



*Dedicated to the memory of
Academician Dr. Eng. Emilian BRATU (1904–1991)*

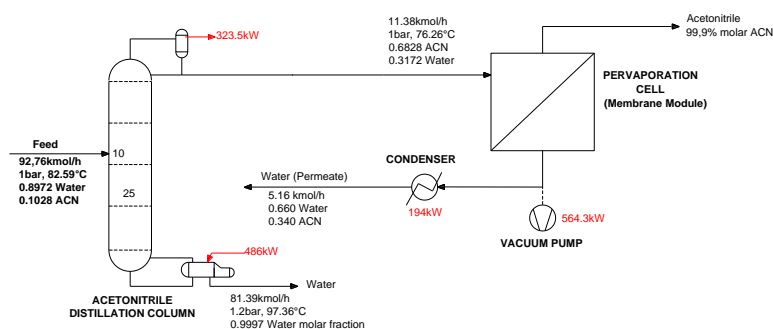
ANALYSIS OF THE SEPARATION OF ACETONITRILE-WATER MIXTURE

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Acetonitrile (ACN) obtained as a by-product in the ammonification process of propene (SOHIO process) is necessary to be dehydrated. The presence of the azeotropic point limits the use of distillation for the separation of the mixture acetonitrile-water. Two alternative approaches are studied: extractive distillation and a hybrid process distillation-pervaporation. The both obtained pure ACN and for the point of view of energy consumption, the hybrid process proved to be more favorable.



INTRODUCTION

The chemical industry is interested in looking for economic ways to reduce energy consumption and to avoid the use of auxiliary agents for the separation of mixtures. Separating non-ideal mixtures has always been a difficult task in the chemical industry. Various approaches have been proposed for a continuous improvement of process performance, choosing between alternate separation

processes. Distillation is one of the technologies often applied in industry to separate multicomponent mixtures, even though it is “the industries’ most energy-intensive technology”.¹ Liquid-liquid extraction² and reactive extraction^{3,4} are also an option, with or without liquid membranes. However, hybrid separations are gaining more and more attention, being used in various combinations.^{1,5} This special interest for some new approach in separation techniques led to

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the organization of an AIChE Annual Meeting in 2011 dedicated only to such processes. Pervaporation (PV) can be considered as an alternative separation method to conventional techniques, with possible industrial applications for separating non-ideal liquid mixtures with near boiling points and for breaking azeotropic mixtures in cases where distillation is energy intensive or requires the use of an auxiliary agent. The procedure is mainly used for the dehydration of organic mixtures, the removal of organic substances from aqueous mixtures and the separation of organic mixtures. As pervaporation is not limited by liquid-vapor equilibrium (L-V) it can realize large separation degrees. More than that it can be simply realized, it is environmental friendly and has high potential for energy-savings. During the separation process, the mixture to be separated is vaporized downstream from the pervaporation membranes at low pressure.^{6,7}

Acetonitrile is an organic solvent widely used in industry.⁸ Consequently, a substantial quantity of acetonitrile-water mixture is generated during

various chemical manufacturing processes. Purifying water contaminated with acetonitrile is particularly important in terms of environmental protection and economic reasons. On the other hand, recovering and recycling acetonitrile from wastewater can contribute to cost savings and resource conservation, making the process more economically viable. Thus, efficient separation methods play a crucial role in recovering ACN and also avoiding environmental contamination.⁹

This study presents a technological comparison between the extractive distillation and the hybrid distillation – pervaporation process using (poly)vinylalcohol membranes. As a case study, dehydration of acetonitrile (ACN) obtained as a byproduct of the propene ammonoxidation process (Fig. 1) is investigated.⁸ The presence of the azeotropic point (Fig. 2) limits the use of distillation, and pervaporation with a (poly)vinylalcohol membrane (PVA) has been shown to be an alternative for acetonitrile separation beyond the azeotropic liquid-vapor equilibrium.

