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Research Article

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Treatment of pharmaceutical process wastewater with hybrid separation method: distillation and hydrophilic pervaporation

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Abstract: The work is motivated by an industrial problem, which is alcohol removal from pharmaceutical process wastewater. The aim of the study was to develop a complete hybrid operation is investigated. Ethanol dehydration, in combination with distillation and hydrophilic pervaporation, is used to investigate about the extent of separation of the ethanol-water mixture. The aim of this research 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. Cost estimation is also examined according to Douglas methodology. Considering our 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.

Keywords: process wastewater, ethanol dehydration, hybrid operation, distillation, hydrophilic pervaporation

1 Introduction

Pervaporation (PV) is a chemical unit operation where the mixture to be separated is vaporized at low pressure on the downstream side of the membranes and the separation of the mixtures takes place by preferential sorption and diffusion of the desired component through the dense membranes. One way of achieving the difference in the partial pressures is to maintain a low vapor pressure using a vacuum pump on the permeate side [1, 2]. Pervaporation is a relatively new technology for the separation of many organic solvent/aqueous mixtures. In recent years, the number of publications, books, and industrial applications of pervaporation have been steadily increasing, pointing to the increasing importance of this unit operation pervaporation as a membrane separation method [3-6]. Pervaporation has the several adavntages in comparison to other/conventional separation techniques. These advantages include: a higher separation effect/efficiency, simple actualization, no-pollution andlower energy demand. Pervaporation can have advantages over distillation because of its lower energy demand and the ability to separate azeotropic mixtures.

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 [7-9], removal of low concentration organics from its aqueous mixtures [10-12] and organic-organic separation [13-15]. Depending on the permeating component two main types of pervaporation can be identified: hydrophilic and organophilic (hydrophobic) pervaporation [16-18].

The first commercial plants for dehydration of alcohol with PV were installed in the late 1980s. While for environmental application organophilic PV with hydrophobic membranes has the highest potential by offering the opportunity to efficiently remove low concentration of organic compounds from wastewater [11]. The first commercial application of such

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a process was reported in 1997 [19]. Separation of organic compounds from water has received less attention [11]. Among the major applications of pervaporation membrane processes, organic separation from organic/water mixtures is becoming more and more important [20]. The removal of organics from aqueous solutions is of particular interest for water recycling processes, fermentation, and the treatment of wastewater [21-24].

For removal of volatile organic compounds (VOCs), other separation technologies such as distillation, liquid–liquid extraction, absorption on carbon and air stripping are not applicable because of feed condition limitations, large volume of by-products or high cost of post-treatments. However, pervaporation can be applied without these limitations [25]. Generally, distillation can be used to remove organic compounds from water [26]. In the case of thermally sensitive organic compounds, however, distillation can not be applied. Furthermore, according to Fleming and Slater [27, 28], pervaporation has several advantages over traditional distillation: (1) reduced energy demand because only the permeating fraction of the liquid should be vaporized, (2) membrane pervaporation has advantages over distillation for liquid separations because of lower operating temperatures, (3) azeotropes can be separated [29], (4) the addition of an extra component is not required to achieve separation (as in extractive and azeotropic distillation [30] (4). Thus, relatively mild operation conditions and high effectiveness make pervaporation an appropriate technique for such separations [27, 31, 32].

Water/alcohol separation is a well-known example of pervaporation process in chemical industry [33, 34]. Although some references reported that pervaporation technology used for separating ethanol (EtOH)/water mixture on an industrial scale, there are virtually no studies on the application on separating methanol/water mixtures. EtOH forms minimal boiling azeotropic mixture with water, which poses a separation problem. Alcohol content above 96 weight% can not be achieved with conventional distillation techniques [35]. If the azeotropic composition can be approached with distillation, then the distillate product (D) can be further purified using hydrophilic pervaporation.

It can be seen that pervaporation is considered a competitive separation alternative for distillation. The aim of this study is to separate the EtOH/water mixture with combination of distillation and hydrophilic pervaporation with rigorous modelling in professional flowsheet environment and to obtain conclusion if the separation can be completed and under what circumstances [36]. These combined separation is called hybrid operations.

