Optimisation of Pressure of the Pressure-Swing Distillation of a Maximum Azeotropic Mixture

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The separation of the maximum-boiling azeotropic mixture water-ethylenediamine by pressure-swing distillation is studied by rigorous simulation and optimisation. Contrary to our former works, the top pressure of the high-pressure column is included as an optimisation variable, as well. First, the total annualised cost (TAC) of the process without Heat Integration is minimised, then different options to reduce the energy demand of the process are applied: partial and full Heat Integration and vapour recompression heat pumps. The different heat-integrated processes are optimised first by optimising only the operational parameters, then with a genetic algorithm (GA; coupled to a flow-sheet simulator) the geometrical parameters (e.g. number of trays), as well. Heat pumps are applied either for only one or both of the columns. The flow rate of the working fluid is optimised to minimise the compressor work (reduction of 24 %). The environmental impact of the different options is evaluated by calculating their CO_2 emissions and Eco-indicator 99 (EI99) values. The optimal pressure does not significantly depend on the application of Heat Integration. The lowest TAC is obtained by the optimal partial Heat Integration, which decreased TAC by 16 % compared to the optimal non-heat integrated process. Although the application of heat pumps is not economical, it is very favourable from the environmental point of view: CO_2 emissions and EI99 can be reduced by 44 and 95 %, respectively.

1. Introduction

Distillation is the most frequently used method to separate liquid mixtures despite its high energy demand: distillation accounts for more than 40 % of the energy demand of the chemical industry (Kiss, 2019). Azeotropic mixtures cannot be separated by conventional distillation methods, while the separation of close-boiling mixtures is possible but usually not economical, and the application of special distillation methods is required. These include extractive distillation (ED, Miranda et al., 2020), heterogeneous azeotropic distillation (HAD, Plesu Popescu et al., 2020) and pressure-swing distillation (PSD).

The advantage of PSD is that it does not require the addition of a new component contrary to the extractive and heteroazeotropic distillation. However, the azeotrope must be pressure-sensitive: Doherty et al. (2008) state that a change of 5 % is required over a moderate pressure interval for practical application. A binary mixture is separated by feeding it into one of two columns (depending on the relation of feed and azeotropic compositions) operating at different pressures. The components of the mixture are obtained in either the bottom product (for minimum-boiling azeotropes) or the distillate (for maximum-boiling azeotropes) of the columns. The other product of each column, which has a composition close to the azeotropic one at the given pressure, is fed or recycled into the other column.

The energy demand of the PSD process can be reduced by performing Heat Integration (HI) between the condenser of the high-pressure column (HPC) and the reboiler of the low-pressure one (LPC). As the heat duties of these two heat exchangers are usually not equal, partial Heat Integration (PHI) is realised; either an auxiliary condenser or a reboiler is needed.

By modifying the operational parameters of the columns, the heat duty of the condenser of HPC and the reboiler of LPC can be made equal, and full Heat Integration (FHI), which is the limiting case of PHI can be performed and the auxiliary heat exchanger can be saved. The optimal extent of Heat Integration in terms of energy demand or total annualised cost (TAC) can be reached by optimising the whole process.

The energy demand can also be reduced by applying mechanical heat pumps (HP) to provide the necessary heat in the reboilers (Kiss, 2019). In vapour compression, the working fluid (WF) compressed and then condensed to heat the reboiler is an external medium; in vapour recompression (VRC), it is the top vapour of the column. In conventional VRC heat pumps, the total amount of the top vapour is used as WF. Modla and Lang (2017) proposed a VRC heat pump with optimal amount of WF. The flow rate of WF was increased by recycling part of it to the compressor. This made it possible to lower the output pressure of the compressor, leading to a reduction of compressor work by 45 % for the separation of a mixture of i- and n-butane. If the total heat offer of WF is not needed, part of WF can by-pass the compressor to reduce its work. This option was studied by Shi et al. (2020) for the separation of the maximum azeotropic mixture methanol-diethylamine.

The mixture of water (A) and ethylenediamine (EDA, B) is a pressure-sensitive maximum-boiling azeotropic one. Its batch separation by PSD was first studied by Modla and Lang (2008), in a double-column batch rectifier. Fulgueras et al. (2016) studied the continuous PSD of this mixture. With fixed numbers of trays (N_1, N_2), the total energy demand of the process was minimised by determining the optimum feeding locations. The energy demand of the process for P_1=0.13 and P_2=6.55 bar was reduced by applying PHI without optimisation. Li et al. (2016) studied the separation of a mixture containing 60 mol% A. The column pressures were fixed at 0.1 and 2.0 bar. With this feed composition and pressures, feeding is only possible into HPC. The TAC of the process was minimised by a sequential iterative procedure, and then PHI without optimisation was applied.

Ferchichi et al. (2020) studied the PSD of this mixture as Li et al. (2016) but performed the optimisation with a GA, reducing TAC by 21 %. The pressures (P_1, P_2) were not included as optimisation variables but taken from Li et al. (2016). By applying PHI, TAC was further reduced by 18 %. The application of VRC heat pumps for one or both columns, with and without optimising the amount of WF was studied, as well. For HPC, partial recycling, for LPC, partial by-pass of WF was found optimal. Even with the optimal amounts of WF, the application of each variant of VRC was uneconomical because of the high cost of the compressors.

