Chemical Engineering Science ■ (■■■■) ■■■–■■■

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Towards a novel process concept for the hydroformylation of higher alkenes: Mini-plant operation strategies via model development and optimal experimental design

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HIGHLIGHTS

- A process concept for the hydroformylation of higher alkenes is presented.
- The mini-plant is simulated with a combined reactor and an empirical decanter model.
- A multiphase surfactant system is modeled.
- An optimal experimental design strategy to determine suitable operating policies is applied.

ARTICLE INFO

Article history:
Received 14 December 2012
Received in revised form
9 May 2013
Accepted 14 May 2013

Keywords:
Reaction engineering
Separations
Mathematical modeling
Dynamic simulation
Optimization
Process systems

ABSTRACT

When developing a new process with expensive and dangerous reaction partners, it is often of interest to keep pilot plant operation time low. A model of the process can aid in achieving this goal. However, the model is generally prone to errors, and thus, leading to deviations from the actual operation. In this contribution, the focus is set on the modeling of a novel process concept for the hydroformylation of long-chained alkenes with particular interest laid on the three phase micellar system. Moreover, a methodology is presented to support operators in determining suitable operating policies for mini-plant operation. Two models of the core units, reactor and decanter, of the constructed mini-plant are presented and linked. With these, an operation policy for the minimization of model parameter uncertainty is determined.

1. Introduction

Major challenges during the development of a novel process are keeping development time and costs low. Furthermore, experimental studies should be especially target-oriented if expensive and dangerous reaction partners are applied. This becomes even more important when pilot plant operation is involved. Here, costs rise exponentially, simply due to the amounts of raw material, man-power, experiment time, and most importantly for safety reasons. One method to tackle the issue of operation time reduction is by modeling the process beforehand. Generally, process models of novel processes involve parameters that are unknown a priori, and thus, creating discrepancies between model and reality. Optimal experimental design strategies can be of assistance here since they aim to improve the subsequent parameter estimation procedure and the corresponding parameter confidence regions. The derived model is used to simulate the process based on preliminary guessed or approximated parameters. Subsequently, optimal control trajectories are calculated so as to raise parameter

Abbreviations: bic, bicontinuous phase; cat, catalyst; doce, 1-dodecene; doca, dodecane; GGW, equilibrium; Hyd, hydration to dodecane; HyfoA/B, hydroformylation to *n*-tridecanal (A) or iso-tridecanal (B); Iso, isomerization; IsoA/B, isomerization to iso-dodecene (A) or 1-dodecene (B); Isoald, iso-aldehydes; IsoDoce, iso-dodecenes; oil, oil phase; TDC, *n*-tridecanal

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0009-2509/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ces.2013.05.022

sensitivities with respect to predefined criteria of the Fisher Information matrix.

In this work, a novel hydroformylation process in a micellar system is of interest. Hydroformylation represents an important application in the field of homogenous catalysis and has been established in industry as a standard process for the production of short-chained aldehydes from alkenes. Its application to higher alkenes (longer than C_{12}) in a biphasic system with a rhodium catalyst, on the other hand, has not yet been established. Thus, a process concept for the hydroformylation of long-chained alkenes in micro-emulsions is investigated and developed. For this purpose, a mini-plant has been built at Berlin University of Technology (TU Berlin) (Müller et al., 2013).

The goal of this contribution is to present a technique so as to support the selection of a suitable operating policy for pilot or mini-plants in order to minimize model parameter uncertainty and thus obtain adequate models for later optimization tasks. This method is applied on the hydroformylation process at TU Berlin. Firstly, the process is modeled based on a rigorous model in combination with an empirical model for the multiphase decanter. Secondly, presenting a possible trajectory for a set of given starting values the plant is simulated. In a final step, a model-based approach is used to determine the optimal operating trajectories for minimizing the model parameter uncertainty. The application of this approach to such a micellar multiphase system has not yet been found in literature.

2. Background information

2.1. Preliminary investigations of the multiphase system

The key idea behind the investigated process concept for the continuous hydroformylation of long-chained alkenes lies in the creation of a micro-emulsion system providing proper reaction and separation conditions, as shown by Kupka (2006). The catalyst required for the reaction is hydrophilic and thus dissolved in water. The applied educt (alkene) is hydrophobic. Without a solubilizer, these two liquids will not mix. By applying a surfactant and creating a micro-emulsion, the hydrophilic rhodium-ligand-complex catalyst is brought into contact with the alkene (Desset et al., 2009). The reaction itself is initiated by injecting syngas (H_2&CO) into the system. This occurs in a continuously stirred tank reactor (CSTR) at pressures of up to 100 bar. The reactants are then led from the CSTR to a decanter, where a phase separation takes place (Müller et al., 2013, 2012a, 2012b). The valuable rhodium catalyst stays in the aqueous phase and is recycled back to the reactor, while the aldehyde (product) creates an oil-rich phase which is then separated for further processing. The crucial aspects with regards to technical and economic feasibility of the overall process concept are the reaction and the phase separation step to recycle the rare and expensive catalyst.