2 Material and methods

In the pharmaceutical industry it is an actual problem that ethanol (EtOH) should be separated from an aqueous mixture [37]. Process wastewater from pharmaceutical industry has to be separated with the following initial composition: 30 % (m/m%) ethanol and 70 m/m% water. The product purity is 99.5 m/m% in both cases and 800 kg/h PWW must be treated. ChemCAD professional flowsheet simulator is used for the investigation of hybrid separation. The complex separation process can be seen in Figure 1.

In the first step, PWW is pumped into the middle of the distillation column and hydrophilic pervaporation

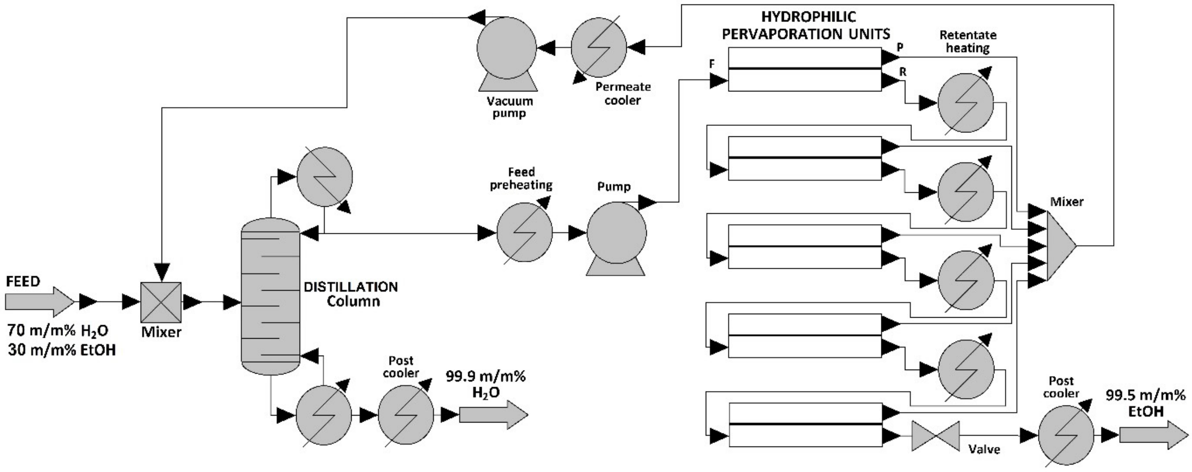

Figure 1. Flowsheet of ethanol-water separation with distillation and hydrophilic pervaporation

separates further the alcohol-rich intermediate product. Water of sufficient purity can be collected as bottom product (W) of distillation. This is actually the purified process wastewater. The alcohol substance can be obtained using this hybrid method as retentate (R) of hydrophilic pervaporation.

Additional apparatuses are also needed for pervaporation process [36]. 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 [38], except for the last module. The applied membrane area per unit should be limited to a site that ensures an acceptable temperature drop. The pervaporation stops, if the temperature decreases below 50°C [36, 39].

Permeate (P) streams leaving the pervaporation 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. Post coolers and valves decreases again in atmospheric temperature and pressure of Water- and Alcohol products [36]. 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 [4] for the hydrophilic pervaporation. Table 1 shows the estimated parameters of this semi empirical model [4].

The objectives function of optimization in the case of distillation are the minimal reflux ratio and number of plates. Furthermore minimal membrane transfer area (A) and total annual cost (TAC) must be found. The methodology of Toth [40] and Douglas equations [41] are used for cost estimation. Current M&S index is used, while pump costs are determined by industrial data. Membrane area-price function is determined on industrial data and used for the calculation of the capital costs of membrane modules [23, 36]. 2.5 years are taken as membrane depreciation time, because membranes should be usually replaced in approximately every 2-5 years. 10-year amortization of capital cost is assumed for the total cost estimation [23, 36].

3 Results and discussion

Results of simulations with distillation and hydrophilic pervaporation process are listed in Table 2. Actually, Table 2 includes the optimized input and output compositions and streams of methods. The feed concentration of distillation is the recycled stream.

The column has 10 theoretical plates and the reflux ratio is 2 in the optimized case. 70 m^2 effective membrane transfer area is required for 99.5 % (m/m) of ethanol. It can be seen the bottom product of distillation is nearly 70% of the feed and the retentate is more than 90% of the feed stream of PV. Figure 2 shows the progression of retentate alcohol concentrations in membrane modules.

