Removal of ethanol from pharmaceutical process wastewater with distillation and hydrophilic pervaporation

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Abstract
The work is motivated by an industrial problem, which is ethanol removal from pharmaceutical process wastewater. To complete this goal hybrid operation is investigated. Ethanol dehydration with combination of distillation and hydrophilic pervaporation is applied. The target of this work is to rigorously model and optimize this hybrid operation in professional flowsheet simulator environment. The number of minimal theoretical plates of distillation column and minimal effective membrane transfer area are determined. Considering the results, it can be concluded that, the distillation and hydrophilic pervaporation processes are suitable for separation ethanol and water in 99.5 weight percent purity and its cumulated heat duty is approx. 48% of extractive distillation.

INTRODUCTION

Water/alcohol separation is a well-known example of pervaporation (PV) process in chemical industry.
Ethanol (EtOH) forms minimal boiling homogeneous azeotropic mixture with water, which means separation problem. Alcohol content above 96 weight% can not be achieved with conventional distillation techniques (Marsden 1954), as it can be seen in **Figure 1**.
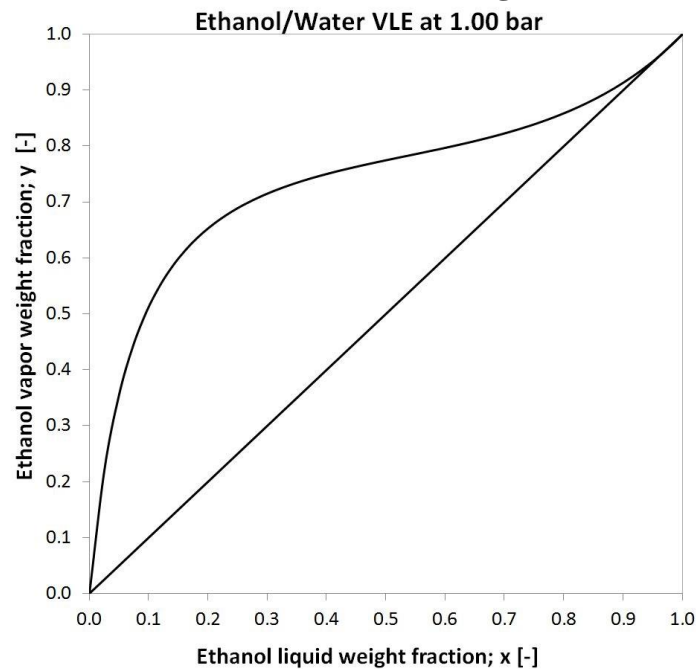

Figure 1 Vapour-liquid equilibrium of EtOH-Water mixture

Ethanol-water mixture can be separated with extractive distillation. The most commonly solvents are ethylene glycol (Meirelles *et al.* 1992; Ravagnani *et al.* 2010; Li & Bai 2012; Rojas *et al.* 2016) and glycerol (Gil *et al.* 2012), which can be used as entrainer. This technique has been widespread in the chemical and environmental industries, but it is not economical in many cases in the reason of its high operation cost. In contrast, the hybrid methods, where the distillation can be combined with other separation method, mainly with membrane processes can open new horizon for the alcohol separation (Koczka *et al.* 2007a; Koczka *et al.* 2007b; Koczka 2009; Koczka & Mizsey 2010; Toth 2015).

The separation process of the pervaporation is determined by the selective sorption, solution and diffusion in the membrane. This process is mainly used for dehydration of organics (Lipnizki *et al.* 1999a; Hsueh *et al.* 2005; Koczka *et al.* 2007a), removal of low concentration organics from its aqueous mixtures (Lipnizki *et al.* 1999b; Aroujalian *et al.* 2003; Konieczny *et al.* 2008) and organic-organic separation (Cunha *et al.* 2002; Smitha *et al.* 2004; Kuila & Ray 2012). Depending on the permeating component two main areas of pervaporation can be identified: hydrophilic and organophilic (hydrophobic) pervaporation (Nguyen & Nobe 1987; Zhang *et al.* 1992; Devaine *et al.* 1995). If the azeotropic composition can be approached with distillation, then the distillate product (D) can be further purified using hydrophilic PV.

