Furthermore, from the reduced flow rate of the recycle streams it was concluded that also the investment costs would be lower compared to the technical reference case. In this previous work, however, the investment costs were not part of the optimization, although they can contribute significantly to the overall economics of a process.

In this work, the plant-wide optimal reactor design is extended toward the treatment of multiphase reaction systems. On the example of the hydroformylation of long chain olefins in thermomorphic solvent systems (TMS) it will be shown that the optimal reaction concept w.r.t. chemical performance measures, such as selectivity, is not necessarily the plant-wide optimal concept.

The performance of a 1-dodecene hydroformylation system is analyzed at first by studying the maximum attainable selectivity to n-tridecanal over conversion without considering recycles and costs. In a second step, a process flowsheet is developed and cost models for utility and investment costs are implemented. The influence of the recycles on the selectivity is investigated in the closed-loop system as well. Finally, a cost optimal trajectory in combination with optimal flowsheet parameters is calculated and the influence of conversion on the minimal overall costs considering operational and investment costs is investigated. Thereby it is possible to identify a unique optimal set of process parameters and distributed flux profiles along the reaction coordinate directly, without further analysis of e.g. Pareto optimal solutions.

2. Example process: hydroformylation of 1-dodecene in TMS

Hydroformylation of olefins: The hydroformylation of olefins is a prominent example for a highly relevant homogeneously catalyzed industrial process. The main products of the hydroformylation reaction are aldehydes which are produced as a mixture of linear (n) and branched (iso) forms. The products of the hydroformylation of long chain olefins are used to produce detergents, surfactants, and plasticizers. Due to the higher biodegradability of the linear aldehyde, its demand is much higher than that for the iso-product. The desired n/iso ratios can be achieved by efficient n/iso separation and by highly selective chemical reaction. Whereas the first option was mainly based on distillation

separation until now, much more effort has been put into the development of highly active and selective catalysts. In general, catalysts for the hydroformylation are based on active transition metals in combination with ligands, which are responsible for the selectivity. The most advanced generation of catalysts are rhodium-based. These catalysts provide an enormous improvement in activity and selectivity, enabling a hydroformylation at much more moderate operating conditions than with catalysts of earlier generations. However, the costs for the Rh-based catalyst are high and a quantitative catalyst separation is a prerequisite for the economical viability of the whole process.

In case of short chain olefins ($\leq C_4$) an efficient process, namely the Ruhrchemie-Rhône/Poulenc (RRP) process has been developed to minimize the rhodium losses via operation at biphasic reaction conditions. The gaseous olefins and the co-reactants hydrogen and carbon monoxide can be solved in an aqueous catalytic phase, whereas the liquid product directly forms a separate organic phase. Since the solubility of long chain olefins ($> C_4$) in an aqueous phase is not sufficient the concept is not applicable for these reactants. Hence, several innovative solvent systems have been developed to overcome the solubility problem in the reactive phase while providing an efficient catalyst separation for the hydroformylation of long chain olefins. Such solvent systems are, e.g. thermomorphic solvent systems (TMS) (Behr and Fangewisch, 2002; Behr et al., 2008), micellar solvent systems (Haumann et al., 2002), gas-expanded liquids (Fang et al., 2007; Subramaniam, 2010a, 2010b), and ionic liquids (Sharma et al., 2010). Except for the ionic liquids, the concept of these solvent systems is that their phase behavior can be tuned via temperature or pressure. In this way homogeneous reaction conditions and temperature or pressure induced phase separation can be combined into one process.

In this work, we focus on the TMS as promising solvent system. Advantages of using a TMS are the mild reaction conditions, absence of additional mass transfer resistances, and a relatively predictable phase behavior.

TMS system: The specific example system of this work is the homogeneously catalyzed hydroformylation of 1-dodecene in a TMS consisting of the polar solvent dimethylformamide (DMF), the nonpolar solvent decane (C10an), and the reactants and products of the hydroformylation. Schäfer et al. (2012) performed an extensive study on this system using a homogeneous Rhodium(acac)(CO₂)/Biphephos catalyst. In their work, they investigated the LLE behavior experimentally and theoretically using the perturbed chain statistically associating fluid theory (PC-SAFT). Furthermore, reaction performance and catalyst recycling were investigated. The availability of this extensive previous work and the knowledge about this particular TMS makes it an excellent example for our reactor design method.

The purpose of using the TMS system in homogeneously catalyzed hydroformylation of long chain olefins was already described in the introduction. While exhibiting a homogeneous phase under reaction conditions, a reduction of the temperature induces a phase split. After the phase split a dense polar phase which contains the catalyst is in equilibrium with a light organic product phase. The polar catalytic phase is recycled into the reactor. It was shown that the catalyst leaching into the product phase is very low and recycling experiments have been conducted successfully. However, while the catalyst leaching is appreciably low, the solubility of the product in the catalytic phase is less favorable. Schäfer et al. (2012) found that a low separation temperature reduces the catalyst leaching. In addition, the biphasic region can only be obtained up to a product mass fraction of 20%. This implies that in case of full conversion around 80% of the product mixture has to be solvent.

In this work, all of the described phenomena have been implemented as constraints into an advanced process model which is explained in the next chapter.

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