As shown above, the PSD of the A-B mixture was optimised either without considering P_1, P_2 as optimisation variables or without a well-defined objective function (Fulgueras et al., 2016). The influence of pressure on the application of HI or HPs was not studied; its optimisation likely leads to a significant reduction in TAC.

The goal of this work is thus to study the influence of varying the pressure of HPC (1) in the process studied by Ferchichi et al. (2020), (2) during the application of the following optimised options to reduce the energy demand: PHI, FHI and VRC heat pumps and (3) to evaluate the environmental impact of the different options studied.

2. Vapour-liquid equilibirum

Fulgueras et al. (2016) pointed out that no azeotrope exists above ca. 4-4.5 bar. However, a tangent azeotrope is still present above this pressure, at low concentrations of A. In this work, VLE calculations are performed with the UNIQUAC model (U_{AB}-U_{BB}=-2,690.424 cal/mol, U_{BA}-U_{AA}=449.932 cal/mol, A_{AB}=-3.4831, A_{BA}=1.5662).

By the VLE calculations, the azeotrope contains 44.1 mol% A (boiling point: 64.7 °C) at 0.10 bar and 25.6 % A (boiling point: 141.7 °C) at 2.02 bar. Figure 1a shows the calculated boiling point of the components and the azeotrope, as well as the azeotropic composition as a function of the pressure. The A content of the azeotrope decreases on the increase of P, and the azeotrope disappears at ca. 4 bar.
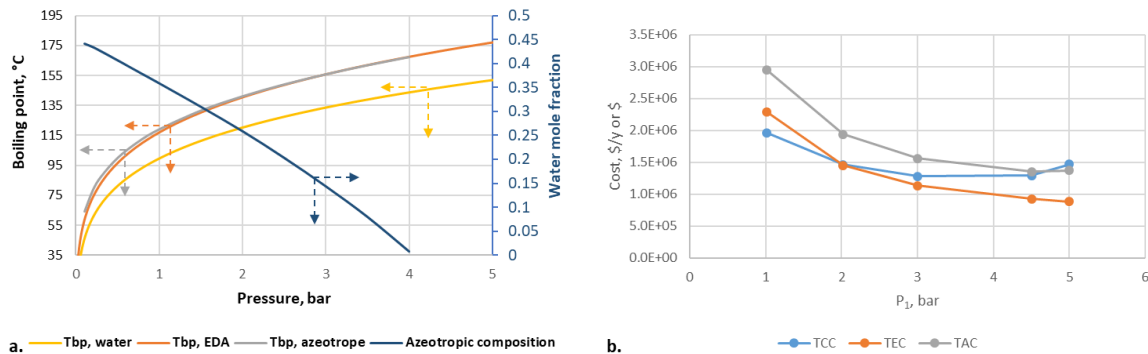

Figure 1: a. The boiling points and the azeotropic composition as the function of pressure; b. Costs of the NHI1a process as a function of P_1

3. Process description

The separation of the maximum-boiling azeotropic A-B mixture is performed in two columns using a PSD system (Figure 2). The fresh feed (F) and the stream recycled from the second column (W_2=F_{rec}) are fed into the first

column (high-pressure column, HPC), which operates with a top pressure of P_1. Ferchichi et al. (2020) used a value of P_1=2.02 bar, while in the present work, it is varied between 2.02 and 5 bar. The flow rate of the feed is 100 kmol/h with a composition of 60 mol% A, fed as a subcooled liquid at a pressure of P_1 and temperature of 46.85 °C. A with a purity of 99.5 % is collected as the distillate of HPC (D_1). The bottom product of HPC is fed into the second, low-pressure column (LPC), whose top pressure is 0.101 bar. B with a purity of 99.5 % is collected as the distillate of LPC (D_2), while the bottom product (W_2), whose composition is near the azeotropic one at the pressure of LPC, is recycled to HPC. The pressure drop of LPC is 0.2407 bar, that of LPC is 0.0492 bar. In HPC, the composition of the distillate and the flow rate of the bottom product (W_1) are specified, whose value from the material balance is $W_1=F+F_{rec}-D_1$ where F_{rec} and D_1 are fixed. In LPC, the specifications are D_1 (whose value, 39.90 kmol/h, is determined from the material balances) and the heat duty of the reboiler (Q_{r2}).
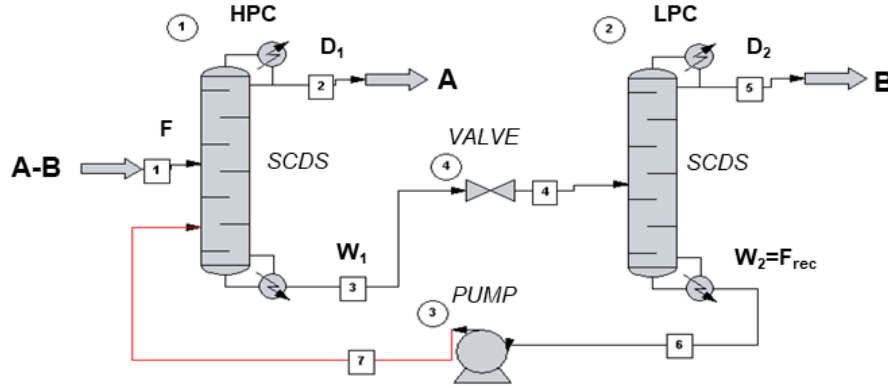