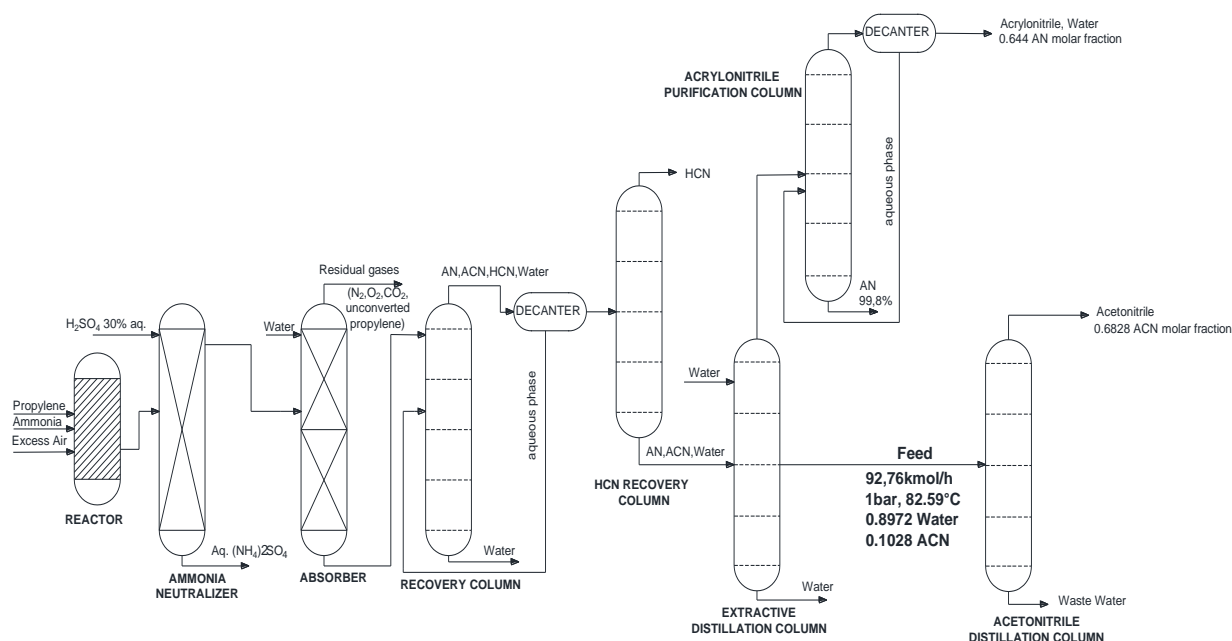


Fig. 1 – Ammonoxidation process (SOHIO).

PROCESS MODELLING

The phase equilibrium (VLE) of the mixture under isobaric conditions was studied in the frame of Aspen Plus simulator, using the NRTL

thermodynamic model. The presence of an azeotrope (69.71% ACN) (Fig. 2a) formed at the temperature of 76.4°C (Fig. 2b) and the pressure of 1bar limits the utilization of distillation for dehydration of acetonitrile.

