

# METHANOL / DIMETHYL CARBONATE (MEOH/DMC) SEPARATION BY PERVAPORATION

**In the industrial dimethyl carbonate (DMC) synthesis, separation of methanol from DMC is an essential step. This white paper describes the use of pervaporation technology to facilitate this separation in a qualitative and quantitative way.**

## What is dimethyl carbonate?

Dimethyl carbonate, or DMC in brief, is a colorless liquid under standard ambient conditions. A major application is in chemical industry as an intermediate in polycarbonate production. Furthermore, it finds its use as a solvent in paints and coatings. DMC is non-poisonous, and due to its low environmental impact, it is considered a green agent.

## DMC synthesis

Traditionally, DMC was industrially produced using highly toxic phosgene. Although the production yield was high, 'green' DMC did not fit in with 'toxic' phosgene and corrosive HCl as reaction by-product, so alternative ways were developed. Nowadays, the most popular synthesis route is by oxidative carbonylation of methanol: carbon monoxide, oxygen and methanol react to form dimethyl carbonate, with water as a by-product. In order to obtain as high a conversion as possible, excess methanol is normally used, resulting in a methanol/DMC reaction product mixture that is rich in methanol content.

An alternative synthesis route is by transesterification of ethylene carbonate and methanol. Another synthesis route is under development where carbon dioxide and ammonia react to form urea, which reacts further with methanol to DMC.

## How to separate a MeOH/DMC mixture?

All these synthesis routes result in a methanol / dimethyl carbonate (MeOH/DMC) mixture. Separating this mixture to obtain high-purity DMC is not pos-

sible with conventional distillation, the 'workhorse' of chemical separation, where the difference in boiling point of the liquids forms the basis for separation. At atmospheric pressure, DMC boils at 90 °C and methanol boils at 65 °C. However, at atmospheric pressure for this mixture a MeOH/DMC binary azeotrope is formed at a weight composition of about 70%/30%. For an azeotrope - a mixture whose vapor has the same composition as the liquid - this composition will not be changed any further by distillation. So due to this fundamental aspect, a practical implication is that conventional distillation cannot separate methanol from dimethyl carbonate with a higher purity beyond the azeotrope.

A practical effort, although, to break the azeotrope is by pressure swing distillation, where two distillation columns in series are used, each at a different operating pressure. The trick here is that the MeOH/DMC binary azeotrope is pressure-sensitive: at a higher pressure the azeotrope is formed at a lower concentration of the low-boiling component, here methanol. In a typical pressure swing distillation setup, the methanol / dimethyl carbonate mixture enters a lower-pressure (atmospheric) column where the overhead compounds are fed to the second higher-pressure column. In this second column, high purity DMC leaves the bottom of the column, and a methanol-rich mixture leaves the column as an overhead stream.

Compared to other distillation processes such as extractive distillation, pressure swing distillation has the

advantage that no additional separating agent ('entrainer') is used. Such an entrainer has to be separated in an additional step, complicating the original MeOH/DMC separation process. For pressure swing distillation, this separation is complicated due to the setup of multiple pressure levels in the distillation columns.

To facilitate the separation of such compositions around the azeotropic composition, pervaporation is very well suitable - preferably in addition to distillation for the regions far away from the azeotropic composition.

## Pervaporation

Pervaporation is a membrane-based technique to selectively separate a desired component out of a mixture of liquids. It is especially suitable for dewatering of organic solvents or removing organic pollutions from (waste) water streams - separations that are otherwise hard or energy-intensive to do. Pervaporation is an alternative for - or an addition to - distillation. Since pervaporation does not rely on the volatility of to-be-separated components, the vapor-liquid equilibrium does not limit its use.

In pervaporation, the affinity of the desired component with the membrane determines its separation performance. If you want to remove water from a mixture, use a membrane that is hydrophilic ('affinity with water'). Conversely, if you want to extract a contamination of non-polar solvent from water, an organophilic membrane ('affinity with organic compounds') is suitable. In pervaporation, the pressure difference between the liquid at the feed side and an artificially induced vapor at the permeate side (by applying a vacuum there) is the driving force for permeation of the

desired component through the membrane. A high pressure difference as well as a high temperature - since permeation is an activated process - will result in a high permeating flux.

