REGENERATION OF ORGANIC SOLVENTS AND VALUABLE COMPONENTS BY MEMBRANE SEPARATION

F.P.CUPERUS

SOLSEP BV VLIETWEG 81 NL-7335JE APELDOORN
cuperus@solsep.com, www.solsep.com

Membrane separation in organic environments offers a great technological and economic potential. However, currently the technology is still in its infancy. Consequently, organic solvent stable membrane technology developments are focused on materials as well as process engineering. In the past five years SolSep BV has been working on nanofiltration of organic solvents to obtain a solvent or a valuable compound from an organic solvent. At this moment our commercial membrane modules are of the spiral wound type. These have been tested in long term tests in solvents like : methanol, ethanol, acetone, ethyl acetate, toluene, chlorobenzene, other chlorinated solvents, many alkanes, alkenes as well as solvent mixtures. Though cut-off values are very approximate, they can be helpful in choosing the right membrane for the right job. Some MWCO values are shown in table 2.

Table 1. Different SolSep membranes and some characteristics.

Solsep designation	Tmax (degC)	Pmax (bar)	Separation characteristic	Remarks – other solvents
UF010104	90	20	Typical retention of larger molecules ca 10,000 Da	Tested in alcohols, aromatics esters, ketones
NF010206	120	20	R(95%) ~300 Da	Alcohols, esters
NF010306	150	40	R(95%) ~500 Da ionics/acetone R(99%)~300 Da	Alcohols, esters, ketones, aromatics, chlorinated solven reducing atmospheres
NF030306	150	40	Acetone:R(95%) ~500 Da Alcohols R(99%) ~300 Da Extremely stable	Alcohols, esters, ketones, aromatics, reducing atmospheres, chlorinated solvents
NF030306F	120	40	Acetone: (R95%)~300Da Ethylacetate: R (95%) ~300 Da Extremely stable	Alcohols, ketones, aromatics, chlorinated solvents
NF030105F	150	20	Ethanol, methanol R(95%) ~300 Acetone R(95%)~750	alcohols, aromatics, ketones

Table 2. Cut-off and retention of several Solsep membranes.
SF: Sunflower oil (MW~990g/mole; 5wt% in solvent), , PS: polystyrene, PIB: polyisobutylene (wt 0.3% in solvent),MCWO tests executed by EMI Twente

Membrane	Retention (%)-SF		MWCO (g/mole)	
	acetone	hexane	acetone/PS	hexane/PIB
SolSep 010206	99+	70	<200	7000
SolSep 010306	95	30	<200	>7000
SolSep 030105	80	50	300	8000
SolSep 030306	70	85+	>1000	1600

A major point in setting up an application is that the performance of membranes in organic solvents can be very much influenced by the type of solvent, as well as the solute(s) or target component. This is probably due to different kinds of interactions of the feed components with the membranes. A remarkable phenomenon that occurs with polymer as well as ceramic membranes. It can be attributed to interaction (adsorption and sorption, swelling) as well as differences in transport mechanisms from sieving to preferred sorption and diffusion. Figure 1 shows an experiment in which one and the same membrane has been subjected to various solvents and solutes. It is clearly shown that solvent as well as solute may have a big influence of the membrane performance. Of course this is an extreme case but it indicates the necessity of a good membrane choice.

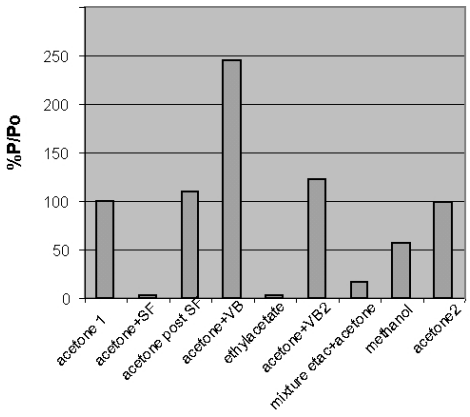

Figure 1. Performance of one membrane sample consecutively subjected to different solvent/solute mixtures.
The experiment starts then: acetone+SF=acetone +sunflower oil, pure acetone, acetone+VB1=acetone + colorant1, pure ethylacetate, acetone+VB2=acetone+colorant2, mixture ethylacetate+acetone, methanol, acetone. Permeability is shown as percentage of first acetone flux.

Recovery systems

The re-use of organic solvent is a general practice in solvent based coating manufacturing. Generally, straight-forward evaporation is being used. However, membrane filtration offers advantage from energy, safety as well as re-use of materials point of view. For high quality coatings a high retention of all components, including resins and fine colorants is necessary. It has been found that NF could be used to upgrade ethyl acetate and acetone mixtures for re-use in industrial application.

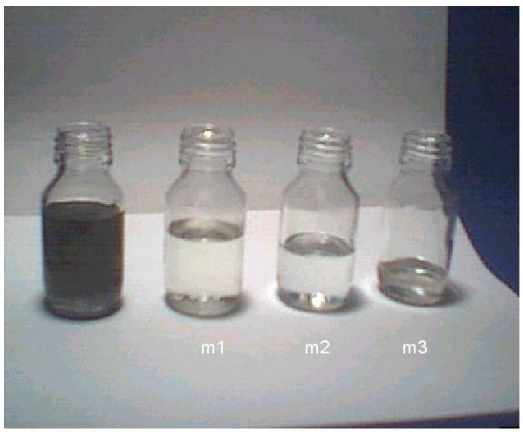

Figure 2. Recovery of solvent from a pigmented -dirty- stream. Black solution is feed, m1..m3 results with 3 different membranes

The reclamation of valuable materials like biomolecules and catalysts are another important field of application for organic solvent stable membranes. For systems that re-use homogeneous catalysts it is vital that the catalysts stays dissolved and active. It has been found in several cases that the insertion of a membrane recovery systems damages the active system and decreases the catalyst's life-time. This phenomenon was studied for a hydroformulation reaction. Figure 3 shows a comparison between a batch operation and a membrane facilitated normalized to equivalent units. The data indicate that the membrane (Solsep010306) has no negative influence on the activity of the catalyst. The membrane retains the cat in the reactor thereby making re-use much easier.

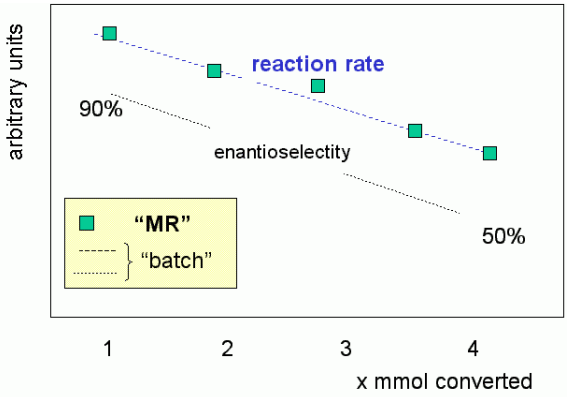

Figure 3. Comparison of a conversion by a homogeneous catalyst: batch and membrane facilitated operation.

Final Remarks

Membranes for separations in organic solvent are an interesting option for existing and new chemical operations. NF and UF are well-developed while RO type of membranes are well underway. NF membranes can be used for the recovery of solvents as well as the purification of valuable target-molecules. The use of membranes in organic solvents can also facilitate new processes with increase efficiency and safety.

Literature

Cuperus. F.P., Ebert, K. Non-aqueous applications of NF (p521-536) in : Nanofiltration: Principles and Applications, Eds: Schaefer, A.I., Fane, A.G., Waite, I.D.. Elsevier 2005