Batch solvent recovery by hybrid separation processes

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ABSTRACT

Solvent recovery of waste streams is now a major issue in most pharmaceutical and specialty chemical companies. Therefore the need of an efficient and sustainable separation process is becoming more and more interesting. This paper presents a hybrid separation process for azeotropic solvent mixtures, which is a combination of a clean, efficient technology (pervaporation) and a more robust technology (azeotropic distillation). Pervaporation as a stand-alone process is not sufficiently selective for these separations, while azeotropic distillation is regarded as insufficiently sustainable. The combination of both in a hybrid system, however, can combine sustainability with selectivity. The developed hybrid concept was evaluated on a real industrial acetonitrile/toluene mixture from the solvent recycler, De Neef Chemical Processing.

Introduction

Many fine chemicals and speciality chemicals are produced in batch processes, which generate solvent mixtures as ‘waste’. Due to the interaction between these solvents, azeotropes frequently occur. Therefore these solvents cannot be easily recovered by conventional distillation, and the solvent mixtures are usually incinerated instead. It is clear that the recovery of these solvents would be a direct cost saving for many chemical manufacturing companies and a large benefit for the environment (Van Baelen et al., 2008). In general the separation of azeotropes in continuous systems occurs by azeotropic or extractive distillation (Hilmen, 2000), in which a third component, the entrainer, is added to break the azeotrope. A second conventional distillation step is needed to purify one of the obtained solvent phases and recover the entrainer.

The increased world-wide competitiveness in production has forced the chemical industry to improve their current processes. Consequently, the reorganization of existing process designs and the development of new processes, with the possible integration of new technologies, is of growing importance to industry. Membrane technologies have emerged as an additional category of separation processes to the well-established thermal separation processes. The advantages of membrane separations include high selectivity, low energy consumption, moderate cost to performance ratio, and compact and modular design.
In recent years, pervaporation has established itself as one of the most promising membrane technologies. It involves the separation of liquid mixtures by selective evaporation of target compounds through a nonporous polymeric or nanoporous inorganic membrane. This selective vaporization is generally achieved by establishing a vacuum at the permeate side of such membrane. Pervaporation offers potential solutions in a wide range of applications from the well-established dehydration of solvents to the recovery of organics from water and the separation of organic/organic mixtures. In contrast to distillation, pervaporation is not governed by the vapour-liquid equilibrium of the mixture to be separated, but by the selectivity of the membrane. The latter is determined by the solubility of the permeants in the membrane and their diffusivity through the membrane.

As pervaporation does not depend on differences in volatility, it is particularly attractive in the separation of azeotropic and close-boiling point mixtures or when heat sensitive molecules are present, all situations where conventional distillation fails, or is at best ineffective or expensive. Thanks to the selectivity introduced by the membrane, only the permeating molecules need to be vaporized, while in distillation the entire feed is subjected to repeated vaporization-condensation cycles. This explains the intrinsically energy-efficient character of pervaporation. The membrane is generally chosen in such way that the minor component in the mixture selectively permeates, thereby minimizing the consumed latent heat of vaporization.

However, pervaporation as a stand-alone process has often to compete with conventional, reliable separation processes like distillation, liquid-liquid extraction, adsorption and stripping, the cost of which can be readily calculated. Despite its clear advantages, in many cases pervaporation alone may not supply products suitable for further processing or waste disposal in accordance with environmental standards. Therefore, hybrid processes are regarded as a means of overcoming these limitations.

In an attempt to combine the advantages of robust standard thermal separation processes and an alternative, energy-efficient separation technology, a hybrid distillation-pervaporation batch process was developed for the separation of azeotropic batch solvent mixtures. This hybrid concept is a combination of separation techniques that, in many cases, individually fail in satisfactorily and/or efficiently separating azeotropic solvent mixtures and purifying the solvents to the requisite level. While azeotropic distillation is regarded as expensive and insufficiently sustainable due to the addition and recovery of entrainers that can moreover contaminate the solvents to be separated, pervaporation as a stand-alone process does often not offer sufficient selectivity in the separation of solvent mixtures. The latter can amongst other reasons be explained by the lack of dedicated pervaporation membranes for organic-organic separations on the market. By combining both separation techniques in a hybrid process, however, it is anticipated that solvents could be recovered from waste streams and purified to the targeted quality in an energy-efficient, thus competitive way.

