



# Optimisation of the higher pressure of pressure-swing distillation of a maximum azeotropic mixture

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## ABSTRACT

The pressure-swing distillation separation of a maximum azeotropic mixture, water-ethylenediamine, is simulated and optimised. In contrast to our previous works, the top pressure of the high-pressure column (HPC) is considered as an optimisation variable. The total annual cost (TAC) is minimised first without heat integration (NHI), then different energy demand reduction options are applied and optimised: partial (PHI) and full (FHI) heat integration and vapour recompression (VRC) heat pumps. For heat pumps, working fluid flow rate is optimised to minimise the work and thus the compressor costs. Environmental impacts are also considered by calculating CO<sub>2</sub> emissions and Eco-indicator 99 (EI99) values. The application of HI does not significantly change the pressure optimum. The lowest TAC is obtained by the optimal PHI, which decreases TAC by 16% compared to the optimal NHI process. Applying VRC is uneconomical, but very favourable environmentally: CO<sub>2</sub> emissions and EI99 are reduced by 44 and 95%, respectively.

## 1. Introduction

Distillation is the most frequent method to separate liquid mixtures despite its high energy demand: distillation accounts for more than 40% of the energy demand of the chemical industry [1]. Azeotropic mixtures cannot be separated by conventional distillation methods, the application of a special distillation method is required such as extractive (ED [2]), heterogeneous azeotropic (HAD) and pressure-swing (PSD) distillation (Doherty et al. [3]). These methods can be combined with reactive distillation, as well, where one of the components of the azeotropic mixture is consumed by a reaction [4].

The advantage of PSD is that it does not require the addition of a new component to the feed, contrary to ED and HAD. However, the azeotrope must be pressure-sensitive. A binary mixture is separated by feeding it into one of the two columns (depending on the relation of the feed and azeotropic compositions) operating at different pressures. The components of the mixture are obtained either in the bottom products (minimum-boiling azeotropes) or distillates (maximum-boiling azeotropes).

The composition of the other products is near the azeotropic one at the pressure of the columns; these products are introduced 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 (HPC) and the reboiler of the low-pressure column (LPC). As the heat duties of these heat exchangers are usually not equal, partial heat integration (PHI) is realised; either an auxiliary condenser or reboiler is needed.

By modifying the operational parameters of the two columns, the heat duty of the condenser of HPC and the reboiler of LPC can be made equal, full heat integration (FHI) can be performed, and the auxiliary heat exchanger can be saved. FHI can be considered as the limiting case of PHI. The optimal extent of heat integration in terms of energy demand or total annual cost (TAC) can be reached by optimising the whole two-column process.

The energy demand can also be reduced by applying mechanical heat pumps (HP) to provide the necessary heat in the reboilers [5]. In vapour recompression (VRC), the working fluid (WF) compressed and then

*Abbreviations:* aux, auxiliary; bp, boiling point; byp, by-pass; CR, compression ratio; EDA, ethylenediamine; EI99, Eco-indicator 99; FHI, full heat integration; GA, genetic algorithm; HI, heat integration; HP, heat pump; HPC, high-pressure column; LP, low pressure; LPC, low-pressure column; MP, medium pressure; NHI, non-heat integrated process; PHI, partial heat integration; PSD, pressure-swing distillation; PSDIC, pressure-swing distillation with an intermediate connection; rc, reboiler-condenser; rec, recycle; TAC, total annual cost; TCC, total capital cost; TEC, total energy cost; THF, tetrahydrofuran; VC, vapour compression; VLE, vapour-liquid equilibrium; VRC, vapour recompression; WF, working fluid.

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condensed to heat the reboiler 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 [6] studied the separation of a mixture of *i*- and *n*-butane and 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. Hence the output pressure of the compressor decreased, leading to a reduction of compressor work by 45%. If the whole latent heat of the top vapour is not needed, part of it can bypass the compressor to reduce its work. For PSD this option was studied by Zhang et al. [7], Shi et al. [8] and Yang et al. [9].