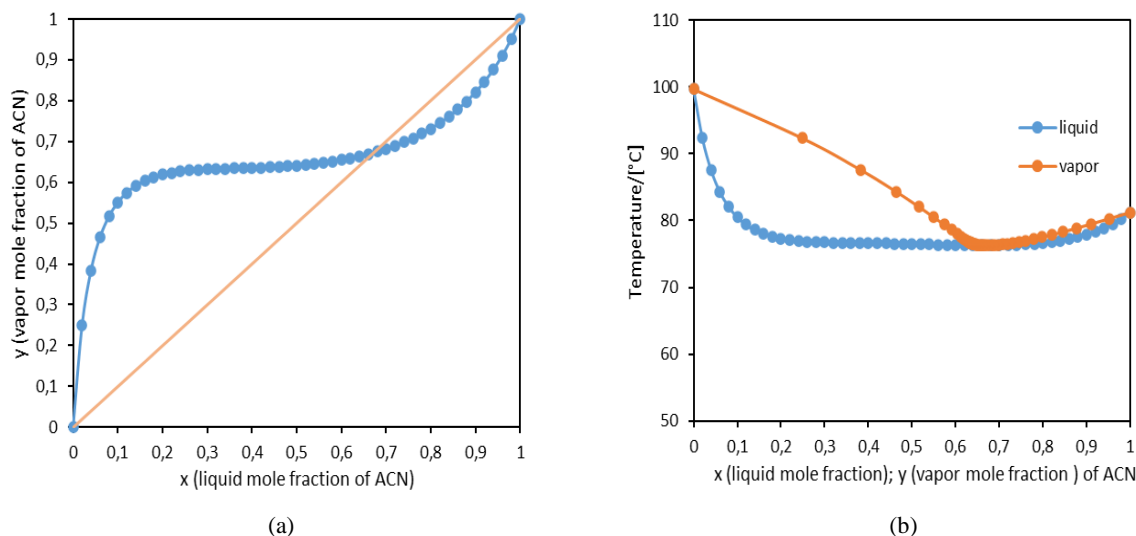


Fig. 2 – Vapor-liquid equilibrium of acetonitrile-water mixture.

Several advanced separation schemes can be chosen to separate this azeotropic mixture. Among the already adopted solutions are the following:⁸ pressure-swing distillation, azeotropic distillation, extractive distillation, membrane separation processes (pervaporation).

Pressure-swing distillation is effective, but generally requires more energy and higher investment costs due to the pressure demands within columns.¹⁰ In extractive and azeotropic distillation a third component is necessary, called entrainer. In azeotropic distillation a light entrainer is used, but this method requires a large additional energy to vaporize the mixture. Extractive distillation employs a heavy entrainer to modify the relative volatility of the components, allowing to produce pure components as the top products without the need for solvent evaporation, as required in azeotropic distillation. Consequently, extractive distillation is generally preferred over azeotropic distillation.¹¹

High-purity acetonitrile can be obtained with the extractive distillation process to separate it from water using ethylene glycol as entrainer.⁸ The entrainer must be compatible with the azeotropic binary system, being able to break the azeotropic point. Additionally, entrainers should have stable properties, high selectivity and low toxicity. Ethylene glycol has qualities such as low viscosity, vapor pressure and toxicity.

RESULTS AND DISCUSSION

The acetonitrile distillation column from Fig.1 is replaced with an extractive distillation followed by a column for solvent recovery, in the first approach of this study, or coupled directly with the pervaporation plant, in the second approach. Both plants must produce ACN of more than 99 % mol purity.

Extractive distillation process

Process simulation in Aspen HYSYS based on the flowsheet presented in Fig. 3 enabled to find out the operating conditions and the extractive distillation column configuration for acetonitrile purity greater than 99% mol: 35 theoretical stages, feed position at 30th stage, entrainer feed stage 5.

The bottom stream of the extractive distillation column was directed to the entrainer recovery column to recover the entrainer. The purified entrainer stream, at the bottom of the recovery column, is cooled and then returned to the extractive distillation column. To compensate the minor losses of the entrainer during the processes, an additional makeup stream is introduced. The makeup stream was mixed with the recycled entrainer before feeding into the extractive distillation column. It should be noted that the

entrainer recovery column requires 15 theoretical stages and an energy consumption of 1215 kW in

reboiler. The recycled entrainer maintains a purity level exceeding 99 % mol.