This hybrid separation process was applied to several industrially relevant binary solvent mixtures. In general, an entrainer forming a heteroazeotrope with one of the solvents in the mixture was added first. The search for suitable entrainers was based on residue curve analysis (Rodríguez-Donis et al. 2001; Gerbaud et al., 2006), using RegSolExpert® (ProSim S.A.) software. The ternary solvent mixture was then separated by heteroazeotropic distillation in which the two liquid phases constituting the heteroazeotrope were split by a decanter. Subsequently, one of these phases was further purified by pervaporation. This contribution will focus on the heteroazeotropic distillation of an acetonitrile/toluene mixture, and the subsequent processing of one of the obtained heteroazeotrope phases by pervaporation.

HETEROAZEOTROPIC Distillation

2.1 Residue curve analysis

Acetonitrile and toluene cannot be separated with conventional distillation because of the appearance of a homogeneous azeotrope at 88 mole% acetonitrile with a boiling point of 80.5°C. The RegSolExpert® software selected hexane as the most suitable entrainer. As can be seen in Figure 1, acetonitrile and hexane form a heterogeneous azeotrope at 39 mole% acetonitrile with a boiling point of 56.0°C. The hexane rich light phase is sent back to the top of the column. The acetonitrile rich heavy phase will be further purified with pervaporation. Toluene will remain in the boiler at the end of the distillation.

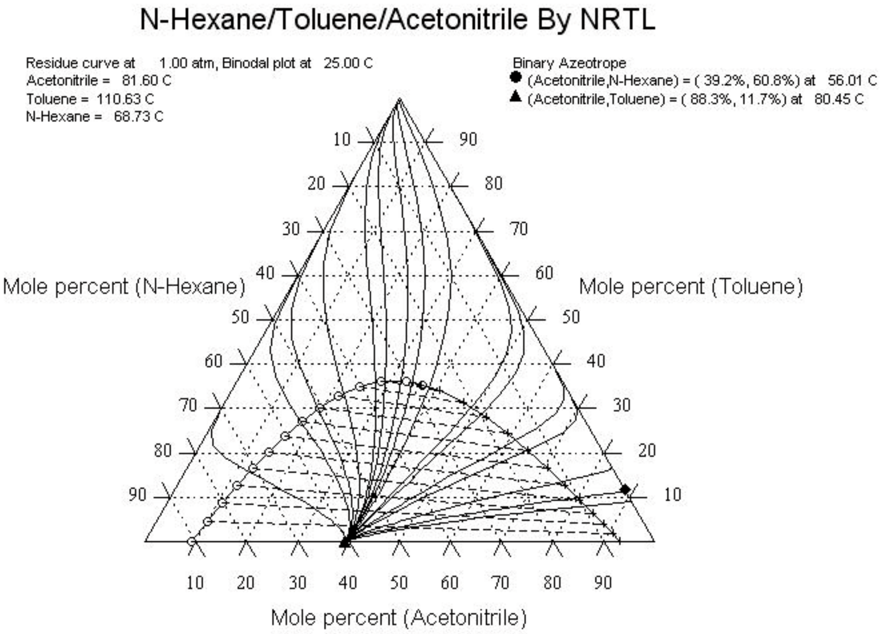

Figure 1. Ternary diagram of acetonitrile, toluene and hexane.

2.2 Materials and methods

2.2.1 Experimental setup

The heteroazeotropic distillation was tested on a small and a large scale experiment. The

chemicals used for the small scale experiment were obtained from VWR Prolabo with a purity of 99.9% on GC assay. The small scale distillation column has a length of 105 cm and a diameter of 3 cm, The column is filled with 3x3cm rashig rings and has 30 theoretical plates. The mixture was heated electrically.
A real industrial toluene/acetonitrile mixture, provided by solvent recycler De Neef Chemical Processing, was used for the large scale experiment. The Heckmann distillation column with 30 real plates is connected to a boiler with a capacity of 80 litres. The mixture was heated with saturated steam.

The left part of Figure 2 shows the distillation setup, which is similar for the small scale and the large scale experiment. The cooled vapour is sent back to the column with a reflux ratio of 10/1 to 1/1. The part of the cooled vapour which is not send back to the column is led to a decanter. The light, hexane rich phase is completely sent back to the column. The heavy phase is collected for pervaporation experiments.

The reflux ratio in the small scale experiment (volume mixture: 0.5 litres, composition: 32.1 vol% acetonitrile, 40.0 vol% hexane, 27.9 vol% toluene) was 10/1 at the start of the distillation, but was gradually lowered to 1/1. The reflux ratio of the large scale experiment (volume mixture: 69 litres, composition: 14.5 vol% acetonitrile, 4.3 vol% hexane, 81.2 vol% toluene was kept constant at 10/2.