**Pervatech's HybSi® membranes for selective methanol removal**

In the case of MeOH/DMC separation, the hydroxyl-group containing methanol is a protic, polar compound, whereas DMC is aprotic and rather non-polar. To selectively remove the polar methanol from the mixture, a hydrophilic pervaporation membrane would be required. To this end, Pervatech's HybSi® hybrid silica AR membranes are used (i.e. acid-resistant organically modified silica membranes), with a maximum operating temperature of 150 °C, a maximum working pressure of 10 bars and an operational pH range of 0.5-8.5.

**Pervaporation membrane evaluation**

[Van Veen 2016] assessed Pervatech's HybSi® hybrid silica AR membranes for MeOH/DMC separation following the urea synthesis route on lab scale as well as pilot scale. They investigated the effect of temperature and feed composition on single membrane performance. Figure 1 [after Van Veen 2016 and Baik 2024] shows that methanol flux increases as the methanol content in the feed increases. This makes sense, since the driving force for methanol permeation increases when the methanol concentration difference or pressure

difference over the membrane increases. Furthermore, the methanol flux increases with temperature, which is in line with the temperature-dependent activated transport through the membrane. Methanol fluxes in the order of magnitude of 10 kg/m²h are obtained.

In addition, [Van Veen 2016] presented results of long-term lab scale tests (120-150 days) on single HybSi® AR membranes with two MeOH/DMC compositions at 125 °C, as can be seen in Table 1. The selectivity of this type of membrane for methanol is clearly visible, as reflected by the high permeate purity.

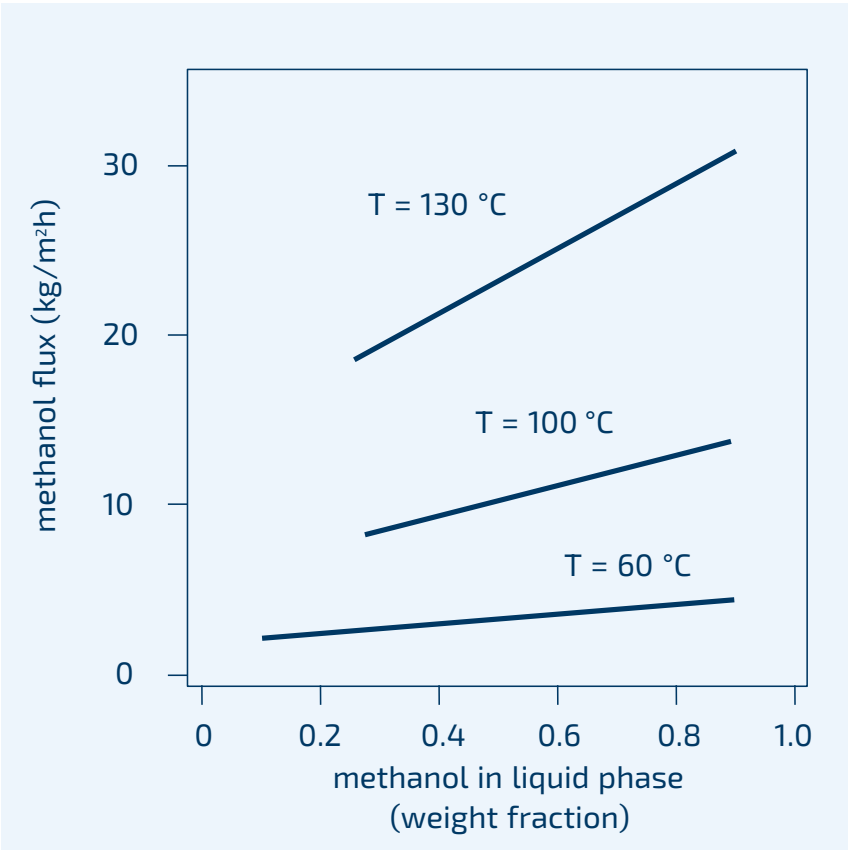


Figure 1: Effect of temperature and feed composition on methanol flux through HybSi® AR pervaporation membranes [after Van Veen 2016 and Baik 2024]

FEED COMPOSITION	MEOH PERMEATE FLUX	DMC PERMEATE FLUX	PERMEATE PURITY
35 wt% MeOH in DMC	~ 7-13 kg/m²h	~ 0.4 kg/m²h	~ 90-95 wt% MeOH
70 wt% MeOH in DMC	~ 22-32 kg/m²h	~ 1-2 kg/m²h	~ 93-97 wt% MeOH