Figure 2: Basic PSD flow sheet for maximum azeotropes

3.1 Partial Heat Integration (PHI)

The PHI consists of heating the reboiler of the LPC with the condensing top vapour of HPC. Due to the difference in the pressures of HPC and LPC, the temperature difference in the new condenser-reboiler is high enough to enable heat transfer. In our case, the heat duty of the condenser of HPC (Q_{c1}) is much higher than that of the reboiler of LPC (Q_{r2}). Therefore, LPC does not need external heating, while an additional condenser is required to condense the top vapour of HPC completely.

3.2 Full Heat Integration (FHI)

By full Heat Integration, the whole heat duty of the condenser of HPC is used to heat the reboiler of LPC. This is achieved by matching Q_{c1} and Q_{r2}. In FHI, the additional condenser present PHI is not necessary.

3.3 Application of heat pumps

The application of heat pumps (HP) might help to reduce the energy cost of the PSD process, as well. In vapour recompression (VRC), the top vapour of a column (whose flow rate is V_{top}) is the working fluid (WF), which is compressed to pressure P_{out} (and temperature T_{out}) and used to heat the reboiler of the same column. After the reboiler, the pressure of WF is reduced to that of the column in an expander, which leads to its partial evaporation.

Three VRC configurations are investigated: VRC in HPC (VRC1), in LPC (VRC2) and in both columns (VRC3). Three different cases can be distinguished based on the value of the ratio of WF compressed to that of leaving the column (β) (Ferchichi et al. 2020). 1. After the expansion, the vapour part of WF is condensed totally in an after-cooler, then it is divided to distillate and reflux. Here the flow rate of WF $V_{WF}=β·V_{top}$ is fixed and β=1.

2. The vapour of the WF is only partially condensed and then divided into liquid (distillate and reflux) and vapour (V_{rec}) streams. V_{rec} is then recycled and mixed with the top vapour in order to increase the quantity of WF compressed. Here β, which is higher than 1.0, is variable and should be optimised.

3. The top vapour leaving the column is divided into the WF and a by-pass stream. After the expansion, WF is condensed totally in an after-cooler and then mixed with the by-pass stream condensed in an auxiliary condenser. Here β is lower than 1.0 and should be optimised.

4. Calculation method

The ChemCAD model of the process is presented in Figure 2. Unit 1 and Unit 2 are the HPC and LPC, respectively (SCDS columns). The optimised non-heat integrated process of Ferchichi et al. (2020) is considered as the base case (NHI0) where the top pressure of HPC is P_1=2.02 and P_2=0.1 bar. The number of theoretical trays in the base case is N_1=90 (counted from the top, including the total condenser and the partial reboiler) for HPC, while N_2=22. The fresh feed is introduced onto stage f_1=6 of HPC, the recycle from LPC onto f_{rec}=20, while W_1 enters LPC on stage f_2=11.

The different options to reduce the energy demand of the process are compared with each other and with the NHI process by calculating the values of an economic indicator, the total annualised cost (TAC, \$/y) and two environmental indicators, the CO_2 emission generated by the process and the Eco-Indicator 99 (EI99) values. TAC is calculated from the total capital cost (TCC, \$) of the equipment and the total energy cost (TEC, \$/y):

$$TAC = \frac{TCC}{PBP} + TEC \tag{1}$$

where PBP is the length of the payback period, here 3 years. The above formula is commonly used for economical evaluation of distillation processes (e.g. by Li et al., 2016).

The method and data for cost calculation are described in detail in Ferchichi et al. (2020), with the exception that the effect of the change of column pressure on the capital cost is included (Eq(2)). TCC consists of the cost of the column vessels, heat exchangers and compressors.

The column vessel cost for each column (Douglas, 1989):

$$C_{CV} = 5{,}547.17 \cdot Di^{1.066} H^{0.802} \left(2.18 + F_p\right) \tag{2}$$

where Di is the column diameter (m), and H is the length of the column (m) calculated from the number of theoretical trays (N) as H=1.2·0.61·(N-2) by taking into account tray spacing (0.61 m) and efficiency (0.833). F_p is a correction factor taking into account the effect of pressure: it is 1.0 below 3.45 bar and 1.05 above that.

The energy cost includes the cost of heating steam and (when a heat pump is applied) electricity. LP steam (4 bar) with a price of 7.78 \$/GJ is used for heating LPC, MP steam (11 bar) with 8.22 \$/GJ for HPC. The price of electricity is taken as four times the price of LP steam: 31.12 \$/GJ.

The CO_2 emission of the process is calculated by taking into account the emissions related to the production of heating steam and electricity. The EI99 values (proposed by Goedkoop and Spriensma (2001)) express the damage caused by the process to human health, the ecosystem quality, as well as its resource consumption. The amount of heating steam, steel used to build the columns and electrical energy are taken into account. Ferchichi et al. (2010) describe the details of the calculation method.