2.2.2 Sample analysis

All samples were analysed in triplicate on a chromopack 9002 GC-FID equipped with a CP-sil-5 CB column with a length of 25 m, thickness of 5 µm and a diameter of 0,39 mm. Samples were dissolved in methanol and iso-octane was used as internal standard. The injection volume was 0,1 µl. The temperature of the GC oven was set at 80°C for 4 min, raised for 2 min at a rate of 40°C/min and held for 2 min at 160°C. The injector and detector temperatures were set at 200°C.

2.3 Results

In a preliminary experiment on the small scale column (reflux ratio: 10/1), the composition of the heavy and light phase of the heteroazeotrope was determined experimentally at 95.2 mole% acetonitrile and 4.8 mole% hexane for the heavy phase, and 94.5 mole% hexane and 5.5 mole% acetonitrile for the light phase. These results were in good correlation with simulation of the ternary diagram in Aspen Plus with the NRTL model.

Table 1 shows the results of the small scale and large scale experiments, conducted as described in paragraph 2.2.1. In the large scale test, a minimum volume of hexane, equalling the hold-up of the column, was used. It can be seen that the vapour compositions of the different fractions of the small scale and large scale experiment are in good agreement with each other, and moreover in line with the compositions measured in the preliminary small scale experiment at a constant reflux ratio of 10/1. The toluene fraction is the condensed vapour with a temperature starting at 109°C. The distillation is stopped when the toluene fraction has a purity above 99 vol%. At this point the residue contains almost pure toluene.

Table 1. Results distillation experiments.

	Start mixture (mole%)	***Heavy phase (mole%)***	***Toluene fraction (mole%)***
Small scale experiment	51,9 acetonitrile 25,9 hexane 22,2 toluene	95,6 acetonitrile 4,4 hexane 0,0 toluene	0,4 acetonitrile 0,5 hexane 99,1 toluene
Large scale experiment	25,8 acetonitrile 3,1 hexane 71,1 toluene	95,4 acetonitrile 4,4 hexane 0,2 toluene	0,8 acetonitrile 0,4 hexane 98,8 toluene

Pervaporation

3.1 Materials and methods

Anticipating on a hybrid separation process, a series of commercial pervaporation membranes was screened on a binary acetonitrile-hexane mixture with composition corresponding to the heavy phase obtained in the heteroazeotropic distillation, i.e. 95.5 mol% acetonitrile and 4.5 mole% hexane. Both flat sheet polymeric and tubular inorganic (silica, zeolite) membranes, with different "philicities", were tested on their selectivity toward hexane, the minor constituent in the mixture. In addition to these commercial membranes, a novel thin film composite membrane with top layer based on the high free volume polyacetylene poly[1-(trimethylsilyl-1-propyne] that was recently developed at VITO and optimised for alcohol/water separations was tested (Claes et al., 2012). Table 2 provides an overview of the tested membranes.

All tests were carried out on a laboratory developed pervaporation set-up system, described elsewhere (Claes et al., 2012). In case of polymeric membranes, measurements were carried out in duplicate

Table 2. Tested pervaporation membranes.

Membrane	***Supplier***	***Top layer material***	***“Philicity”***	***Primary use***
PERVAP 2255-70	Sulzer Chemtech	Polyvinylalcohol (PVA)	Hydrophilic	Solvent dewatering
Microporous titania	Pervatech BV	Titania	Hydrophilic	Solvent dewatering and removal of small organics from solvents
PERVAP 4060	Sulzer Chemtech	Polydimethylsiloxane (PDMS)	Hydrophobic	Organics removal from water
Pervatech PDMS	Pervatech BV	Polydimethylsiloxane (PDMS)	Hydrophobic	Organics removal from water
ZSM-5	Fraunhofer IKTS	ZSM-5 zeolite	Hydrophobic	Organics removal from water
PTMSP-silica	VITO	Poly[(1-trimethylsilyl)-1-propyne] (PTMSP)	Hydrophobic	Organics removal from water
POL_AL_M1	PolyAn GmbH	Unknown	Target-organophilic	Alcohol removal from solvents
POL_OL_M1	PolyAn GmbH	Unknown	Target-organophilic	Olefin removal from solvents
POL_AR_M1	PolyAn GmbH	Unknown	Target-organophilic	Aromatics removal from solvents
Hydrophobic membrane	PolyAn GmbH	Unknown	Target-organophilic	Removal of apolar solvents from solvent mixtures

