Optimal Design and Operation of Hybrid Distillation/Pervaporation Processes

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Abstract. Considerable effort is currently being put into process intensification to design more sustainable and energy-efficient processes. Hybrid distillation/pervaporation processes are prime examples of such an intensified process. In this work, the energy consumption and economic performances of a hybrid distillation/pervaporation process, as well as that of the corresponding traditional extractive distillation process, to separate an azeotropic ethanol/water mixture are compared for different ethanol feed compositions. The results show that the total heat duty for the hybrid process is always lower than that of the extractive process, confirming that the hybrid process is a more energy efficient process. In terms of total annualized cost, the hybrid process is found to be more economically attractive at lower ethanol feed compositions, and the extractive process for higher compositions.

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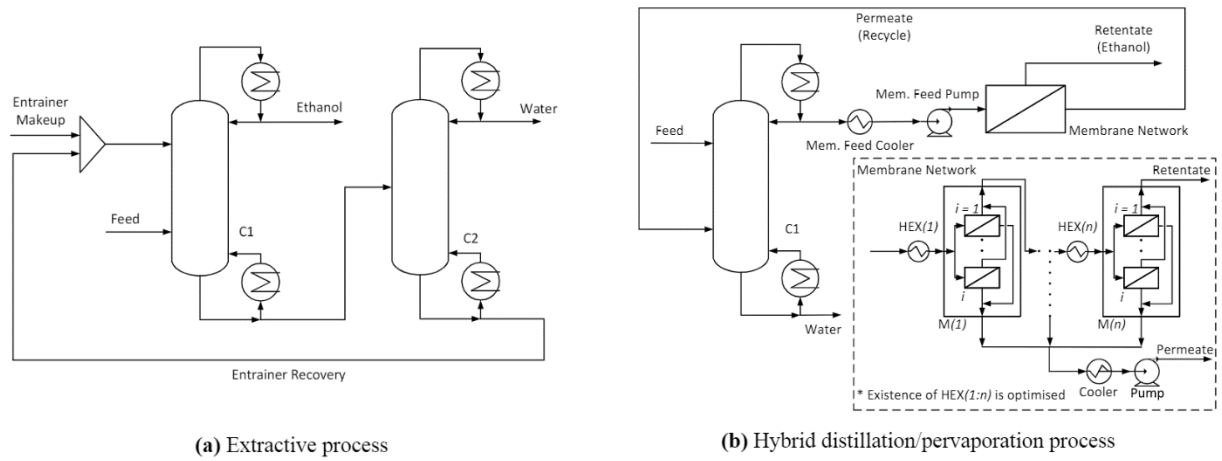
Keywords Distillation, Extractive Distillation, Hybrid Distillation, Pervaporation, Optimization

Introduction

As part of the quest over the past few decades towards a more sustainable and energy efficient process industry, tremendous effort has been put towards process intensification. A prime example of intensification is hybrid separation, often between a distillation column and a membrane process, where the advantages of one process is exploited to counteract the disadvantages of the other. A hybrid distillation/membrane process is for instance capable of separating azeotropic mixtures which cannot be separated by using only conventional distillation columns. An azeotropic mixture is typically separated by the use of an entrainer in an extractive distillation column, but the extractive process is both energy intensive and expensive due to the need for an additional column and separation step for entrainer recovery. Hybrid distillation/membrane processes have been found to save energy [1], but are limited by the low capacity and high capital cost of the membrane unit. Pervaporation and vapor permeation are the most common membrane processes used for hybrid separation/purification for chemical processes, where a pervaporation membrane is used when the membrane feed is in liquid phase and a vapor permeation membrane is used when the membrane feed is in vapor phase. The exact choice of membrane material depends on the availability of the membrane for the specified mixture, and on the configuration of the hybrid process. In this study, the separation of an ethanol/water mixture in a hybrid distillation/pervaporation process is considered as it is one of the most commonly studied and widely applied cases for membrane applications in the separation of azeotropic mixtures [2-4]. So far, however, studies considering the economic feasibility of such a hybrid process have in most cases focused on only a specific feed composition, and there is a lack of consideration and understanding of the effect of the feed composition on the process performance although is clearly likely to have an impact on the performance and therefore the comparison. Thus, in this work, a hybrid distillation/pervaporation process for ethanol/water separation is compared with a traditional extractive distillation process for the same separation for a range of feed compositions, with the objective to minimize the total annualized cost (TAC).