By the NHI process, first, the influence of P_1 from 1.01 to 5.0 bar is studied without changing the geometrical parameters (fixed number of trays, feed locations) (NHI1a). For each P_1, the optimal W_1 and Q_{r2}, where the sum of the two reboiler heat duties are minimal, are determined by iterative optimisation. The upper limit of P_1 is chosen so that there is at least 5 °C difference between the temperature of MP steam (184.5 °C) and T_{r1}. In the next step, the optimal feed locations are determined for a selected P_1 value by minimising Q_{r1} (NHI1b). Subsequently, the minimisation of TAC is performed by a GA twice. 1. NHI2a: the relative feeding locations (f_1/N_1, f_{rec}/N_1, f_2/N_2) are kept constant at their basic values (0.1015, 0.3478 and 0.3704). The optimisation variables: N_1, N_2, W_1 and Q_{r2}. 2. NHI3a: the feeding locations (f_1, f_{rec}, f_2) are optimisation variables, as well. The ranges of the optimisation variables (Table 1, Range 1) are the same for both approaches.

Table 1: Ranges of the optimisation variables for GA

	P_1, bar	N_1	f_1	f_{rec}	N_2	f_2	W_1, kmol/h	Q_{r2} or Q_{rc}, MJ/h
Range 1	2.02-5.0	50-100	3-13	14-45	16-40	4-15	50-250	2,000-12,500
Range 2					10-30	3-10		

The optimisation is performed by an elitist genetic algorithm written in VBA under Excel. The parameters of the GA: mutation probability: 5 %, crossover probability: 70 %, population size: 30, number of generations: 100. To calculate the results necessary for the calculation TAC, the algorithm calls ChemCAD for each individual.

After the optimisation by GA, the feed locations are modified to reduce Q_{r1} and Q_{r2} and thus TAC further (NHI2b and 3b).

Partial Heat Integration is applied to the NHI process with the lowest TAC (NHI1b), first, without changing any parameter (PHI1). Subsequently, PHI is optimised by varying W_1 and the heat duty of the reboiler-condenser (Q_{rc}) only (PHI2). Finally, the optimisation is performed by GA, now including the geometrical parameters (with Range 2) to obtain the optimal partial Heat Integration (PHI3).

F is achieved by adding a feed-forward Controller to the flow-sheet, which increases Q_{r2} so that it is equal to Q_{c1}. Increasing Q_{r2} also makes Q_{c2} and the reflux ratio of LPC (R_2) higher. First, FHI is applied to the optimal NHI, and no other parameters are changed (FHI1), then W_1 is varied to find the minimal TAC without changing the geometrical parameters (FHI2). Finally, GA optimisation is performed, including all the parameters (FHI3). For the application of heat pumps, P_{out} is determined first for $\beta=1$ (VRC1a, 2a, a) and then both P_{out} and β for $\beta\neq1$ (VRC1b, 2b, 3b). If $\beta=1$, P_{out} is chosen so that the temperature of WF (T_{WF}) be higher than the temperature of the bottom liquid (T_r) by the minimum approach temperature $\Delta T_{min}=5$ °. The WF leaving the reboiler can be subcooled or partially uncondensed. The first case is not optimal from the point of view of heat transfer; the second one shows that the flow rate of WF is unnecessarily high.

For $\beta\neq1$, the values of P_{out} and β must be determined, where both of the following requirements are fulfilled:

- The temperature of WF leaving the reboiler should be T_r+5 °C
- The WF leaving the reboiler should be a saturated liquid.

5. Results

5.1 No Heat Integration (NHI)

The optimal values of W_1 and Q_{r2} are determined for several P_1 values (NHI1a, Table 2). On the increase of P_1, the difference between the azeotropic composition increases, which decreases F_{rec} (and hence W_1), the reboiler duties and thus TEC (Figure 1b). TEC decreases in a monotonous way but to a smaller and smaller extent ($|dTEC/dP_1|$ decreases). Most items of the capital costs also decrease due to the following changes: the heat duties of the heat exchangers decrease, the temperature difference in the condenser of HPC increases, and the column diameters decrease because of the lower vapour flow rates. On the other hand, the cost of the reboiler of HPC increases since the temperature difference between the reboiler and the MP steam decreases. Because of these effects, TCC has a minimum at $P_1=3.0$ bar. TAC also has a minimum as a function of P_1, but at a much higher value: 4.5 bar, where $dTAC/dP_1 = dTEC/dP_1 + dTCC/dP_1 = 0$. Compared to the base case (NHI0), TCC decreased by 11.8 %, TEC by 36.2 % and TAC by 30.1 %.