Several preliminary experiments were carried out to gain insights on the system behavior. Based on these results, the assumptions for the reactor and the phase separation model are made. Among these are investigations regarding the phase separation in equilibrium and the reaction within the different phases. Their relevance for the models is discussed in the following.

The first experiments analyze the region of Kahlweit's fish. It represents the plane in the Gibbs phase prism at a water to oil ratio of 1:1. Fig. 1 shows a general image of Kahlweit's fish (Schomäcker et al., 2011) describing the different phase separation states of the system (Rost et al., 2013).

The surfactant molecule is displayed with a hydrophilic (circle) and a hydrophobic part (tail). This is shown in Figs. 1 and 2. These molecules (lipids) bundle together to create micelles. Both

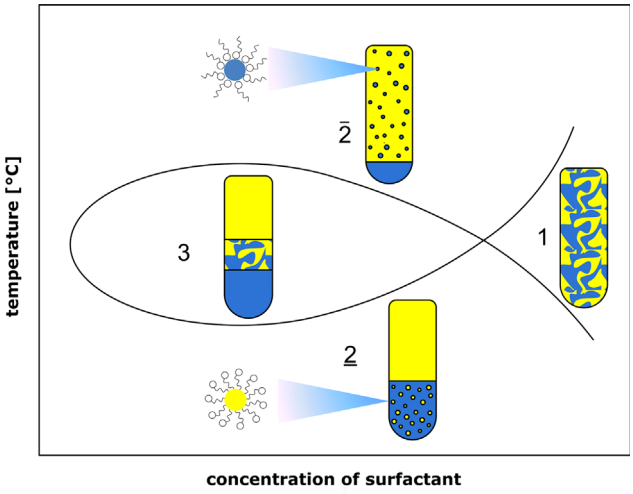

Fig. 1. General image of Kahlweit's fish (Schomäcker et al., 2011). In the 2 region the hydrophilic part of the surfactant (circle) is on the outside and the hydrophobic part (tail) is on the inside of the micelle. In the 2̄ region the hydrophilic part of the surfactant is on the inside and the hydrophobic part on the outside, thus creating a reverse micelle.

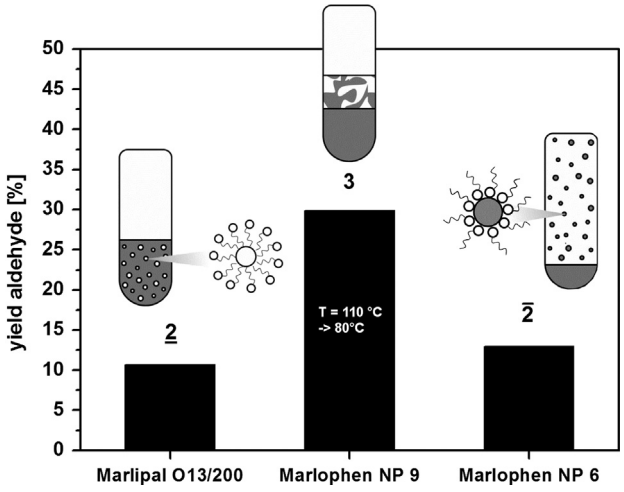

Fig. 2. Conversion after 4 h in different regions of phase diagram (Hamerla et al., 2013).

Figs. 1 and 2 show the different type of micelles. In the lower two phase region (2) the hydrophilic part (circle) is at the outer side of the micelle, while in the upper two phase region (2̄) it is on the inner side of the micelle.

The different separation states are of interest, because they can be applied for various uses during the process. There are basically two desired regions for the process. At low temperatures and low surfactant concentrations a two-phase region is created (2), where the surfactant is mainly dissolved in the lower, aqueous phase. In this case, the top phase mainly consists of aldehyde and alkene. This separation state is desired within the decanter, because a pure product phase can be separated here. If the temperature is increased at this concentration, a three-phase region is then obtained (Fig. 1: the fish's body, state 3). At this point, the lower phase consists of water. The surfactant on the other hand is mainly dissolved in the middle phase. The top phase consists of aldehyde and alkene with small amounts of water and surfactant. This state is also applicable in the decanter. Just as for the lower two-phase state (2), a pure product phase is created. Results from Schrader et al. using a similar surfactant show that the solubility of water in

Please cite this article as: Müller, D., et al., Towards a novel process concept for the hydroformylation of higher alkenes: Mini-plant operation strategies via... Chemical Engineering Science (2013), http://dx.doi.org/10.1016/j.ces.2013.05.022