PERVATECH
selective ceramic membranes
process design

Recovery of aggressive solvents, which are difficult to separate

May 2013

Abstract

The recovery of solvents used for aroma extraction is very difficult, because with distillation the small volatile aromatic compounds will go with the solvent into the vapour phase and goes into the top product of the distillation column.

With pervaporation the solvent passes through the membrane and the small aromatic compounds are retained. To achieve this the standard pervaporation membrane has to be modified, making the pore slightly larger, enabling the solvent to pass through, meanwhile retaining the aromatic compounds. Several pervaporation tests and membrane modifications were performed at Pervatech. These tests showed that it was possible to tailor the membrane to an optimum for the separation of volatile aromatic organic components from an Ethanol/Water stream by pervaporation. This separation process results in an increase in the reusability of the ethanol from only 2 times to approximately 50 times. Therefore a cost reduction of more than 90% on ethanol purchase and incineration could be achieved.

Introduction

The recovery of solvents used for aroma extraction is carried out as case study for a.o. Food Industry. In this case the goal is the separation of volatiles from a solvent in a situation conventional techniques do not suffice. These are mixtures of Ethanol/Water with an undesirable odorous organic aromatic dissolved. The goal is to remove the dissolved organic aromatic components by means of pervaporation so the Ethanol can be recycled more often, resulting in a significant cost reduction and to demonstrate the feasibility of pervaporation with ceramic membranes to the industry.

Theory

Pervaporation is a membrane technique where one component of a mixture selectively permeates through the membrane leaving the other component in the retentate. The feed and retentate are in liquid phase and the permeate is in vapour phase in a vacuum which ensures a driving force over the membrane. There will be a driving force as long as the pressure at the permeate side is below the vapour pressure of the permeating component. A lower concentration of the desired component results in a lower vapour pressure and therefore in a lower flux through the membrane since the driving force, pressure difference, will be lower. The permeate is condensed in a condenser and then collected.

The solvents, which have to be separated, are Ethanol/Water from an organic aromatic component. This organic aromatic component is dissolved in the Ethanol/Water mixture at ppm level and has to be rejected by the membrane, enriching the organic aromatic component concentration in the retentate. This principle is depicted in figure 1, which clearly shows that the larger components are rejected by the membrane.

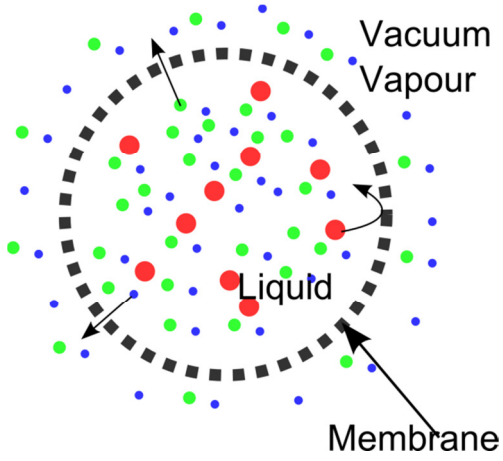

Figure 1: Membrane principle of pervaporation

The membrane has a certain selectivity, which means that not all organic aromatic components are rejected. Therefore it can be favourable to do a second pervaporation step over an organophilic membrane to remove the last traces of the organic aromatic components.

Methods

Samples with industrial feed are being used for the testing. In total three different mixtures consisting of Ethanol/Water plus an organic aromatic substance have been tested on several different modified HybSi® membranes. The tests were carried out on an specifically for this task designed test apparatus. This "Application tester" is depicted in figure 2.

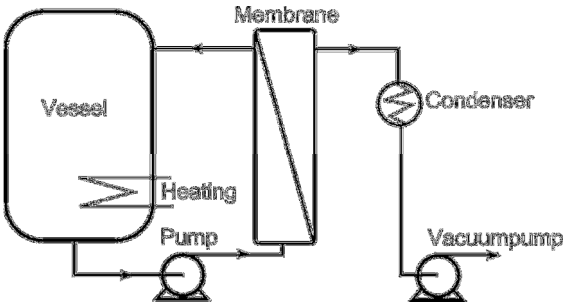

Figure 2: Application tester

First the Vessel of the application tester is filled with the mixture, and then the heating is started together with the pumping of liquid over the membrane. When the desired temperature is reached, vacuum is applied to start the pervaporation process. Next to a sample of the initial feed, samples of permeate and of the end feed are collected for further analysis. The process is stopped when enough permeate is collected or the desired end concentration is achieved. Analysis is typically done by means of refractive index or Karl Fischer. When more data is required samples are being send to the customer for further analysis.

Results

Initially, with the current treatment, the ethanol can be reused in the process 2-3 times. After the first trial on a more open modified HybSi® membrane, the Ethanol could be reused 5-6 times, which is already a huge increase. Then after another modification of the membrane in which the pore size was reduced slightly, almost no traces were found of the aromatic organic component, the organoleptic concentration is now 30-60 times weaker than the initial feed concentration, therefore the Ethanol can be reused approximately 30-50 times and the costs for Ethanol can be reduced considerably.