Table 2: Results of the NHI process with optimisation of P_1, W_1, Q_{r2}, f_1, f_{rec} and f_2 ($N_1=69$, $N_2=27$)

Case	NHI0		NHI1a		NHI1b	
	Ferchichi et al. (2020)		Optimised operational parameters		Optimised feed locations	
Parameter	HPC	LPC	HPC	LPC	HPC	LPC
P (bar)	2.02	0.1	4.5	0.1	4.5	0.1
f_i	5	10	5	10	7	10
f_{rec}	17	-	17	-	24	-
Di (m)	1.37	1.98	0.914	1.52	0.914	1.52
W (kmol/h)	108.8	68.9	66.0	26.1	66.0	26.1
x_{W2}		0.434		0.432		0.432
T_c (°C)	120.8	58.3	148.1	58.3	148.1	58.3
T_r (°C)	145.6	72.6	174.1	72.6	174.1	72.6
R	4.65	2.79	2.74	1.24	2.69	1.24
Q_c (MJ/h)	13,475	6,666	8,623	3,905	8,525	3,905
Q_r (MJ/h)	15,258	5,301	10,373	2,700	10,275	2,700
TCC (10^5 \$)		14.64		12.91		12.88
TEC (10^5 \$/y)		14.52		9.26		9.19
TAC (10^5 \$/y)		19.40		13.56		13.48

Subsequently, the feeding locations are modified to reduce the energy demand even further (Table 2, NHI1b). The feed tray of the feed is moved slightly, while that of the recycle stream considerably lower in the column (f_1 and f_{rec} increased). As a result, a slight further decrease of TAC (by 0.6 %) is reached.

GA optimisation is first performed by keeping the relative feed locations fixed (Table 3, NHI2a, optimisation variables: P_1, N_1, N_2, W_1, Q_{r2}). P_1 is remarkably close to that of NH1b. N_1 also has a similar value, while N_2 is lower. The decrease of N_1 and N_2 is accompanied by higher W_1, Q_{r1} and Q_{r2}, especially Q_{r2}. Although TCC is reduced by 2.3 %, TEC is higher by 5.8 %, and TAC by 3.2 %, meaning that GA was not capable to decrease TAC in this case (even after increasing the number of generations to 300). To verify whether using fixed relative feeding locations is appropriate, the feeding locations are optimised subsequently by minimising Q_{r1} (NHI2b). f_1 and f_2 are only slightly changed; however, f_{rec} is placed considerably lower in the column, showing that fixing f_{rec}/N_1 is not optimal. By modifying the feed locations, only a slight decrease of TAC (by 0.96 %) is achieved.

Performing the optimisation with variable feed locations resulted in parameter values similar to those obtained with fixed relative feed locations (Table 3, NHI3a). The energy demand is slightly lower, leading to a TAC lower by 1.3 %. The feeding locations are only 1-2 trays away from their optimal positions (NHI3b).

Table 3: Results of the NHI process optimised by GA (variable number of trays)

Case	NHI2a		NHI2b		NHI3a		NHI3b	
	Fix relative feed locations		Optimised feed locations		Variable feed locations		Optimised feed locations	
Parameter	HPC	LPC	HPC	LPC	HPC	LPC	HPC	LPC
P (bar)	4.49	0.1	4.49	0.1	4.53	0.1	4.53	0.1
N	64	22	64	22	65	21	65	21
f_i	6	8	7	8	6	9	7	9
f_{rec}	22	-	31	-	28	-	30	-
Di (m)	0.914	1.68	0.914	1.68	0.914	1.68	0.914	1.68
W (kmol/h)	80.1	40.2	80.1	40.2	77.1	37.2	77.1	37.2
x_{W2}		0.418		0.421		0.421		0.421
T_c (°C)	148.0	58.3	148.0	58.3	148.4	58.3	148.4	58.3
T_r (°C)	173.8	72.6	173.8	72.6	174.2	72.6	174.2	72.6
R	2.65	1.75	2.59	1.75	2.69	1.68	2.59	1.68
Q_c (MJ/h)	8,433	4,782	8,289	4,780	8,300	4,668	8,285	4,668
Q_r (MJ/h)	10,381	3,379	10,235	3,379	10,212	3,302	10,197	3,302
TCC (10^5 $)		12.58		12.53		12.56		12.56
TEC (10^5 $/y)		9.72		9.62		9.55		9.54
TAC (10^5 $/y)		13.92		13.80		13.74		13.73

The lowest TAC is reached not by using GA but by optimising first W_1 and Q_{r1}, then all feeding locations at P_1=4.5 bar. Nevertheless, the best GA result is only by 1.9 % higher than this optimum. The main differences are that the results of GA have lower N_1 and N_2, slightly higher W_1 and higher Q_{r2}. The results also show that while fixing the relative feed locations is clearly not optimal, it does not result in a significantly higher TAC.

5.2 Partial Heat Integration (PHI)

First, PHI is applied to the optimal NHI process NHI1b (Table 4, PHI1). Since Q_{c1} is higher than Q_{r2}, an auxiliary condenser is needed (with a heat duty of Q_{aux}) to condense the top vapour of HPC not used for heating the reboiler of LPC. By applying PHI, LPC does not require heating steam, leading to a decrease of TEC by 19.9 %. TCC is practically unchanged, and thus TAC is decreased by 13.8 %.