Methodology

The flux equations and parameters used in this work for the pervaporation membrane model is that of a hollow fiber membrane considered by Tsuyumoto et al. for the separation of an ethanol/water mixture [2], where ethanol leaves the membrane in the retentate while water leaves the membrane in the permeate. The process is modelled using gPROMS Process [5], which has a built-in distillation model, whilst the pervaporation unit model is user-defined and has been validated against experimental results by Tsuyumoto et al. [2]. The pervaporation unit model is described by a membrane network model (shown in the inset figure of Figure 1b), and this membrane network (including the cooler and pump at the permeate stream) is represented as a single unit in the overall hybrid/pervaporation process shown in Figure 1b. To reduce the computational burden of the optimization, the membrane network has been simplified by making a few assumptions. First of all, the membrane network is assumed to contain



(a) Extractive process **(b)** Hybrid distillation/pervaporation process

Fig. 1 Flowsheets of the (a) extractive process, and (b) hybrid distillation/pervaporation process.

n membrane stages in series, and i_n membrane modules in parallel in each membrane stage n. Secondly, the possible recycle streams within the membrane network (e.g. part of the retentate stream being recycled back to the current and/or previous membrane stage) are not considered. For this system, it has been reported that recycle streams within the membrane network may increase the product quality slightly but with a greater energy usage [3]. Next, in each membrane stage n, the feed stream is assumed to be equally distributed between the i_n number of membrane modules. By applying this strategy, the $n \times i_n^{max}$, where i_n^{max} is the maximum number of membrane modules allowed in membrane stage n, split fraction variables which would otherwise be needed, are removed from the optimization problem (this strategy has been found to be effective [3]). The existence of the heater before each membrane stage is determined during optimization, and theoretically, the temperature of the outlet stream from the heater or duty of the heater should also be an optimization variable. However, this will introduce n more variables into the system, leading to difficulty in terms of simulation and optimization convergence. Thus, another simplification is made where the temperature of the heater is fixed at the maximum allowable temperature (for the case study considered at $70\ °C$, which is the maximum temperature tested during the experiments for this membrane system [2]). This is because the separation performance of a membrane is generally better when the temperature is higher (i.e. higher permeate flux at higher temperature), so it is reasonable to operate the membrane at its maximum allowable temperature [6]. Finally, the pressure on the permeate side of the membrane module is fixed (here at $400\ Pa$, which is the value used by Tsuyumoto et al. [2] in their experiments). The permeate stream is recycled back into the distillation column for further purification to meet the overall product specifications, and at a location determined by the optimization. As the total permeate stream is a low pressure vapor stream, a cooler and a pump are installed to condense the stream to a saturated liquid phase with the pressure matching that of the pressure of the distillation column. A membrane feed cooler and a membrane feed pump is also necessary to ensure that the temperature of the distillate from the column unit does not exceed the allowable temperature of the membrane unit and to prevent phase changes on the retentate side of the membrane. For the extractive process (see Figure 1a), ethylene glycol is chosen as the entrainer as it is one of the most commonly used entrainers for ethanol/water separation. The lightest component (i.e. ethanol) leaves the system in the distillate of the first column. The entrainer is recovered in the second column (the recovery column) from water, and is recycled back into the first column after mixing with the fresh entrainer makeup stream to compensate for any entrainer lost in the product streams.