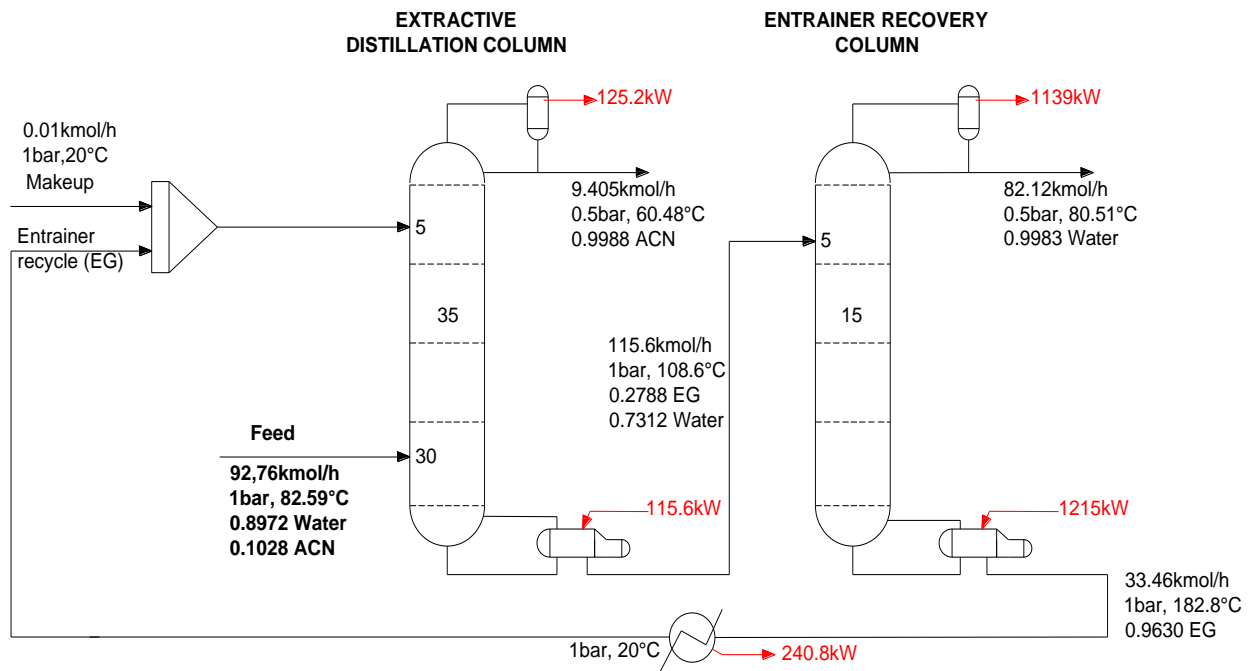


Fig. 3 – Extractive distillation process.

Pervaporation process

The separation by pervaporation is based on partial pressure difference between the two sides of the membrane. No additional extraction agent or extensive heat is involved during the separation

process. The membrane preferentially facilitates the transport of the component with higher permeability. Due to the low pressure in the downstream, the permeate is obtained in the vapor phase.

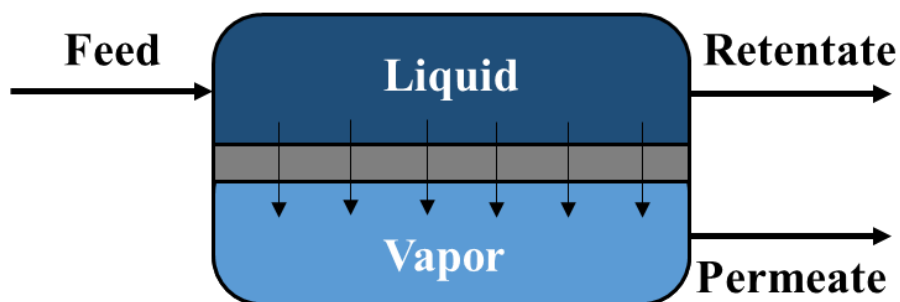


Fig. 4 – Schematic of pervaporation process.

The permeate flux for component i (ACN or water) can be calculated from the equation

$$J_i = \frac{P_{mi}}{\delta_m} \cdot (P_{vi} \cdot x_i \cdot \gamma_i - p_p \cdot y_i)$$

where J_i – permeate flux for component i ; P_{mi} – permeability of membrane for component i ; δ_m – membrane thickness; P_{vi} – vapor pressure of component

i ; γ_i – activity coefficients; x_i , y_i – molar fraction of component i in retentate and permeate, respectively.