The aim of this study is to separate of EtOH-water process wastewater (PWW) with combination of distillation and hydrophilic PV and to compare the heat duty with extractive distillation in professional flowsheet environment.

MATERIAL AND METHODS

In the pharmaceutical industry it is an actual problem that EtOH should be separated from an aqueous mixture (Toth & Mizsey 2015). PWW from pharmaceutical industry has to be separated with the following initial composition: 10 weight percent (m/m%) EtOH and 90 m/m% water. The product purity is 99.5 m/m% in both cases and 1000 kg/h PWW must be treated.

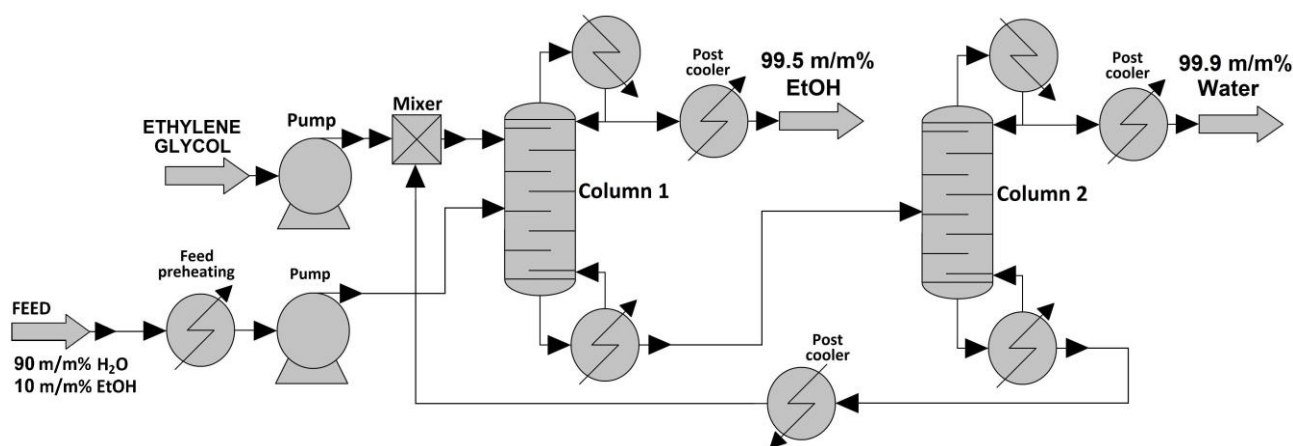The ChemCAD flowsheet of extractive distillation can be seen in **Figure 2**.

Figure 2 Flowsheet of ethanol-water separation with extractive distillation

The first column is the extractive column, where the azeotropic mixture can be separated with ethylene glycol as entrainer. The second column treats the water-ethylene glycol mixture, the entrainer can be recycled and mixed into the feed stream. The optimal reflux ratio, the mass- and bottom flow rates, heating and cooling requirements, number of theoretical plates (N) and feed plate have to be optimized. As an equilibrium model for the calculation of the non-ideal vapour-liquid equilibria (VLE) the UNIQUAC model is applied.