Two circular disks with a diameter of 25 mm were cut from the same membrane sheet, placed into two parallel test cells and sealed with Kalrez o-rings. The tubular membranes, all with length of 250 mm, external diameter of 10 mm, internal diameter of 7 mm, and active separation layer at the lumen side, were applied in a special test cell and also sealed with Kalrez o-rings. Subsequently, the feed mixture was circulated through the membrane test cells at approximately 12 L.h^{-1}. The feed was kept at 30°C, 50 °C or 70°C using a thermostat-controlled oil bath, and the vapour-side pressure was maintained at approximately 0.04 mbar. The permeates were condensed in two stainless steel vessels, each immersed in a cooling cylinder filled with liquid nitrogen. During the tests the feed, permeates and retentate were sampled at regular intervals. Membrane fluxes J (kg m^{-2} h^{-1}) were determined by weighing the permeate samples and calculated according to Eq. 1:

$$J = \frac{m}{A \times t} \qquad (1)$$

where m represents the weight of permeated liquid per unit membrane area A and time t. The hexane/acetonitrile separation factorwas calculated according to Eq. 2:

$$\alpha_{Hex/ACN} = \frac{Y_{Hex}}{Y_{ACN}} \times \frac{X_{ACN}}{X_{Hex}} \qquad (2)$$

In which X and Y refer to concentrations (wt.%) in the feed and permeate, respectively. All samples were analysed as described in paragraph 2.2.2.

3.2 Results

From the ten screened membranes, all tested at 30°C, 50°C and 70°C, the four hydrophobic membranes, i.e. the PDMS based membranes PERVAP 4060 and Pervatech PDMS, the ZSM-5 zeolite membrane and the VITO developmental membrane, clearly showed the most promising separation performance, in terms of total permeate flux and acetonitrile/hexane separation factor. Permeate fluxes up to 40 kg m^{-2} h^{-1} at 30°C (PERVAP 4060 and VITO membrane) and values up to about 35 (VITO membrane), corresponding to a hexane permeate concentration of about 47 mole% were measured. With all other membranes, including the PolyAn membranes that are specifically marketed for the separation of organic-organic mixtures, no significant hexane enrichment could be achieved and fluxes were generally low.

Further tests at 30°C with these four hexane selective membranes, using a test cell with an active membrane area of 44 cm^2, confirmed these results and allowed to get insight in the concentration dependency of the fluxes and separation factors, anticipating on a batch pervaporation process. These tests also demonstrated the chemical integrity and performance stability of the membranes.

Hybrid concept

The vapour from the top of the distillation column has to be cooled to get a phase separation. Therefore it cannot be led directly to the pervaporation unit. The hybrid concept is thus a cascade of two separation processes and is shown in Figure 2.

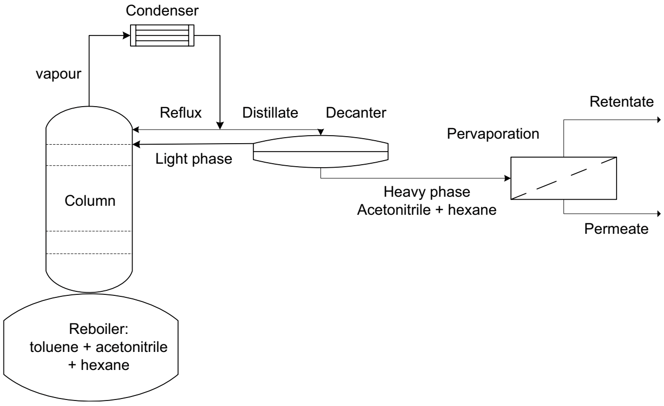

Figure 2.Scheme of the hybrid concept.

CONCLUSIONS

A hybrid concept, which is a combination of a heteroazeotropic distillation and pervaporation, was evaluated on a real industrial acetonitrile/toluene mixture from the solvent recycler, De Neef Chemical Processing. Hexane was used as entrainer to form a new, low boiling acetonitrile/hexane heteroazeotrope. The light, hexane rich phase was send back to the column and the heavy, acetonitrile rich phase was purified by pervaporation. Hydrophobic membranes clearly showed the most promising separation performance, in terms of total permeate flux and hexane/acetonitrile separation factor.

ACKNOWLEDGEMENTS

This work was funded by The Environmental & Energy Technology Innovation Platform (MIP), founded by the Flemish Government.

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