**Membrane separation of co-products in hydroaminomethylation reactions in thermomorphic multiphase systems**

Stefan Schlueter1, Annika Koenig1, Bettina Scharzec1, Jens Dreimann2, Mirko Skiborowski\*1

*1 TU Dortmund University, Department of Biochemical and Chemical Engineering, Laboratory of Fluid Separations, Emil-Figge-Str. 70, 44227 Dortmund, Germany*

*2 TU Dortmund University, Department of Biochemical and Chemical Engineering, Laboratory of Industrial Chemistry, Emil-Figge-Str. 66, 44227 Dortmund, Germany*

*\*Corresponding author: mirko.skiborowski@tu-dortmund.de*

**Highlights**

* Innovative separation of co-products by membrane filtration
* Applicability to aqueous and organic solvent systems
* Polyamide membranes favorable in aqueous solvent systems
* Low MWCO membranes required for separation in organic solvent systems

**1. Introduction**

Homogeneous catalysis offers high yields and selectivity at mild reaction conditions but requires the challenging separation and recovery of the valuable homogeneous catalyst. In previous work, it was shown that a combination of thermomorphic multiphase systems (TMS) and organic solvent nanofiltration (OSN) enables effective catalyst recovery in the hydroformylation of long chain olefins [1]. In this combination, a TMS of at least two solvents, which are homogeneous at high temperature in the reactor, forms a two-phase system at lower temperature. This system is first separated by a decanter into a catalyst-rich polar phase and a product-rich apolar phase, which is further processed by OSN to recover remaining catalyst and recycle it back to the reactor.

This contribution focuses on an alternative membrane-assisted TMS concept, which addresses the separation of polar co-products, such as water in hydroaminomethylation (HAM) reactions. Due to its high polarity water accumulates in the polar catalyst phase. Since this accumulation can influence the phase stability of the mixture and thereby negatively affect the reaction as well as the subsequent phase separation, the water content should be controlled. For this purpose, the implementation of a second pressure-driven membrane separation in the recycle stream is proposed. However, the specific type of membrane separation and membrane material selection depend on the TMS for the HAM. This consists of different solvents, depending on the substrates, which are two organic solvents, if the substrates are rather non-polar [2], or an organic solvent and water if more polar substrates are used [3]. In the case of an organic system, OSN is a possible choice, whereas reverse osmosis (RO) represents a suitable choice in case of the aqueous system. The current work presents the results of dedicated membrane-screening experiments for organic and aqueous solvent systems. For a range of solvents, which were selected based on literature data [2 - 4], a number of membranes were screened based on high rejection of the catalyst and selective water removal.

**2. Methods**

Concentrations of the catalyst and the co-product were estimated based on literature data and mass balances. Several commercially available membranes were selected. The experiments were conducted in cross-flow pressure cells. At least three different membrane sheets were measured for each membrane. For the organic system, dimethylformamide (DMF) and methanol (MeOH) as polar solvents were investigated, while a combination of water as the polar and 1-butanol (1-BuOH) as the non-polar solvent was investigated for the aqueous system. The applied ligands were the comparatively small triphenylphosphine (TPP) and tri-sulfonated triphenylphosphine (TPPTS), respectively.

**3. Results and discussion**

For the aqueous system, TPPTS rejections above 99% were measured for all membranes in water. Rejections decreased slightly when 1-BuOH was present in the mixture (Fig. 1a). Membranes made of polyamides are preferential for the selective separation of water since they combine a high rejection of TPPTS with a high rejection of 1-BuOH. Cellulose acetate membranes, however, show a negative rejection of 1-BuOH (Fig. 1b). For both membrane types, a high flux decrease was observed when 1-BuOH was present in the system (Fig. 1c). Based on the screening results a suitable PA membrane was identified and can be used for further investigations.



**Figure 1.** Rejection of TPPTS (a), rejection of 1-butanol (b) and total flux (c) for the aqueous solvent system. Feed pressure pFeed=30 bar, ligand concentration wLigand=0.003 g g-1, w1-BuOH=0.04 g g-1.

For the organic system, several commercial membranes were screened in a similar way. TPP rejections of 97% and higher were observed for a polyimide membrane with a molecular weight cut-off (MWCO) of 150 Da. The same membrane showed the best results in MeOH as well as DMF. Furthermore, selective water separation was possible with water rejections down to – 50%.

**4. Conclusions**

The current results show high prospect for the realization of the targeted co-product separation in HAM reactions in aqueous and organic solvent mixtures. Different OSN and RO membranes were suitable in the corresponding solvent systems. High catalyst rejections and selective water separation were achieved leading to a feasible process concept. Further investigations will focus on the implementation of the membrane separation into a continuously operated miniplant.

**References**

1. J. Dreimann et al., Ind. Eng. Chem. Res. 56 (2017) 1354–1359.
2. A. Vorholt et al., Eur. J. Lipid Sci. Technol. 119 (2017) 1600211.
3. T. Faßbach et al., Adv. Synth. Catal. 360 (2018) 1473-1482.
4. A. Vorholt et al., Chem. Ing. Tech. 85 (2013) 1540-1547.