The column pressures are usually selected either arbitrarily or based on heuristics. One of the columns, generally LPC, is often atmospheric. In this way, operation in vacuum is avoided, despite its potential economic benefits [10]. If the decrease of pressure is advantageous from the point of view of VLE conditions, LPC is operated in vacuum. The minimum of its top pressure ( $P_{LPC}$ ) is determined so that its condenser can be cooled with (inexpensive) cooling water. Increasing the pressure difference between the columns is advantageous from the point of view of energy demand since it increases the difference between the azeotropic compositions and thus decreases the flow rates of the intercolumn streams. Therefore, the pressure of HPC ( $P_{HPC}$ ) is usually selected as the maximum value possible given by the temperature of the (saturated) heating steam available. However, the possibility of using different steam qualities (low-, medium- and high-pressure) is not always considered, according to Risco et al. [11]. For each steam quality, there is a local minimum of the energy demand at the maximum  $P_{HPC}$  possible. On the other hand, Abu-Eishal and Luyben [12] for the separation of THF-water, found that  $P_{HPC}$  had an optimal value if PHI was applied, because, on the increase of  $P_{HPC}$ , the reboiler duty of LPC decreased, but so did the condenser duty of HPC, that is, the amount of heat available for HI.

From an economic point of view, the optimal pressure values are lower than the maximal ones since the capital cost of the HPC reboiler increases on the increase of  $P_{HPC}$ . Therefore, it is important to select  $P_{HPC}$  by minimising the TAC of the PSD system. In most works that consider the effect of  $P_{HPC}$  on TAC, a two-step approach is followed. The values of geometrical and operational parameters are determined by performing sensitivity studies or using a sequential iterative approach for fixed column pressures, and the calculations are repeated by changing the pressures. Yu et al. [13] studied the separation of methylal and methanol. FHI was applied, and although the energy demand decreased monotonously on the increase of  $P_{HPC}$ , TAC had an optimum at 12 bar instead of the maximum (14 bar). Zhu et al. [14] varied the pressure of both columns for the separation of ethanol and toluene without HI.  $P_{LPC}$  was optimal at its lowest possible value (0.4 bar), yet 0.5 bar was chosen for safety reasons. For PHI and FHI, only  $P_{HPC}$  was varied. Ghuge et al. [15] determined the optimal  $P_{HPC}$  for the separation of a THF-water mixture without HI. PHI and FHI were then applied without changing  $P_{HPC}$ . Wang et al. [16] proposed the application of an intermediate connection between the columns (PSDIC), which is taken as a side stream from one column and fed to the other one. Separation of the mixtures of ethyl acetate-ethanol, chloroform-methanol and water-ethylenediamine were studied without HI and with PHI. The PHI processes were not optimised.  $P_{LPC}$  was selected based on the temperature of the cooling water, while  $P_{HPC}$  was varied within the sequential iterative optimisation. Li et al. [17] studied the separation of a ternary mixture consisting of acetonitrile, isopropanol, and water. After eliminating water, the acetonitrile-isopropanol mixture was separated in a conventional two-column PSD system. Both column sequences were possible.  $P_{LPC}$  was determined by the cooling water temperature. As a function of  $P_{HPC}$ , TAC had a minimum at 7 or 7.5 bar depending on the column sequence. PHI and VRC heat pumps were applied without studying the influence of column pressures or optimisation.

By using the optimisation methods (sensitivity study or sequential iterative optimisation) applied in the above works, local optima are likely to be found. In works using more sophisticated optimisation