The simulations are carried out in gPROMS Process [5], where the membrane is a user-defined model while the other equipment (columns, coolers, and pumps) are modelled with the built-in library models. The library model used for the distillation column is an equilibrium-based model. All the design and operating variables (except for the column pressure which is fixed at 1 bar) are optimized using genetic algorithm (GA) coded in MATLAB [7] with the settings proposed in our previous work [8]. A desktop with an AMD Ryzen 9 3900X CPU with 3.79 GHz and 64 GB memory is used to perform all the optimizations. The parfeval function (a parallel computing function) in MATLAB is used with 18 workers to speed up the optimization for GA. gO:MATLAB [9] is used to transfer data between gPROMS Process and MATLAB. The objective function is to minimize the total annualized cost (TAC), where the

Table 1. Optimal design variables and costs of the extractive process at different feed ethanol molar compositions (0.1 to 0.8 $mol\ mol^{-1}$).

Item	Feed Ethanol Molar Composition					Units
	0.1	**0.3**	**0.5**	**0.7**	**0.8**	
Column C1 (Extractive Column)						
Total stages	32	42	39	37	33	-
Feed stage *	28/3	37/3	33/3	30/3	25/4	-
Makeup flowrate	0.61	0.94	0.37	0.89	0.12	*kmol h-1*
Distillate	46.49	148.84	250.35	353.03	403.34	*kmol h-1*
Reflux ratio	2.82	1.88	1.62	1.47	1.39	*kmol h-1*
Reboiler duty	1748.29	4092.53	6093.23	8209.06	9163.18	*kW*
Condenser duty	1881.00	4539.82	6946.61	9250.01	10188.94	*kW*
Solvent-to-feed ratio	0.09	0.23	0.45	0.67	0.81	-
Column C2 (Recovery Column)						
Total stages	9	9	11	15	12	-
Feed stage	5	5	6	10	6	-
Recovery flowrate	42.73	114.59	223.81	332.98	403.67	*kmol h-1*
Reflux ratio	0.01	0.03	0.08	0.17	0.34	*mol mol-1*
Reboiler duty	5443.08	4705.66	4018.95	3081.41	2548.42	*kW*
Condenser duty	5212.26	4140.54	3066.32	1969.42	1470.05	*kW*
Total Duty						
Heating	7191.37	8798.19	10112.18	11290.47	11711.60	*kW*
Cooling	7093.26	8680.36	10012.93	11219.43	11658.99	*kW*
Capital Cost (CAPEX)						
Column	1.0850	1.9446	2.1341	2.1937	2.1017	*M $*
Reboiler	1.2128	1.4144	1.5648	1.6885	1.7276	*M $*
Condenser	1.0909	1.2909	1.5057	1.7372	1.8353	*M $*
Operating Cost (OPEX)						
Heating	3.6562	4.2575	4.7400	5.1371	5.2572	*M $ year-1*
Cooling	0.0759	0.0929	0.1072	0.1201	0.1248	*M $ year-1*
Overall						
CAPEX	3.3888	4.6498	5.2045	5.6194	5.6645	*M $*
Ann. CAPEX	0.4236	0.5812	0.6506	0.7024	0.7081	*M $ year-1*
OPEX	3.7321	4.3504	4.8472	5.2572	5.3820	*M $ year-1*
TAC	4.1557	4.9317	5.4977	5.9597	6.0901	*M $ year-1*

* Displayed as Feed Stage/Recycle Stage

TAC takes into account the capital cost and operating costs of all the equipment (except for the entrainer mixer in the extractive process which is ignored). The sizing equations used for the calculation of the capital costs are taken from Seider et al. [10], while the capital cost equations for the equipment (including the Lang factors) are taken from Sinnott and Towler [11]. The utility costs (heating, cooling, and electricity) are taken from Turton et al. [12], and the choice of the heating and cooling utility (e.g. high/medium/low pressure steam, cooling water, chilled water, refrigerants) are automatically selected during the optimization based on the heating and cooling conditions.