Table 4: Results of the PHI process

Case	PHI1		PHI2		PHI3	
	Non-optimised		Optimised operational parameters		Full optimisation	
Parameter	HPC	LPC	HPC	LPC	HPC	LPC
P (bar)	4.5	0.1	4.5	0.1	4.39	0.1
N	69	27	69	27	62	15
f_i	7	10	7	10	6	7
f_{rec}	24	-	24	-	30	-
Di (m)	0.914	1.52	0.914	1.52	0.914	1.83
W (kmol/h)	66.0	26.1	39.0	29.1	85.5	45.6
x_{W2}		0.432		0.429		0.429
T_c (°C)	148.1	58.3	148.1	58.3	147.2	58.3
T_r (°C)	174.1	72.6	174.1	72.6	172.8	72.6
R	2.69	1.24	2.59	1.75	2.56	3.40
Q_c (MJ/h)	-	3,905	-	4,087	-	7,568
Q_r (MJ/h)	10,275	-	10,194	-	10,231	-
Q_{aux} (MJ/h)	5,825	-	5,602	-	2,033	-
Q_{rc} (MJ/h)	-	2,700	-	2,800	-	6,198
TCC (10^5 $)		12.79		12.78		11.95
TEC (10^5 $/y)		7.36		7.30		7.33
TAC (10^5 $/y)		11.62		11.56		11.31

Without changing the geometrical parameters (PHI2), it is possible to further reduce Q_{r1} by slightly increasing both F_{rec} (through W_1) and Q_{rc} (Table 4). TEC decreased by 0.82, TAC by 0.52 %.

Performing full optimisation with GA (PHI3) decreases N_1 and N_2 (N_2 is almost halved). This is possible since Q_{rc} can be increased by increasing considerably the level of heat integration between the columns. This results in higher F_{rec} and R_2, as well as an increased column diameter (Di_2). The capital cost of LPC becomes lower due to the much lower N_2. P_1 is only slightly changed, suggesting that HI does not significantly change the optimal column pressure. Compared to PHI1, TCC decreases by 6.5 %, TEC is virtually unchanged, and TAC decreases by 2.7 %. By applying the optimal HI, TAC decreases by 16.1 % compared to NHI1b.

5.3 Full Heat Integration (FHI)

By applying FHI without changing either operational or geometrical parameters (FHI1), Q_{rc} is increased to the 3.12 times of that of the optimal NHI process (NHI1b) (Table 5). Consequently, R_2 and the diameter of LPC are also considerably higher. TCC increases by 19.5 % because of the higher cost of the shell and condenser of LPC. The reduction of the energy demand (by 20.8 %) is similar to that of PHI1. As a result, TAC is decreased by 7.9 % compared to NH1b, meaning that (without optimisation) applying only partial Heat Integration is more favourable than FHI.

Table 5: Results of the FHI process

Case	FHI1		FHI2		FHI3	
	Non-optimised		Optimised recycle flow rate		Full optimisation	
Parameter	HPC	LPC	HPC	LPC	HPC	LPC
P (bar)	4.5	0.1	4.5	0.1	4.37	0.1
N	69	27	69	27	62	13
f_i	7	10	7	10	7	6
f_{rec}	24	-	24	-	30	-
Di (m)	0.914	2.44	0.914	2.44	0.914	2.44
W (kmol/h)	66.0	26.1	79.0	39.1	87.1	47.2
x_{W2}	0.438		0.438		0.426	
T_c (°C)	148.1	58.3	148.1	58.3	147.0	58.3
T_r (°C)	174.1	72.6	174.1	72.6	172.7	72.6
R	2.65	4.53	2.47	4.40	2.57	4.59
Q_c (MJ/h)	-	9,624	-	9,398	-	9,730
Q_r (MJ/h)	10,170	-	9,943	-	10,270	-
Q_{rc} (MJ/h)	-	8,422	-	8,018	-	8,249
TCC (10^5 $)	15.39		15.20		12.48	
TEC (10^5 $/y)	7.28		7.12		7.35	
TAC (10^5 $/y)	12.41		12.19		11.51	

By increasing the recycle flow rate to minimise TAC (by 50 %) (Table 5, FHI2), the heat duties can be slightly decreased, resulting in a lower TEC (by 2.2 %) and TCC (1.2 %). TAC is thus decreased by 1.8 %.

By the optimisation with GA (FHI3), the numbers of trays are decreased to values very close to those of the optimal PHI (PHI3). Q_{rc} is between the values of FHI1 and FHI2, while F_{rec} is increased even further. P_1 is only slightly changed, to a value almost equal to that of the optimal PHI. Due to the smaller numbers of trays, TCC decreases by 18.9 % compared to FHI1. Although Q_{r1} increases slightly (by 0.96 %), TAC is lower by 7.3 %. Compared to PHI3, the TAC of the optimal FHI3 is higher if only slightly (by 1.8 %), even if the cost of the auxiliary condenser is saved.

5.4 Application of heat pumps

The application of VRC heat pumps to the optimal NHI process (NHI1b) is studied. First, heat pumps are applied to either to only HPC or LPC (VRC1 and VRC2), then for both columns (VRC3). In each case, calculations are performed first with $\beta=1$ then with optimal β.

5.4.1 Heat pump for HPC only

The results of the application of a VRC heat pump for HPC (VRC1) are shown in Table 6. By the conventional operation ($\beta=1$, VRC1a), $P_{out}=31.4$ bar corresponding to a relatively high compression ratio of CR=6.98. The temperature of the WF leaving the reboiler takes its desired value: $T_{WF}=T_{r1}+5=179.1$ °C. However, the WF is strongly subcooled by 40 °C. Increasing P_1 from 2.02 to 4.5 bar does not increase P_{out} proportionally since CR was 4.75 for P_1=2.02 bar (Ferchichi et al., 2020).