methods, the column pressures were only occasionally included as an optimisation variable. Wang et al. [18] optimised with simulated annealing the PSD of the mixtures of acetone-methanol and chloroform-methanol without and with HI. Either PHI (acetone-methanol) or FHI (chloroform-methanol) was applied. In all the cases, the optimisation was performed first with fixed  $P_{LPC}$  and  $P_{HPC}$  and then with including both pressures as optimisation variables. By optimising the pressures, TAC was further reduced by 12% (acetone-methanol) and 7.4% (chloroform-methanol) if HI was not applied, by 7.2% for PHI (acetone-methanol) and 3.7% for FHI (chloroform-methanol). Ma et al. [19] developed an optimisation method based on a pseudo-transient continuation approach, which was applied to the separation problem of Abu-Eishal and Luyben [12] with PHI.  $P_{LPC}$  was fixed,  $P_{HPC}$  was an optimisation variable. The new method gave by 2.7% lower TAC than the sequential iterative optimisation. Yang et al. [20] proposed a two-step optimisation procedure for a three-column system for the separation of the ternary mixture THF-ethanol-water. In the first step, optimisation was performed by SQP for different, fixed values of the top pressure of the second and third column. All the possible combinations of the integer multiples of 0.5 bar were studied. In the second step, the same approach was used to refine the location of the optimum but with pressure intervals of 0.1 bar. The pressure of the first column was always atmospheric. Álvarez et al. [21] used a genetic algorithm (GA) to optimise the PSD of an ethyl acetate-ethanol mixture, including  $P_{HPC}$  as an optimisation variable. The heat integration of the columns was not studied. Gu et al. [22] applied a GA (NSGA-II), for the multi-objective (TAC and CO<sub>2</sub> emission) optimisation of the separation of a methanol-THF-water mixture. At the given feed composition, two feasible column sequences, both consisting of three columns, were identified. The optimisation was performed without and with HI, and the column pressures were included as optimisation variables. The top pressure of the two LPCs were 0.6 bar instead of the minimum value (0.5 bar).  $P_{HPC}$  was slightly lower than the maximal (13.2 bar) value.

The mixture water (A)-ethylenediamine (EDA, B) is a pressure-sensitive maximum-boiling azeotropic one. PSD separation of this mixture in batch was first studied by Modla and Lang [23] at pressures 0.1 and 8.0 bar. Fulgueras et al. [24] studied the continuous PSD of this mixture (containing 40 mol% A). For different pressures, the number of trays of the columns were selected by shortcut simulation. With fixed numbers of trays ( $N_1$ ,  $N_2$ ), the total energy demand 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.

The feed in Li et al. [25] contained 60 mol% A. The pressures were fixed at 0.1 and 2.0 bar. In this case feeding is only possible into HPC. TAC was minimised by a sequential iterative procedure, and then PHI was applied without optimisation. For the same feed Wang et al. [16] by applying PSDIC configuration obtained by 8.6% lower TAC than the conventional PSD process. The difference in TAC was 14% between the PHI processes. By optimising pressures, they obtained 0.08 and 8 bars. Hence TAC of PSDIC was reduced by 44% without HI and by 31% with PHI.

Environmental impact of the PSD processes was evaluated by the CO<sub>2</sub> emission in Refs. [7–9]. For this purpose, Eco-indicator 99 (EI99, [26]) was first used by You et al. [27]. Sánchez-Ramírez et al. [28] applied EI99 as one of the objective functions in the multi-objective optimisation of a NHI process.

Ferchichi et al. [29] studied the PSD of the mixture of Li et al. [25] but performed the optimisation with a GA, reducing TAC by 21%. The pressures (0.1 and 2 bar) were not optimised. By applying optimal PHI, TAC was further reduced by 24%. By optimal FHI, the decrease of TAC is only slightly lower (23%). 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. The compressor work was reduced by 31% (HPC) and 20% (LPC), respectively. On the basis of CO<sub>2</sub> emission and

EI99 VRC options were favourable but they were uneconomical because of the high compressor costs.

In this work, optimisation of the pressure of HPC is performed for PSD separation of mixture water(A)-ethylenediamine(B) studied by Ferchichi et al. [29]. The following research gaps will be addressed. In the literature, optimisation of the pressures was performed either for non-heat integrated (NHI) processes or for only one HI option; therefore, a comparison of different options to reduce the energy demand (PHI, FHI, VRC) with optimised pressures is not available. Moreover, in the case of the water-ethylenediamine mixture, the influence of optimising the pressures was only studied for PHI, and only by using the local, sequential iterative method.

The goal of this work is thus to study the influence of optimising the pressure of HPC (1) in the process studied by Ferchichi et al. [29], (2) for the application of the following optimised options to decrease the energy demand: PHI, FHI and VRC heat pumps, (3) to calculate the environmental impact of the above options and (4) to study the economy of the different options as a function of utility prices.