Case Study

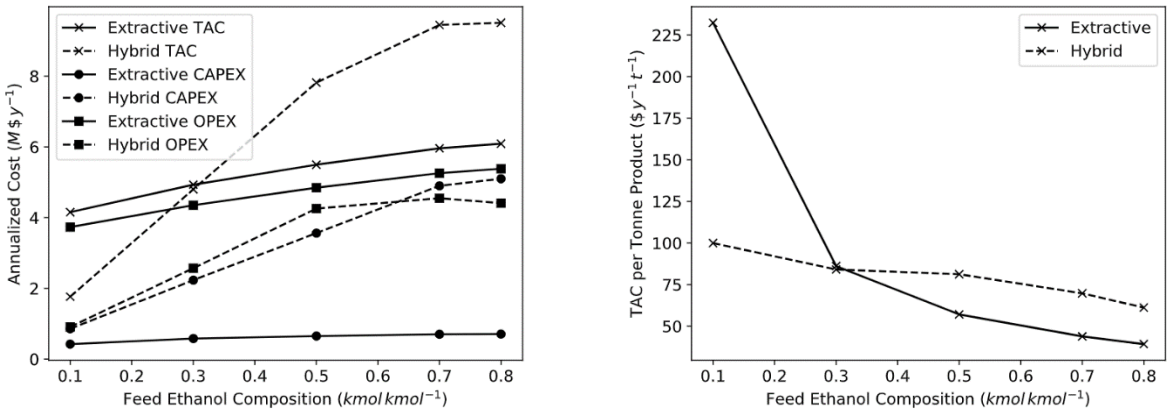
The comparison between the performances of the hybrid distillation/pervaporation process and the extractive process in terms of energy and economics are based on the separation of an azeotropic ethanol/mixture with different feed ethanol molar compositions (0.1, 0.3, 0.5, 0.7, and 0.8 $mol\ mol^{-1}$). The maximum ethanol feed composition is chosen as 0.8 $mol\ mol^{-1}$, as this is close to the ethanol/water azeotropic point (0.85 $mol\ mol^{-1}$). The feed is provided at 500 $kmol\ h^{-1}$, and it is assumed to be a saturated liquid at 1 bar. The UNIQUAC model is used to describe the liquid phase properties, while ideal gas is used to describe the gas phase properties. The membrane model used in this work is a hollow fiber pervaporation membrane described by Tsuyumoto et al. [2], and the model has previously been validated against the experimental data provided in that study. The product purities are assumed to be at least 99 mol % of product. The distillation column is assumed to be operating at 1 bar, and no pressure drop is considered. It is assumed that the plant will operate for 8400 $h\ year^{-1}$ with a payback period of 8 $years$.

Table 2. Optimal design variables and costs of the hybrid distillation/pervaporation process at different feed ethanol molar compositions (0.1 to 0.8 $mol\ mol^{-1}$).

Item	Feed Ethanol Molar Composition					Units
	0.10	**0.30**	**0.50**	**0.70**	**0.80**	
Column C1						
Total stages	20	28	25	21	18	-
Feed stage/Recycle stage	17/18	21/26	20/22	10/19	2/16	-
Distillate	56.73	184.94	311.14	457.51	490.38	*kmol* h^{-1}
Reflux ratio	1.35	1.04	1.03	0.17	0.11	*mol* mol^{-1}
Reboiler duty	1559.42	4261.85	7029.38	6060.91	6052.00	*kW*
Condenser duty	1441.23	4075.84	6820.62	5801.60	5842.09	*kW*
Membrane Network						
No. membrane stages	5	9	10 *	10 *	10 *	-
No. modules in stage 1	18	32	42	46	69	-
No. modules in stage 2	21	21	65	79	65	-
No. modules in stage 3	20	25	40	80	91	-
No. modules in stage 4	43	37	64	99	83	-
No. modules in stage 5	49	42	50	105	112	-
No. modules in stage 6	-	52	98	106	148	-
No. modules in stage 7	-	96	58	124	141	-
No. modules in stage 8	-	58	90	139	129	-
No. modules in stage 9	-	70	82	140	141	-
No. modules in stage 10	-	-	136	146	138	-
Total no. modules	151	433	725	1064	1117	-
Total membrane area	906	2598	4350	6384	6702	m^2
Total heater duty	134.20	470.38	783.22	1397.35	1102.70	*kW*
Permeate cooler duty	142.93	483.43	808.33	1393.95	1146.02	*kW*
Total Duty						
Heating	1693.62	4732.23	7812.60	7458.26	7154.70	*kW*
Cooling	1584.16	4559.27	7628.95	7195.55	6988.11	*kW*
Capital Cost (CAPEX)						
Column	0.3735	0.8619	0.283	0.1967	0.5934	*M $*
Membrane	4.9664	14.2414	23.8452	34.995	36.7381	*M $*
Reboiler	0.3604	0.6912	1.0073	0.8984	0.8974	*M $*
Condenser	0.2674	0.6079	1.0163	0.8599	0.8660	*M $*
Auxiliary	0.8831	1.4549	2.3496	2.2426	1.7066	*M $*
Operating Cost (OPEX)						
Heating	0.7196	2.0106	3.3194	3.1688	3.0398	*M $* $year^{-1}$
Cooling	0.0501	0.1609	0.2691	0.4000	0.3408	*M $* $year^{-1}$
Electricity	0.0002	0.0007	0.0011	0.0016	0.0018	*M $* $year^{-1}$
Mem. Replacement	0.1390	0.3986	0.6673	0.9794	1.0282	*M $* $year^{-1}$
Overall						
CAPEX	6.8507	17.8573	28.5014	39.1926	40.8015	*M $*
Ann. CAPEX	0.8563	2.2322	3.5627	4.8991	5.1002	*M $* $year^{-1}$
OPEX	0.9089	2.5707	4.2569	4.5498	4.4105	*M $* $year^{-1}$
TAC	1.7652	4.8029	7.8196	9.4489	9.5107	*M $* $year^{-1}$

