

Cyclic Operation of a Semibatch Reactor for the Hydroformylation of Long-Chain Olefins and Integration in a Continuous Production Process

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Highlights

- New reactor concept for hydroformylation of long-chain olefins
- Quasi-continuous process operation using a cyclically operated semibatch reactor
- Dynamic reactor simulation and experimental investigation within an integrated process

1. Introduction

An important recent trend in chemicals production is the diversification of feedstocks, in particular the increasing use of renewable resources in processes formerly based on oil and gas. Direct substitution of the processes' raw materials is rarely possible due to broader fluctuations in the substrate quality when using renewable sources. The hydroformylation of olefins is one such example in which established processes like the Ruhrchemie/Rhône-Poulenc process for short-chain olefins is not directly applicable to renewable feedstocks containing long-chain olefins because of the limited solubility of the olefins in the catalyst-containing aqueous phase. Therefore, new catalyst systems [1], alternative solvent systems [2], reaction mechanisms [3,4] and reactor [5] as well as separator designs [6] for using long-chain olefins in the hydroformylation process are under investigation. In [5] an alternative to conventional continuous reactor operation is proposed in the context of hydroformylation of long-chain olefins. A cyclically operated semibatch reactor (CSBR) in combination with additional, continuous reactors and a continuously operated downstream process is proposed. The comparison of this quasi-continuous process with a fully continuous process involving a plug flow reactor instead of the CSBR shows comparable performance in terms of conversion and selectivity w.r.t. the desired linear aldehyde (nC13al). However, in terms of process flexibility, the quasi-continuous process provides better adaptability to external perturbations due to the better controllability of the CSBR. The technical design proposed in [5], which is based on steady-state simulations of the quasi-continuous process, was realized and experimentally tested. The present contribution focuses on the dynamic simulation of the cyclically operated SBR, including the downstream processes, as well as on the comparison to experimental results.

2. Methods

For the dynamic simulation of the process shown in Figure 1, a rigorous process model is derived. It consists of the repeatedly operated CSBR as well as a continuous separation process containing two buffer tanks and a decanter for liquid-liquid separation of the product-rich apolar phase from the catalyst-rich polar phase. The reactor model is based on the reaction kinetics reported in [4]. For recycling of the homogeneous catalyst rhodium-biphephos, a thermomorphic solvent system (TMS) consisting of n-decane (nC10an) and n,n-dimethylformamide (DMF) is chosen. The liquid-liquid phase separation was described by means of a Kriging surrogate model proposed in [6].

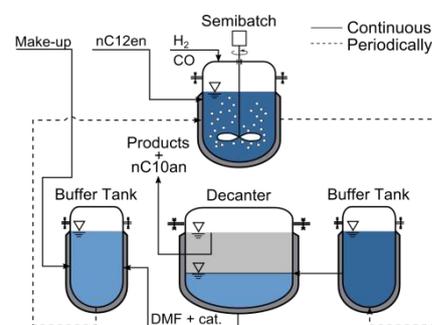


Figure 1. Process flowsheet with the CSBR.

The dynamic simulation of the process is divided into three separate simulations accounting for the CSBR preparation (period 1), chemical reaction (period 2) and downstream process (period 1 + 2). Consideration of the preparation period is necessary because of time delays occurring during operation due to

discharging/charging the CSBR and to perform additional tasks, e.g., taking samples. Subsequently, the reaction period is initiated by dosing substrate (1-dodecene: nC12en) into the reactor. The whole downstream process is operated simultaneously to the preparation and reaction period, so that the separation time and, therefore, the necessary volumetric fluxes are determined by the combination of preparation and reaction time as well as the liquid volume in the downstream (post CSBR) buffer tank. Missing solvent components are fed as make-up stream into the upstream buffer tank (pre CSBR) to ensure a constant substrate-to-solvent component ratio during the reaction.

3. Results and discussion

The dynamic simulation and the experiments are performed using a preparation time of 30 minutes and a semibatch time of 60 minutes. Figure 2 shows 15 cycles covering the start-up process as well as steady-state operation. The experimental data shown are taken from steady-state operation. For matching the trajectories of the dynamic simulation, the experimental process parameters are chosen for the simulation. In addition to that, a shortcut stream needed to be added to the decanter model for replicating the accumulation of the linear aldehyde and isomers of the substrate (iC12en) in the process.

By choosing a shortcut stream of 42% of the total molar flow entering the decanter, the initial concentration of nC13al and iC12en in each cycle can be approximated. Under the chosen operating conditions, deviations between the simulated and experimental concentrations persist. The underestimation of the nC13al production and iC12en conversion during a batch cycle indicate that an adjustment of the reaction mechanism and rate laws at high catalyst and product concentrations in the feed stream is necessary.

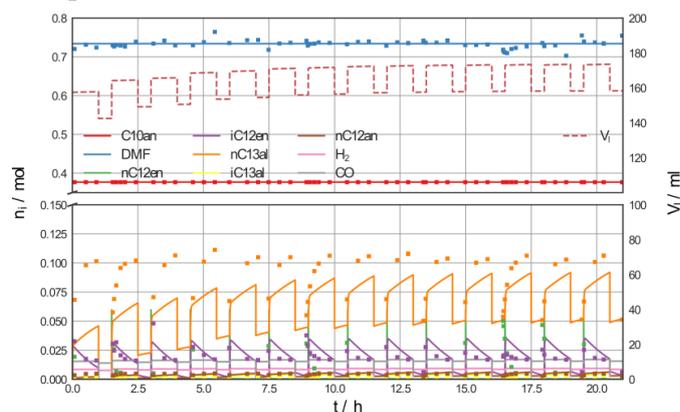


Figure 2. Dynamic simulation and experimental results

4. Conclusions

The dynamic simulation model of the cyclically operated CSBR and the downstream process is able to qualitatively reproduce the experimental results. In the next step, online IR-spectroscopy with six probe heads will be utilized to accurately determine concentration trajectories of the involved species. As a consequence, process parameters can be adjusted online which is necessary for model-based process control and the investigation of the reaction under different operating conditions. With regard to varying feedstock quality and process control, the cyclically operated CSBR allows for adjustment of control profiles (e.g., temperature, partial pressure of H₂ and CO) on a per-batch basis which combines the flexibility of a batch process with the throughput of a continuously operated reactor.

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Keywords

Hydroformylation, Dynamic simulation, Cyclic semibatch reactor operation, Optimization