## 2. The process and energy reduction options

The mixture water(A)-EDA(B) forms a pressure sensitive maximum boiling azeotrope. Fig. 1 shows as a function of the pressure the calculated boiling point ( $T_{bp}$ ) of the pure components and azeotrope, with the A content of the azeotrope ( $x_{az}$ ).

By VLE calculations [29], at 0.10 bar  $x_{az} = 44.1$  mol% ( $T_{bp} = 64.7$  °C) and at 2.02 bar  $x_{az} = 25.6$  mol% ( $T_{bp} = 141.7$  °C). On the increase of P,  $x_{az}$  monotonously decreases. The azeotrope disappears at ca. 4 bar [24], but a tangent azeotrope is still present above 4 bar, at low A contents.

The flow rate of the feed (F) is 100 kmol/h it contains 60 mol% A ( $x_F = 0.6$ ) and its temperature is 46.85 °C. The purity requirements are 99.5 mol% for both products (distillates). Since  $x_F$  is higher than  $x_{az}$  at any pressure, it is introduced into HPC (Column 1 in Fig. 2), whose top pressure ( $P_1$ ), is varied between 1.01 and 5 bar. The top pressure of LPC:  $P_2 = 0.101$  bar. The pressure drop of HPC is 0.24, that of LPC is 0.05 bar.

Both bottom products, whose composition is close to the azeotropic one at the given pressure, are fed into the other column ( $W_1 = F_2$ ,  $W_2 = F_{rec}$ ). For HPC, the composition of the distillate ( $x_{D,1}$ ) and the flow rate of the bottom product ( $W_1$ ) are specified:  $W_1 = F + F_{rec} - D_1$ , where  $F_{rec}$  and  $D_1$  are fixed. For LPC, the specifications are  $D_2$  (whose value from the material balances is 39.90 kmol/h) and heat duty of the reboiler ( $Q_{r2}$ ).

### 2.1. Heat integration

By partial heat integration (PHI) the reboiler of LPC is heated with the condensing top vapour of HPC. In our case, since the condenser heat duty of HPC ( $Q_{c1}$ ) is much higher than the reboiler heat duty of LPC

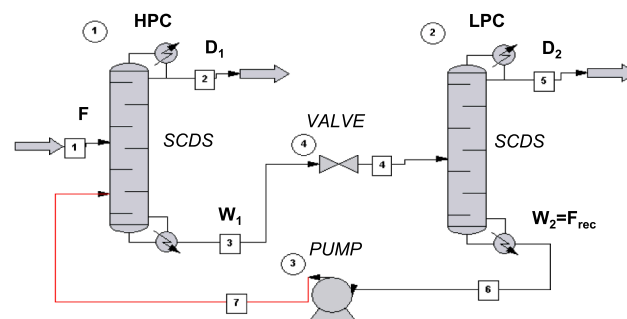


Fig. 2. Basic PSD flow-sheet for maximum azeotropes.

( $Q_{r2}$ ), an auxiliary condenser is needed, while LPC requires no external heating. A flow-sheet and detailed explanation of heat integration was given in Ferchichi et al. [29].

By full heat integration (FHI)  $Q_{c1} = Q_{r2}$ . Both heat duties are covered in the condenser-reboiler, no auxiliary heat exchanger is needed. FHI can be achieved by varying  $R_1$ ,  $R_2$  and  $W_2$ .

### 2.2. Heat pump (HP)

By vapour recompression (VRC) the top vapour of the column, whose flow rate is  $V_{top}$ , provides the working fluid (WF), which is compressed to pressure  $P_{out}$  (and temperature  $T_{out}$ ) then heats the reboiler. After its condensation in the reboiler, the pressure of WF is reduced to that of the column top in an expander, through which it is partially evaporated. The resulting vapour ( $V_{WF,v}$ ) is totally or partially condensed in an after-cooler. The liquid leaving the after-cooler is divided into distillate and reflux.