Table 1: Effect of feed composition on methanol flux through HybSi® AR pervaporation membranes, long term results at 125 °C [after Van Veen 2016]

### Pilot tests

[Van Veen 2016] conducted pilot tests at Research Institute of Industrial Science & Technology (RIST) in Korea with a HybSi® AR membrane surface area of about 0.7 m<sup>2</sup> and variations in temperature, permeate pressure, feed flow and feed composition. This resulted in a typical total permeate flux of 15 kg/m<sup>2</sup>h @ 105 °C @ 8 bar @ 600 mbar, with details in Figure 2. Again, the high selectivity of the HybSi® AR pervaporation membrane for methanol is demonstrated with a permeate containing 95 wt% methanol.

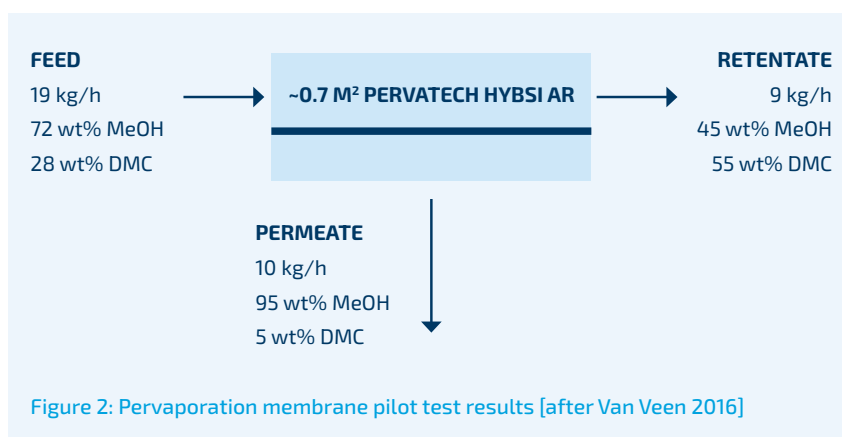


Figure 2: Pervaporation membrane pilot test results [after Van Veen 2016]

### In-house application tests

Pervatech's HybSi® hybrid silica AR membranes were tested in-house to separate methanol / dimethyl carbonate mixtures using different feed temperatures (100 - 125 °C) and permeate vacuum pressures. For a 58 wt%/42 wt% MeOH/DMC mixture this resulted in a typical methanol permeate flux of 19 kg/m<sup>2</sup>h @ 125 °C @ 6 bar @ 220 mbar containing 96 wt% methanol. This is in the same order of magnitude as the external results given above. Figure 3 shows streams if these results are scaled-up to a pervaporation system with a membrane surface area of 22.3 m<sup>2</sup>.

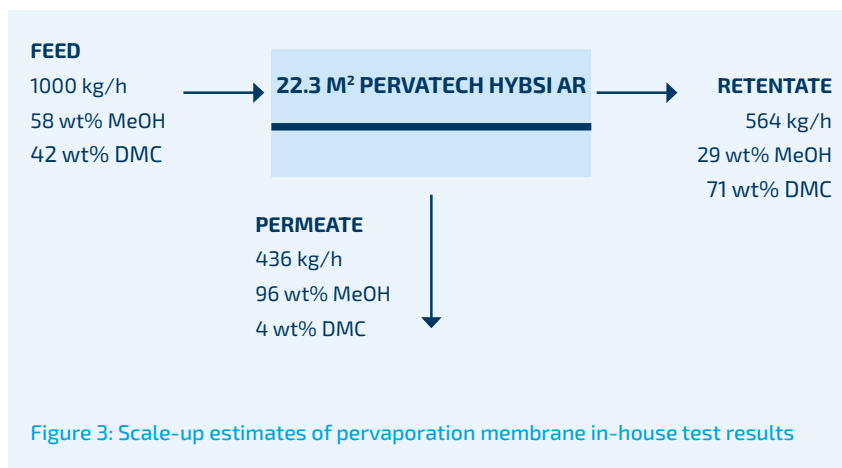


Figure 3: Scale-up estimates of pervaporation membrane in-house test results

### Economics in MeOH/DMC separation by pervaporation

[Van Veen 2016] conducted computer simulations to evaluate the potential reduction in investments and operational costs when a HybSi® AR pervaporation module is included in the purification process to separate the MeOH/DMC mixture. They compared 'standard' pressure swing distillation (PSD) to a hybrid process with a pervaporation membrane module between the two distillation columns, where the overhead components of the first lower-pressure column form the feed stream for the pervaporation membrane, of which the retentate is fed to the second higher-pressure distillation column. This is visualised in Figure 4 [after Van Veen 2016].