ChemCAD professional flowsheet simulator is used for the investigation of hybrid separation (see **Figure 3**).
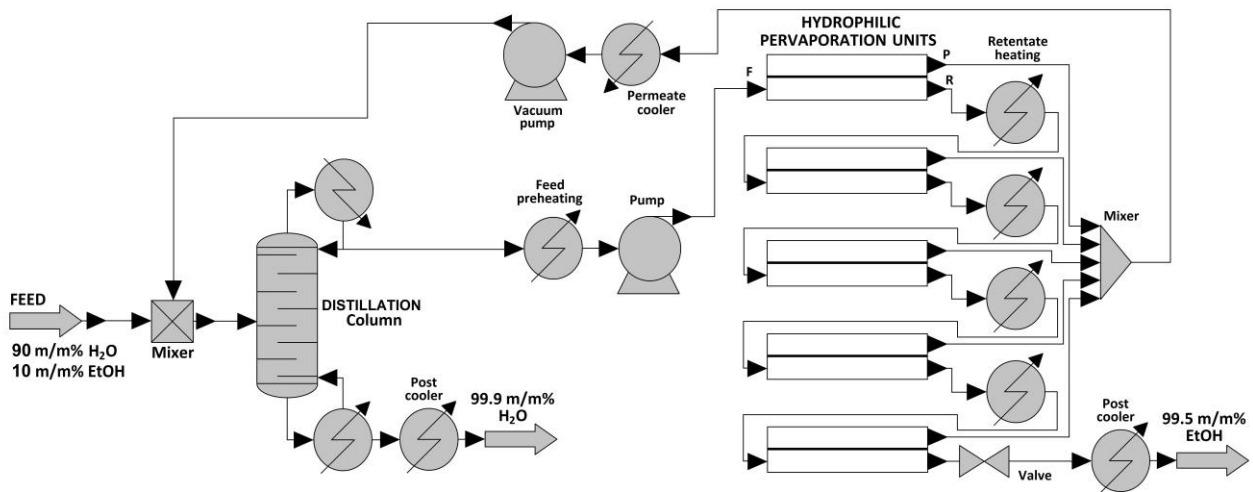

Figure 3 Flowsheet of ethanol-water separation with distillation and hydrophilic pervaporation

First step, PWW is pumped into the middle of the distillation column and hydrophilic PV separates further the alcohol-rich intermediate product. It can be determined the suitable water can be received as bottom product (W) of distillation. Actually it is the purified PWW. The ethanol substance can be appropriate using this hybrid method as retentate (R) of hydrophilic PV.

Additional apparatuses are also needed for PV process (Toth *et al.* 2015). The temperature and the pressure must be increased for the operational level prior to the first membrane unit, because the feed (F) has atmospheric conditions, 20°C and 1 bar. Heat exchanger adjusts the temperate and pump increases the pressure prior to the first PV unit, too. Retentate stream is reheated after each membrane unit by further heat exchangers (Tusel & Brüschke 1985), except for the last module. Permeate (P) streams leaving the PV units are collected, mixed, condensed with cooler and its pressure is increased again from vacuum with pump. This stream is mixed into feed stream of distillation column. The applied feed temperature in membrane modules is 70°C. Feed and permeate pressures are the following, 3 bar and 0.008 bar.

UNIQUAC thermodynamic model is applied in the case of SCDS distillation column and exponential Rautenbach model (Rautenbach *et al.* 1990; Valentínyi *et al.* 2013) for the hydrophilic PV. According to the methodology of Valentínyi *et al.* (2013) the pervaporation can be described with the following semi-empirical model:

$$J_i = \frac{1}{1+\{[\bar{D}_i \cdot exp(B \cdot x_{i1})]/(Q_0 \cdot p_{io} \cdot \bar{\gamma}_i)\}} \cdot \frac{[\bar{D}_i \cdot exp(B \cdot x_{i1})]}{\bar{\gamma}_i} \cdot \left(\frac{p_{i1}-p_{i3}}{p_{io}}\right) \qquad i = (1, ..., k) \tag{3}$$

Table 1 shows the estimated parameters of this semi empirical model.

Table 1 Estimated parameters for ethanol–water mixture with Sulzer PERVAP™ 4510 membrane (Valentínyi *et al.* 2013)

	EtOH	Water
B: Exponential parameter [-]	8.68	2.63
E_i: Activation energy [kJ/kmol]	128572	77877
D_i: Transport coefficient [kmol/m^{2}h]	$1{,}93*10^{-5}$	$2{,}02*10^{-4}$

RESULTS AND DISCUSSION

Table 2 shows the optimized results of extractive distillation separation.