* This is the upper bound of the optimized variable

The optimal design and operating parameters for the extractive process and the hybrid distillation/pervaporation process at different feed ethanol compositions are shown in Table 1 and Table 2, respectively. Looking first at the traditional extractive process, from Table 1 it can be seen that as the ethanol feed composition increases, the reflux ratio decreases. This is due to the increasing fraction of ethanol (light component) in the total feed (i.e. sum of feed, entrainer recovery/recycle, and makeup flowrates) into the extractive column (from 9 % to 44 % as feed ethanol composition increases), which allows for smaller reflux ratios. The reboiler duty for the extractive column, however, shows the opposite trend, with the duty increasing as the feed composition of ethanol increases. The increase in reboiler duty is due to the larger amount of ethanol (as ethanol composition increases in the feed stream), thus more energy is needed to vaporize the light component in the extractive column. On the other hand, the decrease in the



(a) Annualized cost **(b)** Total annualized cost per tonne product

Fig. 2 Economic performance of hybrid distillation/pervaporation processes, indicated by (a) total annualized cost (TAC), capital cost (CAPEX), and operating cost (OPEX), respectively, and (b) TAC per ton product (ethanol).

amount of water in the feed means that less energy is needed to vaporize the water in the recovery column, thus a lower reboiler duty is needed in the recovery column as the feed ethanol composition increases, although the number of stages and the reflux ratio increases. The solvent-to-feed ratio increases with the increasing composition of ethanol in the feed but the ratio between amount of solvent and amount of ethanol in the feed remains almost constant at about 0.9 (not shown in the table). The total number of stages in the extractive column reaches a peak (42 stages) at around 0.3 molar composition of ethanol and drops gradually as the feed ethanol composition increases (note that a peak in number of stages was also seen by Luyben [13]). For the recovery column, the reflux ratio increases as the ethanol feed composition increases due to the lower fraction of water (i.e. the light component of the water/ethylene glycol mixture in the recovery column) in the column.