The vapor pressure of the pure components was calculated using the Antoine Equation:

$$\lg P_{vi} = A - \frac{B}{T + C},$$

where the temperature is in K, and vapor pressure results in Pa

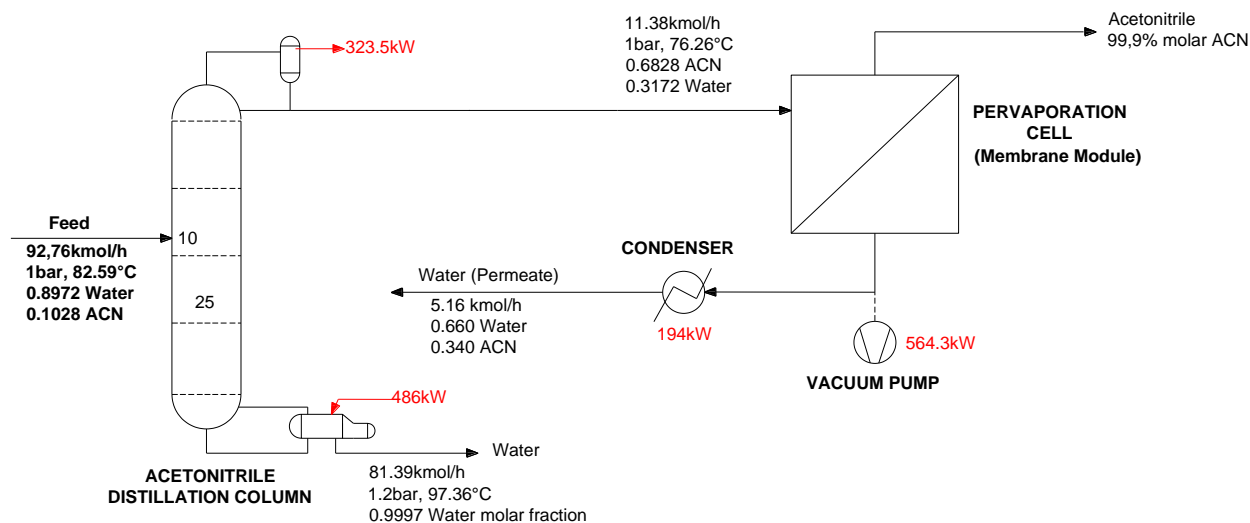


Fig. 5 – Diagram of hybrid distillation-pervaporation process.

Table 1

Constants used in calculations for the Antoine Equation¹²

	A	B	C
Acetonitrile	7.33986	1482.290	250.523
Water	8.07131	1730.630	233.426

The permeance of components through membrane was calculated with the below equation:¹²

$$\frac{P_{mi}}{\delta_m} = a \cdot \omega_w^2 + b \cdot \omega_w + c, \text{ where } \omega_w \text{ is the water}$$

mass fraction, and the permeance results in

$$\frac{\text{kg}}{\text{m}^2 \cdot \text{s} \cdot \text{Pa}}$$

Table 2

The constants of the above correlation used to evaluate the membrane permeance¹²

	a	b	c
Acetonitrile	5.75E-07	-1.02E-07	5.26E-09
Water	5.61E-06	-9.06E-07	5.67E-08

In the membrane plant, with a membrane area of 95 m², an acceptable recovery (80 %) of acetonitrile with a purity of about 99 % is ensured. However, a significant amount is lost in the permeate stream. For this reason, the permeate must be either recirculated to the distillation column or further treated to ensure the environmental regulation referring to the wastewater quality.

CONCLUSIONS

Although the recovery rate of acetonitrile is only 80% in case of pervaporation compared to 98% in case of extractive distillation, using pervaporation as a method of separation of azeotropic mixture presents major advantages, by consuming much less energy. In the case of ethyleneglycol extractive distillation, the total energy consumption for column reboilers is 1330 kW. In the case of pervaporation the energy consumption is much lower, mainly necessary for the vacuum pump to maintain the permeate pressure condition. Pervaporation has other features such as: it is not limited by the L-V equilibrium, simple achievement, lack of additional pollution caused by the extractant. These characteristics are often difficult to obtain in many cases with traditional processes.

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