Helically Coiled Segmented Flow Tubular Reactor for the Hydroformylation of Long-Chain Olefins in a Thermomorphic Multicomponent Solvent System

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Highlights
- Hydroformylation of 1-dodecene is performed in a helically coiled tubular reactor.
- A thermomorphic solvent system for efficient catalyst recovery is used.
- The coiled reactor operates in the segmented gas-liquid flow regime.

1. Introduction

Aldehydes are produced via the hydroformylation of olefins and are an important class of intermediates for the synthesis of alcohols, plasticizers and surfactants. Currently the most important industrial process is the Ruhrchemie / Rhône-Poulenc (RCH/RP) process where a water-soluble rhodium catalyst is used [1]. Due to low water solubility of olefins and the synthesis gas components, this process is only economical for short-chain olefins (C<=6) [1]. Thus, for the hydroformylation of long-chain olefins a different solvent system has to be used which allows high reaction rates and efficient catalyst recovery after the reaction. For this purpose, Thermomorphic Multicomponent Solvent (TMS) systems, e.g. composed of n,n-Dimehtylformamide (DMF)/n-decane, are very promising. At reaction temperature (>85°C) is the mixture one-phasic; afterwards the mixture is cooled down and splits up into two liquid phases: a polar phase containing the homogenously dissolved catalyst, and an apolar phase containing the aldehyde, non-converted olefins and small amounts of byproducts. The TMS concept enables a simple catalyst recycling via decantation and overcomes mass transfer limitations, which are often limiting the performance of two-phase reaction processes. This opens the door for the hydroformylation of long-chain olefins coming from renewable feedstocks.

2. Methods

In our group, based on the detailed reaction kinetics determined for the hydroformylation of 1-dodecene in the TMS-system DMF/n-decane, a flux profile analysis (FPA) was used to optimize a reactor system for the integration into a continuously operated miniplant process [2]. The objective was to maximize the selectivity with respect to the linear aldehyde (tridecanal) at high conversion (> 90%) of the olefin 1-dodecene. The results of the FPA-analysis reveal that two different reaction zones are needed: zone I with low axial dispersion followed by zone II with intense backmixing. For the realization of zone II a continuous stirred tank reactor (CSTR) is used. For reaction zone I, a tubular reactor is favored, wherein high gas-liquid mass transfer rates and lowest possible axial dispersion are to achieved. Both features can be realized in a tubular reactor operated in gas-liquid segmented flow regime. The separated gas and liquid slugs reduces the axial dispersion to a minimum level, whereas the internal flow circulation of the slugs enhance the gas-liquid mass transfer. The segmented flow regime exists only for small tube diameters. Preliminary experiments have shown that at given reaction and process conditions a maximum tube diameter of 3 mm is required to obtain the desired segmented gas-liquid flow. Because the reactor should later be integrated into an existing miniplant, restrictions regarding the feed flow rate of the plant had to be considered. Under these constraints, the tubular reactor has a length of approximately 200 – 300 m. For compact reactor design the tube was coiled in a helical way.
3. Results and discussion

The helically coiled segmented flow tubular reactor (Fig 1) was built in stainless steel (pressure to 30 bar) and applied for the hydroformylation of 1-dodecene in the TMS system DMF/n-decane using a homogeneous dissolved Rhodium-BiPhePhos-catalyst. The heating of the helix is separated into three zones which can be regulated independently. To achieve a high flexibility regarding the residence time inside the coiled tube it is also possible to shorten the length of the reactor. For the characterization of the hydroformylation reaction progress, samples can be taken along the tube at discrete spots. The samples are afterwards analyzed by GC and GC-MS.

The reactor is operated continuously, thereby closing the recycle line for the catalyst. The impact of the different heating zones on the reaction performance is determined. Additionally, the influence of the pressure drop caused by friction and the chemical reaction on the performance of the reaction will be characterized. The flow rates used for the experiments are chosen in the same manner, that a comparison to already published results (see [3]) is possible. Additionally, a study is made to characterize the gas-liquid mass transfer and the backmixing of the coiled reactor using the same operating flow rates as for the experiments. Finally the results of the experiments are compared with simulations and the predictions of [2], helping to optimize the operation conditions of the reactor system further to maximize the selectivity with respect to the linear aldehyde.

4. Conclusions

For the homogeneously catalyzed hydroformylation of 1-dodecene, using a TMS system for high efficient catalyst recovery, a novel reactor concept is developed with the FPA-study. Form the analysis a tubular reactor was derived which is operated in the segmented flow regime leading to low axial backmixing and adequate gas liquid mass transfer. Due to the coiling of the tube is the reactor very compact and it is also possible to shorten the length of the tube for an adjustment of the residence time. The different heating zones make it possible to optimize the performance of the reactor further. This reactor concept is a very promising approach for the hydroformylation of long chained olefins. A transfer into bigger scales can be realized via the numbering up of the reactor.

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References


Keywords
“coiled tubular reactor”; “hydroformylation”; “long-chain olefins”