Three VRC configurations are investigated: the application of VRC in HPC (VRC1), in LPC (VRC2) and in both columns (VRC3).

The flow rate of WF compressed ( $V_{WF}$ ) is conventionally equal to that of top vapour ( $V_{top}$ ). However, this is not the only option for the operation of VRC. Ferchichi et al. [29] distinguished three different cases based on the ratio of the flow rates:  $\beta = V_{WF}/V_{top}$ :

- $\beta = 1$ :  $V_{WF} = V_{top}$ . In the after-cooler,  $V_{WF,v}$  is condensed totally.
- $\beta > 1$ :  $V_{WF} > V_{top}$ .  $V_{WF,v}$  is only partially condensed. The remaining vapour ( $V_{rec}$ ) is mixed with  $V_{top}$  before the compressor and increases the amount of WF:  $V_{WF} = V_{top} + V_{rec}$ .  $\beta$  can be optimised.
- $\beta < 1$ .  $V_{top}$  is divided into  $V_{WF}$  and a by-pass stream ( $V_{byp} = V_{top} - V_{WF}$ ). After the expansion, WF enters an after-cooler, where it is condensed totally.  $V_{byp}$  is condensed in an auxiliary condenser. After condensation,  $V_{WF}$  and  $V_{byp}$  are mixed.  $\beta$  can be optimised. A flow-sheet and detailed explanation of the different heat pump configurations was given in Ferchichi et al. [29].

## 3. Calculation method

The ChemCAD model of the process is presented in Fig. 2. Unit 1 and Unit 2 are the HPC and LPC, respectively (SCDS columns). The optimised NHI process of Ferchichi et al. [29] is considered as the base case (NHI0), where the top pressure of HPC is  $P_1 = 2.02$  and  $P_2 = 0.1$  bar. In the base case, the number of theoretical trays is  $N_1 = 90$  for HPC, while  $N_2 = 22$ . (The tray numbers include the total condenser and the partial reboiler and are counted from the top.) 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 the NHI process and with each other by calculating the values of an economic (TAC, \$/y) and two environmental indicators (the CO<sub>2</sub> emission and the Eco-indicator 99 (EI99)).

TAC is calculated from the total capital cost (TCC, \$) of the equip-

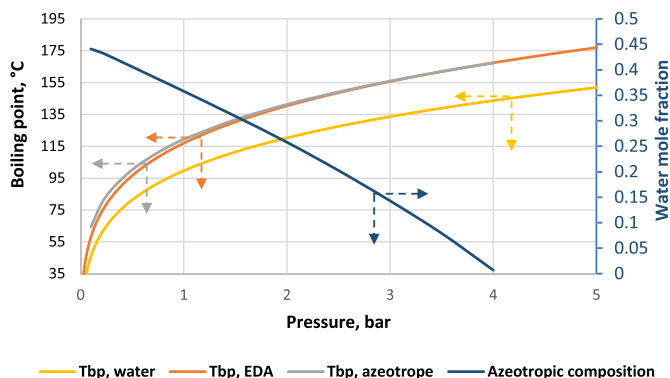


Fig. 1. The boiling points and the composition of the azeotrope as the function of pressure.

ment and the total energy cost (TEC, \$/y):

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

where PBP is the length of the payback period (3 years). TCC includes the costs of column vessels, heat exchangers and compressors.

The method and data for cost calculations are described in detail in Ferchichi et al. [29], with the exception that the effect of the change of column pressure on the cost of the column vessel is now included through a correction factor  $F_p$  [30]:

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

where  $Di$  is the inner diameter (m) and  $H$  is the height of the column;  $F_p$  is 1.0 below 3.45 bar and 1.05 above it.

TEC consists of costs of heating steam and (in the case of heat pumps) electricity. LPC is heated with LP steam (4 bar), while for HPC MP steam (11 bar) is applied. The steam prices are LP steam:  $p_{st} = 7.78$  \$/GJ, MP steam: 8.22 \$/GJ [25]. Electricity is assumed to be four times more expensive than LP steam:  $p_{el} = 31.12$  \$/GJ [29].