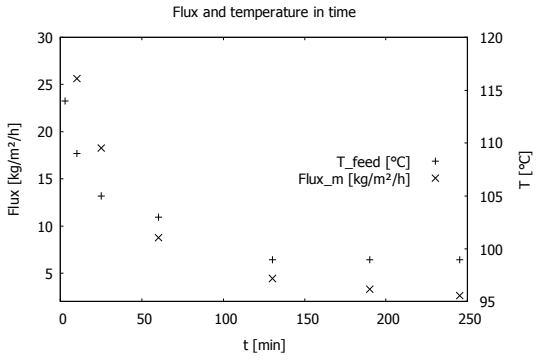

Figure 3: Flux and Temperature in time volatile organic component 1

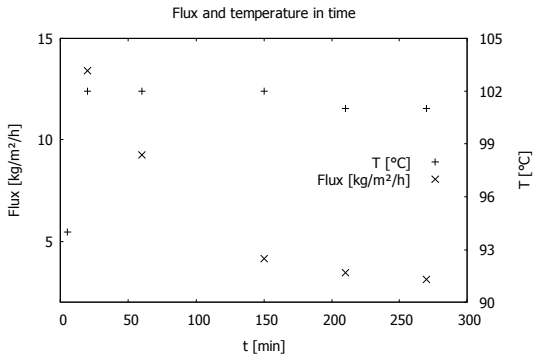

Figure 4: Flux and Temperature in time volatile organic component 2

Figure 3 and figure 4 show an initial decrease in flux due to the decreasing water content in the feed. The flux of mixture 1 and 2 finally goes to an Ethanol flux of around 3 kg/m^2/h.

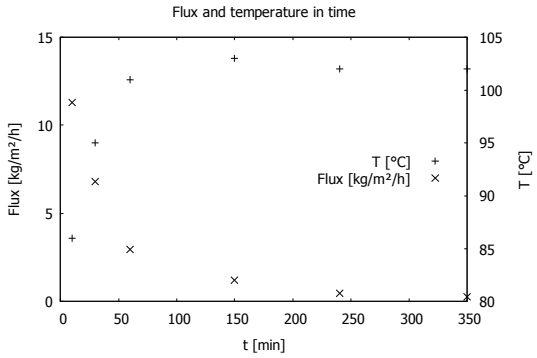

Figure 5: Flux and Temperature in time volatile aromatic component 3

Figure 5 on the other hand shows the pervaporation of mixture 3 of which the flux in time goes to zero because of the clogging of the membrane by particles present in the feed.

After these tests new tests were performed on PDMS membranes to remove the last traces of aromatic organic components in the permeate. In order to do so, permeate is produced by running the application tester with the 3 different feeds until enough permeate is collected for conducting the organophilic pervaporation. For one mixture it was not possible to produce enough permeate due to clogging of the membrane by particles in the feed and therefore a lowered flux.

After the tests were finished the samples were analysed, both organoleptic and by Gas Chromatography. The results from the organoleptic analysis are more promising than the results from the Gas Chromatography since there is always pollution in a test system which is being used for different separation processes. Therefore the concentration of unwanted components from the Gas Chromatography analysis is higher than expected from the organoleptic analysis, which declares the Ethanol from the pervaporation almost technical grade.

With an usage of about 90 ton/year with a maximum of 3x recycle the direct operational costs for the Ethanol case are about k€ 220/year. These costs can be reduced with the newly developed membrane modifications for the recovery of ethanol to a mere k€ 13/year as is depicted in table 1. Therefore reducing the costs by > 90%.

For the process intensification with membranes, calculations have been made for a feed stream of approximately 270 ton/year resulting from the 3 times recycle for the current situation. When 8000 hour/year operating time is used for the calculation of the feed stream to the membrane process, the feed will be approximately 34 kg/hour. For this feed stream, an approximate 8 m^2 of membrane surface area can purify this feed stream.

Table 1: Approximation of costs for and after process intensification

Step	Price/ton [€/ton]	Actual price 3 times recycle [€/year]	Price 50 times recycle [€/year]
EtOH purchase	900	81.000	4.860
Transport	150	13.500	810
Incineration	1.400	126.000	7.560
Total	2.450	220.500	13.230

Discussion

For this case the tests went really well and with each modification the membrane was better equipped to keep the volatile organic components in the retentate. Therefore it is possible with this pervaporation step to clean the ethanol to a technical grade so it can be reused for approximately 50 times resulting in an approximate cost reduction of 200.000 €/year.

Although the Ethanol can be reused approximately 50 times, the removal of “last traces” was not accomplished. This could be accomplished with an additional polishing step.

In order to validate the organoleptic findings with gas chromatography analysis, extra tests have to be performed on the volatile aromatic organic mixtures. These test will be dedicated towards optimising the separation, continuously running capacity and enabling CAPEX-OPEX calculations.

Conclusions

Tests performed at Pervatech on the industrial feed shows the potential of the pervaporation membrane technology for the cleaning of Ethanol streams and the possibilities for tailoring the membrane to the desired output.

In order to scale the process to a real production plant, extra tests have to be performed at Pervatech.