**Membrane Filtration of Pickering Emulsions for Continuous Liquid/liquid Catalysis – Influence of Membrane Material and Nanoparticle Type**

Anja Drews1, Maresa Kempin1, Tina Skale1

*1 HTW Berlin, School of Life Science Engineering, Wilhelminenhofstr. 75A, 12459 Berlin, Germany*

*\*Corresponding author: anja.drews@htw-berlin.de*

**Highlights**

* Membrane/nanoparticle/solvent combination influences nature of filtration behaviour.
* Gel-forming HDK H20 nanoparticles result in increased permeabilities.
* Suspension filtration can help to explain interactions of solid and liquid phases.

**1. Introduction**

Water-in-oil Pickering emulsions (PE) are currently receiving increased interest as a promising alternative to dispersions or surfactant stabilized emulsions in two-phase (bio-)catalysis. While batch PE catalysis has been demonstrated for a variety of reactions and catalysts, the separation of the two liquid phases and thus continuous operation has been identified as a main challenge [1]. Since then, the feasibility of using membrane filtration for the retention of catalyst containing droplets has been demonstrated [2-3]. In a proof-of-concept, the biocatalyst was still active after more than 8 residence times with feasible space-time-yields of 0.64 g/(Lh) [4]. After these first results, this works aims at investigating the influences of membrane material and type of stabilizing nanoparticles (NP) to yield more generally valid conclusions and to be able to explain individual interactions of present liquid and solid phases.

**2. Methods**

The desired amount of silica NP (HDK H20, H18 or H2000 by Wacker AG) was dispersed in the continuous phase (e.g., dodecene, CPME etc.) and PE were prepared by emulsifying the desired water phase fraction using a rotor/stator homogenizer Ultra-Turrax (UT, IKA GmbH) or ultrasonication (US, Branson Sonifier). In addition, NP suspensions were investigated.

A stirred cell (Merck, Vmax = 91 mL, Aeff = 1.23∙10-3 m2) was used for filtration trials. When pressure was applied to a connected surge tank, solvent was continuously transported to the completely filled stirred cell, which displaced permeate at the same rate. Recorded permeate weight was used to calculate flow rate. Membranes were soaked in solvent and pre-pressurized prior to use. Different ultrafiltration and organic solvent nanofiltration (OSN) membranes were used. Microscopic pictures of PE samples before and after filtration were taken and image analysis software (SOPAT GmbH) was used to measure droplet size distribution. Rheology was measured using a MCR 302 rotational rheometer (Anton Paar GmbH).

**3. Results and discussion**

First results showed that with permeabilities of up to around 40 L/(m² h bar) a large variety of PE could be filtered and concentrated to up to 80% water phase fraction [2-4]. As can be seen in Fig. 1 (left), an unexpected disproportionate flux behaviour with increasing pressure was repeatedly observed for filtration of different PE through a 1 kD PVDF membrane [2-3] which could neither be explained by drop coalescence nor membrane abrasion or swelling. In addition, filtration of a dodecene/H20-PE resulted in higher permeabilities than filtering dodecene alone. This was confirmed for a CPME/H20-PE and a 10 kD membrane [4] and might due to the gel- and network-forming nature of these NP [5]. In contrast, H2000 do not form such networks and result in different behaviour in both emulsion and suspension filtration as well as in rheology.

 

Inhouse NP

pure CPME

**Figure 1.** Left: Pressure stepping (dodecene PE, 2 g/Ldispersed phase HDK H20, US, PVDF 1 kD, [3]).
Right: Flux over time for different NPs (CPME PE, UT, PES 10 kD, 2 bar, [4]).

For all suspensions, almost linear flux increases were found. This means that drops add to the inter-actions, e.g., by adsorbing otherwise unbound residual NP at their interface but also by influencing the rheological behaviour. As opposed to the 1 kD ultrafiltration data shown above, first results indicate that using an OSN membrane with a similar MWCO (900 D) yields feasible permeabilities of around 3 L/(m² h bar), linear relationships and PE fluxes that are lower than pure solvent fluxes.

**4. Conclusions**

Membrane filtration was shown to be a promising process concept for the separation of aqueous PE droplets from continuous organic phases and thus for continuous liquid/liquid reactions in PE. The gel-forming H20 particles yield unexpected and different filtration behavior than other NP. Separating the influences of all present materials will help to understand individual interactions of all phases which is required for optimum material selection and robust process design.

**Acknowledgments**

Financial support by the German Research Foundation DFG (collaborative research centre InPROMPT TRR 63, B6) is gratefully acknowledged. We thank Wacker Chemie AG for kindly providing free particle samples.

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