The CO<sub>2</sub> emission of the process is calculated by taking into account the emissions related to the production of heating steam and electricity. EI99 value [26] expresses 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 for the construction of the columns and electrical energy are considered. Ferchichi et al. [29] describe the details of the calculation method.

By the NHI process, first, the influence of varying  $P_1$  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  $Q_{r2}$  values, 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). 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 optimisation variables (Table 1, Range 1) are the same for both approaches.

For the optimisation, a GA written in Visual Basic for Applications under Excel is used with a population size of 30 and a maximum number of generations of 100 [29]. To receive the results necessary for the calculation TAC, the algorithm calls ChemCAD for each individual.

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

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 all the five geometrical parameters and  $P_1$  (with Range 2) to obtain the optimal partial heat integration (PHI3).

Full heat integration 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 (NHI1b), 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

**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	2000–12,500
Range 2					10–30	3–10		

optimisation is performed, including all the parameters (FHI3).

The application of heat pumps is studied for the best NHI process. The parameters of heat pumps, whose values must be determined, are  $P_{out}$  and  $\beta$ . These values are chosen so that 1. the temperature difference in the reboiler (between WF and the bottom liquid) is equal to the minimum approach temperature ( $\Delta T_{min} = 5$  °C), 2. the WF leaves the reboiler as a saturated liquid [29]. If  $\beta$  is fixed at 1.0 (VRC1a, 2a, 3a), only the first condition can be satisfied, and WF will leave the reboiler either subcooled or partially uncondensed. This indicates that  $V_{WF}$  is either too low (the heat transfer is not optimal) or too high. By using  $\beta \neq 1$  (VRC1b, 2 b, 3 b), both conditions can be met simultaneously, although this might require additional heating of the expanded WF to reach the necessary  $\beta$  value, which is undesirable [29].

Since the top pressure of the columns strongly influence the heat pumps, the simultaneous optimisation of the PSD system and the heat pump applied for HPC is performed (VRC1a\*) to verify whether a further reduction in TAC can be achieved. The details of the calculation are given in Part 2 of the Supporting information.

## 4. Results

### 4.1. 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  $F_{rec}(=W_2)$  and hence  $W_1$ , the reboiler duties and thus TEC (Fig. 3). As expected, 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 difference between the temperature of the reboiler and that of the MP steam decreases. Because of these effects, TCC has a minimum at  $P_1 = 3.5$  bar. TAC also has a minimum as a function of  $P_1$ , but at a much

**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. [29]		Optimised operational parameters		Optimised feed locations	
	HPC	LPC	HPC	LPC	HPC	LPC
P (bar)	2.02	0.1	4.5	0.1	4.5	0.1
f	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	6666	8623	3905	8525	3905
$Q_r$ (MJ/h)	15,258	5301	10,373	2700	10,275	2700
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	–



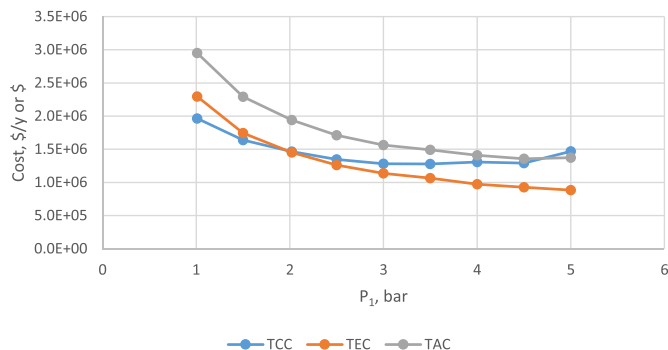


Fig. 3. Costs of the NHI1a process as a function of  $P_1$ .

higher value: 4.5 bar, where  $dTAC/dP_1 = dTEC/dP_1 + dTCC/dP_1 \bullet 1/PBP = 0$ . Compared to the base case (NHI0), TCC decreased by 11.8%, TEC by 36.2% and TAC by 30.1%.