By applying the heat pump with β=1, TCC increases by 161 % because of the high investment cost of the compressor (it is 71.1 % of TCC). The steam cost is reduced to its 19.9 %, while TEC decreases by 12.4 %. However, the high capital cost makes the application of VRC uneconomical by increasing TAC by 42.9 %.

By recycling one part of the WF (VRC1b), P_{out} can be reduced. The flow rate of recycled WF is determined by the heat duty of the after-cooler. The lower this heat duty, the lower the amount of WF condensed and the higher the amount of WF recycled. An upper limit of β thus exists where $Q_{after-cooler}$ is zero: β could be further increased only by heating in the after-cooler, which is undesirable to avoid using external heating energy. The actual value of this upper limit is a function of P_{out}. As in the work of Ferchichi et al. (2020), WF cannot be a saturated liquid and have the desired temperature (179.1 °C) at the same time without heating, and two cases can be distinguished:

1. The temperature difference in the reboiler is ΔT_{rc}=5 °C, but WF is subcooled (its boiling point is 211.48 °C). P_{out} is 19.55 bar (CR=4.35), β=1.068, W is 486.0 kW.
2. The WF leaving the reboiler-condenser is saturated liquid (its temperature is 207.44 °C). P_{out} is lower in this case: 18.043 bar (CR=4.01), while the amount of WF recycled is higher: β=1.141.

Table 6: Comparison of results of the application of heat pumps without and with recycling or by-pass

Parameter	VRC1a	VRC1b	VRC2a	VRC2b	VRC3a HPC	VRC3a LPC	VRC3b HPC	VRC3b LPC
β	1	1.141	1	0.697	1	1	1.141	0.697
W (kW)	637.0	485.9	76.1	53.3	637.0	76.1	485.9	53.3
$Q_{after-cooler}$ (MJ/h)	543.1	-	1,343.4	76.21	543.1	1,343.4	-	76.21
Q_c (MJ/h)	-	-	-	1,185	-	-	-	1,185
TCC (10^5 $)	33.65	28.88	19.26	18.15	39.70		34.15	
Steam cost (10^5 $/y)	1.83	1.83	7.36	7.36	-		-	
Electricity cost (10^5 $/y)	6.22	4.74	0.74	0.52	6.96		5.26	
TEC (10^5 $/y)	8.05	6.57	8.10	7.88	6.96		5.26	
TAC (10^5 $/y)	19.26	16.20	14.52	13.93	20.19		16.65	

The compressor work is slightly lower in the second case; thus, it is the one shown in Table 6. By the recycling, P_{out} is reduced considerably, leading to a decrease in the cost of the compressor, and thus TCC (TCC is lower by 14.2 %). TEC is also lower by 18.4 %. In consequence, the TAC is reduced by 15.9 %; however, the application of the heat pump is still not economical.

5.4.2 Heat pump for LPC only

The results of the VRC heat pump for LPC (VRC2) are shown in Table 6. With the conventional heat pump (VRC2a, β=1), WF must be compressed to 0.24 bar (CR=2.40) so that its temperature when leaving the reboiler is 72.62 °C (T_{r2}+5 °C). However, WF is only partially condensed in the reboiler-condenser, and an after-cooler is need after the expansion to completely condense WF. Since Q_{r2} is much lower than Q_{r1}, the compressor work is also lower than in VRC1. TCC increases by 49.5 % because of the cost of the compressor, TEC is reduced by 11.9 %, and TAC becomes higher by 7.7 %.

By by-passing the compressor with the WF (VRC2b), the compressor work can be reduced. Although the P_{out} does not change (0.24 bar), V_{WF} is lower. The by-pass stream, which is 30.3 % of the top vaour, is condensed in a condenser. The vapour part of WF evaporated during expansion is condensed in an after-cooler. The cost of the compressor and thus TCC is reduced (TCC by 5.8 %). TEC is only slightly lower (by 2.7 %). In consequence, the TAC is slightly reduced (by 4.1 %). The application of the heat pump is still not economical, but the difference in the TAC values is small (3.3 % of the TAC of NHI1b).

5.4.3 Heat pump for both columns

The simultaneous application of two heat pumps with β=1 (VRC3a) decreases TEC by 24.3 %; however, the high cost of the compressors increase TAC by 49.8 % (Table 6). By optimizing V_{WF1} and V_{WF2} (VRC3b, β≠1), TEC is further decreased by 24.4 %, to a value that is 57.2 % of the TEC of the optimal NHI. TAC is decreased by 17.5 %, but it is still higher than that of NHI1b.

5.5 Economic comparison of the cases studied

The total capital, energy, and annualised costs are summarised in Table 7 for the optimal case of each option to reduce the energy demand of the process. The lowest TCC is obtained with PHI, while TEC is the lowest if heat pumps (with optimal WF flow rate) are applied by both columns (VRC3b). The lowest TAC is reached by PHI, although that of FHI is only slightly higher. The application of the heat pumps is not economical.

5.6 Environmental evaluation

The environmental indicators (CO_2 emissions and EI99 values) calculated are shown in Table 10. The EI99 values depend principally on the steam consumption and, to a lower degree, on electricity consumption, while the contribution of the amount of steel used to build the columns is negligible.