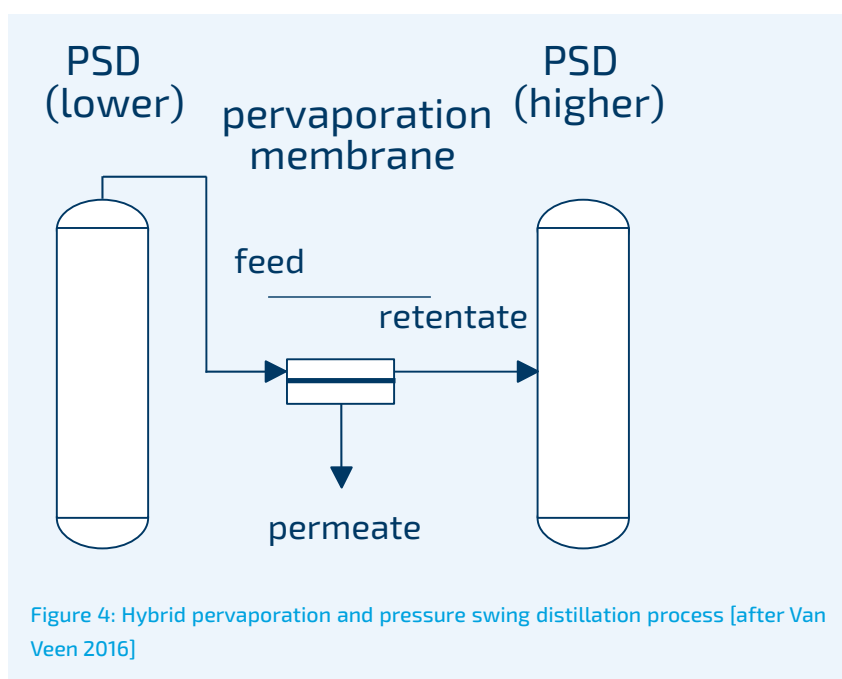


Figure 4: Hybrid pervaporation and pressure swing distillation process [after Van Veen 2016]

Although the DMC production rate of the hybrid system is 16% lower than the standard pressure swing distillation case, the cost saving on purification per ton of DMC produced is as much as 45%, both CAPEX and OPEX related. The simulation results show that capital investments are reduced due to process intensification with a compact design with smaller distillation columns. Operational costs are lower because the energy consumption is lower in the hybrid case. [Van Veen 2016, Baik 2024]

#### To summarize ...

The effective use of pervaporation membrane technology in methanol / dimethyl carbonate separation is clearly demonstrated. Pervatech's HybSi® AR pervaporation membranes are highly

effective in removing methanol selectively from a MeOH/DMC mixture (even) at the azeotropic composition. They perform best at conditions with relatively high temperatures and high methanol concentrations in the feed stream - as is the case in industrial dimethyl carbonate synthesis.

This hybrid solution is a typical example of process intensification to combine the best of both worlds: pervaporation to break the MeOH/DMC azeotrope, and distillation for the separation far away from the azeotropic composition.

#### References

[Van Veen 2016] Henk van Veen, Marc van Tuel, Anatolie Motelica, Jaap Vente, Joon Hyun Baik and Jungho Cho, 'Lab and

*pilot scale pervaporation process for the purification of dimethyl carbonate*', report ECN-M--16-070, conference paper presented at Advanced Membrane Technology VII, Cork, Ireland, September 11 - 16, 2016, publicly available via <https://repository.tno.nl>, retrieved on 2 March 2022

[Baik 2024] Joon Hyun Baik, Kyungtae Park, Cheonwoo Jeong, Joonwoo Kim, Dong Jun Koh, Jung Ho Cho, Henk van Veen, Marc van Tuel, Anatolie Motelica, Jaap F. Vente, 'Pilot-scale azeotrope purification of dimethyl carbonate by cost-efficient pervaporation-assisted distillation', Journal of Cleaner Production 434 (2024) 139963

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