Considering the hybrid distillation process in Table 2, the table shows that the total number of stages reaches a peak at 0.3 feed ethanol composition, which is the same trend observed for the extractive column (Table 1). In general, the reflux ratio decreases as the ethanol feed composition increases, again for the same reason as explained for the extractive column. Table 2 also shows that the total number of membrane modules/area required increases almost linearly with the ethanol feed composition. This is because as the feed composition increases, more ethanol needs to be processed by the membrane network, and the only way to do so in this design is by increasing the number of membrane modules (under the condition of fixed permeate pressure and fixed maximum membrane temperature). The reboiler duty and total heater duty of the membrane network in the hybrid distillation process reaches a peak around 0.5 and 0.7 feed ethanol molar composition, respectively, which is a result of the trade-off between the capital and operating costs of the distillation column and of the membrane network. For the hybrid process, the water can be separated from the binary mixture from both the distillation and the membrane unit. Separating more water using the distillation column (i.e. distillate composition closer to the azeotropic point) may lead to larger column design and reboiler duty for the column, but lower capital and utility cost for the membrane network.

A comparison between the extractive process and the hybrid process shows that the total number of distillation stages required by the hybrid process is much smaller for all the feed composition cases. It can also be seen that the total heat duty (i.e. reboiler and total membrane heater duties) for the hybrid process is always lower than that of the total reboiler duty of the extractive process. This means that the hybrid distillation column is always superior in terms of energy consumption, which is consistent with other findings in the literature [1]. The energy saving is larger when the ethanol feed composition is lower.

Moving on to the economic performances of the extractive and hybrid processes, the operating cost (OPEX) typically contributes to about 90 % of the total annualized cost (TAC) in the extractive process, where the majority of the OPEX is from the heating utilities. For the hybrid process, the OPEX is about half of the TAC, and dominated by the reboiler duty of the distillation column. The capital costs (CAPEX) of the hybrid process in each case shows that the main contributor of CAPEX is the membrane unit, totaling about 73 % to 90 % of the total CAPEX as the ethanol feed composition increases from 0.1 $mol\,mol^{-1}$ to 0.8 $mol\,mol^{-1}$. This finding is clearly a function of the cost considered for the membrane, and the impact on membrane costs will be explored in future work.

A comparison between the TAC, annualized CAPEX, and OPEX for the two processes can be seen in Figure 2a. The OPEX of the extractive distillation process is always higher than the OPEX of the hybrid distillation process, but the CAPEX of the hybrid distillation process is always higher than the CAPEX of the extractive distillation process. This shows that the hybrid distillation is capable of saving more OPEX in terms of energy duties, but the CAPEX increases due to the membrane. The capital costs found for the hybrid process is clearly a function of the membrane costs considered in this work. It is clear that the CAPEX of the hybrid process could be further reduced, making hybrid distillation more advantageous than extractive distillation, if the membrane costs can be reduced. Overall, looking at the TAC, the hybrid distillation process is much cheaper (savings up to about 58 %) than the extractive distillation process when the ethanol feed composition is lower than the cut-off point at about 0.3 $mol\ mol^{-1}$. Beyond the cut-off point, the hybrid process becomes more expensive (up to about 59 %) than the extractive process. Figure 2b shows that the TAC per ton of ethanol product in the extractive distillation process greatly decreases from about 232 $\$\ y^{-1}\ t^{-1}$ to about 39 $\$\ y^{-1}\ t^{-1}$ as the feed ethanol composition increases, while the TAC per ton of ethanol product for hybrid distillation decreases only slightly from about 100 $\$\ y^{-1}\ t^{-1}$ to about 61 $\$\ y^{-1}\ t^{-1}$ as the feed ethanol composition increases. The comparison indicates that the TAC per ton of ethanol product in the hybrid process stays relatively constant for the ethanol feed compositions considered, but the ethanol feed composition has a higher impact on TAC per ton of ethanol product for the extractive process.

Conclusions

This work considered the optimal design of a hybrid distillation/pervaporation process and has compared its performance in terms of total annualized costs (TAC) with that of the corresponding traditional extractive distillation process for the separation of an ethanol-water mixture. The performance has been considered for different systems with increasing amount of ethanol in the feed. For the membrane considered, it is found that the hybrid process is economically superior at low ethanol feed compositions, while the extractive process is more attractive at higher compositions. With the continuing advances in membrane technology, with better and cheaper membranes, hybrid distillation/pervaporation processes will become increasingly attractive. Future work will consider different mixtures, membrane permeability, membrane costs, and membrane replacement costs for a more comprehensive study.

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