Table 2 Optimized results of ethanol-water separation with extractive distillation method

		Extractive column	Recovery column
N [-]		20	15
Feed stage (PWW)		12	8
Feed stage (Ethylene glycol)		2	-
Reflux ratio [-]		2	1
D	EtOH [m/m%]	99.5	0.04
	Water [m/m%]	0.4	99.9
	Ethylene glycol [m/m%]	0.1	0.06

The results of simulations with distillation and hydrophilic PV process are listed in **Table 3**.

Table 3 Optimized results of ethanol-water separation with hybrid D+PV method

	Distillation			Pervaporation	
	F	W	D	P	R
EtOH [m/m%]	10	0.5	92	1	99.5
Water [m/m%]	90	99.5	8	99	0.5

Figure 4 depicts the EtOH concentrations of retentate stream in the function of membrane module numbers.
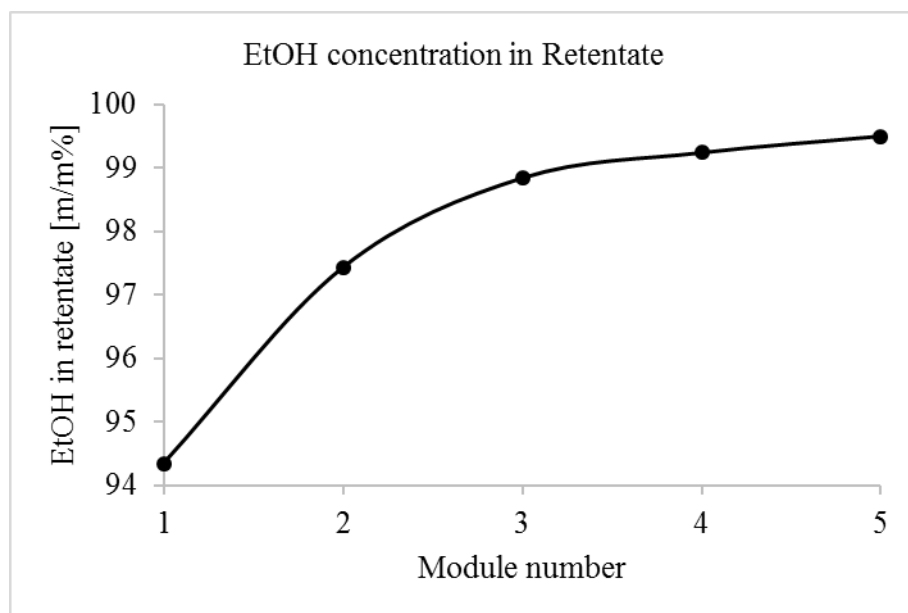

Figure 4 Ethanol concentration in retentate stream

It can be seen 5 membrane module is sufficient for reach the enrichment limit, which is 99.5 m/m% ethanol.
The column has 15 theoretical plates and the reflux ratio is 2 in the optimized case. 80 m^2 effective membrane transfer area is required for removal EtOH from PWW. It can be seen both method can

be removal ethanol from water. **Table 4** summarises the cumulated heat duties.

Table 4 Heat duties of separation methods

Calculated heat duties	MJ/h
Extractive distillation	1491
Distillation + Hydrophilic PV	710

It can be concluded that heat duty of extractive distillation is approx. twice of hybrid separation.

SUMMARY

The combination of distillation and hydrophilic pervaporation is investigated in professional flowsheet environment. It can be concluded ethanol-water mixture can be separated into pure components with this hybrid operation and with extractive distillation too. The target composition, which is 99.5 m/m% in both product case, can be reached and the heat duty of extractive distillation is significantly higher than hybrid method.

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