The process design and the evaluation of the design alternatives need to be evaluated for the energy demands at the different separation steps [36]. Table 3 shows the calculated heat duties. It can be seen that the reboiler of distillation column has the highest energy requirement and the post cooler is almost significant, this is consistent with the material streams.

Table 1. Estimated parameters for ethanol–water mixture with Sulzer PERVAP™ 4510 membrane [4]

	Water	**Ethanol**
Permeability coefficient [kmol/m^{2}hbar]	10^8	10^8
Transport coefficient [kmol/m^{2}h]	0,000202	$1{,}93 \cdot 10^{-5}$
Activation energy [kJ/kmol]	77877	128572
Exponential parameter [-]	2.63	-8.68

Table 2. Optimized results of ethanol-water separation

	Distillation			**Pervaporation**	
	F	**W**	**D**	**P**	**R**
EtOH [m/m%]	29	0.5	93	1	99.5
Water [m/m%]	71	99.5	7	99	0.5
Stream [kg/h]	816	562	254	16	233

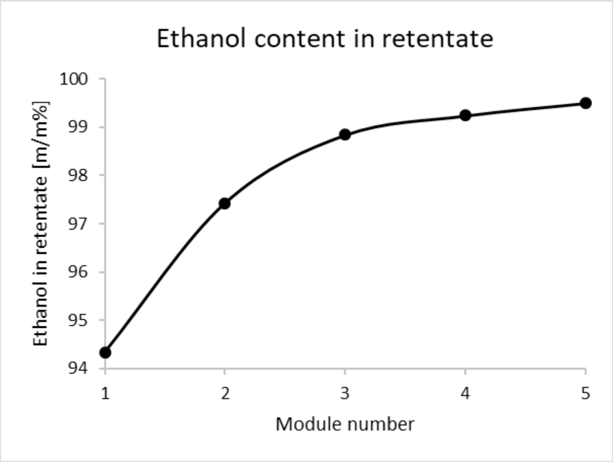

Figure 2. Ethanol weight percent in retentate

The conceptual design of an industrial process takes a small part of the project costs but offers a huge cost reduction opportunity for the whole project [36], therefore this hybrid operation should be investigated also from an economic point of view. Table 4 presents the main cost elements of hybrid operation. The cost of feed preheating, retentate heating and post coolers are summarized and nominated as Heat exchangers in Table 4 [36].

It can be concluded that the biggest part of investment cost is membrane modules and heat-energy is the most significant part of operating cost.

4 Conclusions

The combination of distillation and hydrophilic pervaporation is investigated in professional flowsheet environment. It can be concluded that the ethanol-water mixture can be separated into pure components with this hybrid operation. The simulations suggest that this separation process is able to remove the ethanol from pharmaceutical process wastewater. The target composition, which is 99.5 % (w/w) in both product case can be reached with 10 theoretical plate's distillation column and 70 m^2 effective membrane transfer area. Cost estimation is also justified the competiveness of hybrid operation.

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Table 3. Calculated heat duties of hybrid operation

Calculated heat duties		**$Q_{Heating}$ [MJ/h]**	**$Q_{Cooling}$ [MJ/h]**
Distillation	Reboiler	461	
	Condenser		-152
	Post cooler		-310
Pervaporation	Feed preheating	17	
	Retentate heating	28	
	Permeate cooler		-31
	Post cooler		-13

Table 4. Cost elements of hybrid operation

10 years amortization	**Investment cost**		**Operating cost**		**TAC**
	1000$/year	%	1000$/year	%	1000$/year
Distillation column	4.0	4	–	–	4.0
Heat exchangers	18.6	17	144.6	71	163.3
Membrane modules	80.5	75	18.0	9	98.5
Permeate cooling	3.9	4	41.3	20	45.1
Pumps	0.1	<0.5	0.4	<0.5	0.5
Total	107.1		204.3		311.4

Nomenclature

A	Membrane transfer area
D	Distillate product
EtOH	Ethanol
F	Feed
P	Permeate
PV	Pervaporation
R	Retentate
TAC	Total annual cost
PWW	Process wastewater
Q	Heat duty [MJ/h]
VOC	Volatile organic compounds
W	Bottom product weight percent m/m%

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