Table 9: Economic comparison of the cases studied

Case	NHI1b	PHI3	FHI3	VRC1b	VRC2b	VRC3b
TCC (10^5 \$/y)	12.88	11.95	12.48	28.88	18.15	34.15
TEC (10^5 \$/y)	9.19	7.33	7.35	6.57	7.88	5.26
TAC (10^5 \$/y)	13.48	11.31	11.51	16.20	13.93	16.65

Table 10: CO_2 emissions and EI99 values of the configurations studied

Case	CO_2 emissions (kg/h)	Specific CO_2 emissions (kg CO_2/kg feed)	(kmol CO_2/kmol feed)	EI99 (point/y)
NHI0	273.9	0.079	0.062	135,038
NHI1b	178.0	0.051	0.040	85,502
PHI1	158.1	0.045	0.036	68,628
PHI3	157.4	0.045	0.036	68,334
FHI1	156.4	0.045	0.036	67,927
FHI3	158.0	0.045	0.036	68,594
VRC1a	137.1	0.039	0.031	21,802
VRC1b	109.3	0.031	0.025	20,633
VRC2a	172.1	0.049	0.039	69,217
VRC2b	167.8	0.048	0.038	69,040
VRC3a	131.2	0.038	0.030	5,517
VRC3b	99.18	0.028	0.023	4,171

By optimising NHI, the CO_2 emissions are reduced by 35.0 %, the EI99 values by 36.7 %. Applying either PHI or FHI, without or with optimisation, further reduces the CO_2 emissions by 11-12 % and EI99 by 20 %. Applying a heat pump for HPC is highly recommended from an environmental point of view: with $\beta=1$, the CO_2 emissions decrease by 22.9 %, EI99 by a remarkable 74.5 %. By optimising β, further reductions of 20.3 and 5.4 % can be achieved, respectively. In the case of LPC, only slight reductions can be reached by the application of the heat pump. The most environmentally friendly option is VRC3b: its CO_2 emission is 55.7 %, its EI99 value is only 4.88 % of that of the optimal NHI1b process.

Considering both TAC and the environmental indicators, four options are non-dominated, meaning that no other configuration exists, having both lower TAC and lower environmental impact: PHI3, FHI1, VRC1b and VRC3b.

6. Conclusions

The separation of the maximum-boiling azeotropic mixture water-EDA by pressure-swing distillation was studied by simulation and optimised. The influence of varying the top pressure (P_1) of the high-pressure column (HPC) was also investigated. First, the total annualised cost (TAC; with a payback period of 3 years) of the separation process was minimised without applying Heat Integration (NHI) by using different optimisation approaches. By NH1b, only the operational parameters (P_1, the flow rate of the bottom product of HPC (W_1), reboiler heat duty of the low-pressure column LPC (Q_{r2})) and the feeding locations were optimised. Subsequently, the optimisation was performed by a genetic algorithm (GA) including the numbers of trays as optimisation variables, with either fixed (NHI2a) or variable (NHI3a), relative feeding locations then further optimised (NHI2b and NHI3b). The lowest TAC was reached by NHI1b (optimal NHI), where P_1 increased from 2.02 to 4.5 bar, and TAC was decreased by 30.5 % compared to the results without optimising P_1.

Partial (PHI1) and full Heat Integration (FHI1) were applied to the optimal NHI process and further optimised by varying either the operational parameters (W_1 and only for PHI, Q_{r2}; PHI2 and FHI2) only or geometrical parameters (numbers of tray, feed locations), as well (PHI3 and FHI3). The lowest TAC was reached by PHI3 (by 16.1 % lower than that of the optimal NHI process), that of FHI3 was only slightly higher (by 1.8 %). The optimal P_1 for PHI and FHI did not differ significantly from 4.5 bar.

Finally, vapour recompression (VRC) heat pumps were applied to one (VRC1a and 2a) or both columns (VRC3a). The flow rate of the working fluid (WF) of the heat pumps was optimised to minimise the compressor power (VRC1b, 2b, 3b), and thus its cost by either recycling or by-passing one part of the WF. Although the

application of heat pumps reduced the total energy cost considerably, it was not economical because of the high investment cost of the compressor. Increasing P_1 was unfavourable for the heat-pump assisted distillation: by VRC1a, the WF had to be compressed to 31.4 bar. By optimising the flow rate of WF (VRC1b), this value was reduced to 18.0 bar, resulting in a 17.5 % decrease in TAC. This highlights the importance of optimising the amount of the WF.

The environmental impact of the different options was evaluated by calculating their CO_2 emission and Eco-indicator 99 (EI99) values. By optimising NHI, both values were considerably reduced (by 35 and 37 %, respectively). By either PHI or FHI, the CO_2 emissions can be further reduced by ca. 12 %, while EI99 by 20%. Although the application of heat pumps was uneconomical, it was very favourable from the environmental point of view, particularly for the HPC. For example, the CO_2 emission and EI99 values of VRC3b (with optimal flow rate of WF) are lower than those of the optimal NHI process by 44 and 95 %, respectively.

Future works might include the simultaneous optimisation of the PSD system and the heat pump(s) since P_1 influences the compression ratio, the study of the effect of the payback period or equipment lifetime on the order of the different options with respect to TAC, as well as the influence of feed composition (relative to the azeotropic ones) on the results of energy-saving options.

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