Subsequently, the feeding locations are modified to reduce the energy demand even further (Table 2, NHI1b). The feed tray of the feed ( $f_1$ ) is moved slightly, while that of the recycle stream ( $f_{rec}$ ) is 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 (NHI2a), then the feeding locations are optimised subsequently (NHI2b). GA was not capable to decrease TAC in this case (even after increasing the number of generations to 300). Detailed results are given in Part 1 of the Supporting information.

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 by 1–2 trays away from their optimal positions (NHI3b).

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.

4.2. 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

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

Case Parameter	NHI3a Variable feed locations		NHI3b Optimised feed locations	
	HPC	LPC	HPC	LPC
	P (bar)	4.53	0.1	4.53
N	65	21	65	21
f	6	9	7	9
$f_{rec}$	28	–	30	–
Di (m)	0.914	1.68	0.914	1.68
W (kmol/h)	77.1	37.2	77.1	37.2
$x_{w2}$	0.421	–	0.421	–
$T_c$ (°C)	148.4	58.3	148.4	58.3
$T_r$ (°C)	174.2	72.6	174.2	72.6
R	2.69	1.68	2.59	1.68
$Q_c$ (MJ/h)	8300	4668	8285	4668
$Q_r$ (MJ/h)	10,212	3302	10,197	3302
TCC ( $10^5$ \$)	12.56	–	12.56	–
TEC ( $10^5$ \$/y)	9.55	–	9.54	–
TAC ( $10^5$ \$/y)	13.74	–	13.73	–

Table 4 Results of the PHI process.

Case Parameter	PHI1 Non-optimised		PHI2 Optimised operational parameters		PHI3 Full optimisation	
	HPC	LPC	HPC	LPC	HPC	LPC
	P (bar)	4.5	0.1	4.5	0.1	4.39
N	69	27	69	27	62	15
f	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)	–	3905	–	4087	–	7568
$Q_r$ (MJ/h)	10,275	–	10,194	–	10,231	–
$Q_{aux}$ (MJ/h)	5825	–	5602	–	2033	–
$Q_{rc}$ (MJ/h)	–	2700	–	2800	–	6198
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	–

(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%.

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 PHI, TAC decreases by 16.1% compared to NHI1b.

4.3. Full heat integration (FHI)

Without changing either operational or geometrical parameters

Table 5 Results of the FHI process.

Case Parameter	FHI1 Non-optimised		FHI2 Optimised recycle flow rate		FHI3 Full optimisation	
	HPC	LPC	HPC	LPC	HPC	LPC
	P (bar)	4.5	0.1	4.5	0.1	4.37
N	69	27	69	27	62	13
f	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)	–	9624	–	9398	–	9730
$Q_r$ (MJ/h)	10,170	–	9943	–	10,270	–
$Q_{rc}$ (MJ/h)	–	8422	–	8018	–	8249
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	–

(FHI1),  $Q_{rc}$  is increased to the 3.12 times of  $Q_{r2}$  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 NHI1b, meaning that (without optimisation) FHI is slightly less favourable than applying only partial heat integration.

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 very close 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, TAC of the optimal FHI3 is slightly (by 1.8%) higher, even if the cost of the auxiliary condenser is saved.

#### 4.4. Application of heat pumps

VRC heat pumps are applied to the optimal NHI process (NHI1b): first, either to only HPC (VRC1) or LPC (VRC2), then to both columns (VRC3). In each case, calculations are performed first with  $\beta = 1$  then with optimal  $\beta$ .

##### 4.4.1. Heat pump for HPC only

The results of applying a VRC heat pump for HPC (VRC1) are shown in Table 6. By the conventional operation ( $\beta = 1$ , VRC1a),  $P_{out} = 31.4$  bar, which corresponds to a relatively high compression ratio of  $CR = 6.98$ . WF leaves the reboiler with the desired temperature:  $T_{WF} = T_{r1} + 5 = 179.1$  °C. However, the WF is strongly (by 40 °C) subcooled. 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 [29].

By applying the heat pump with  $\beta = 1$ , TCC increases by 165% because of the high capital cost of the compressor (it is 69.8% 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 44.1%.

Since  $Q_{c1}$  is considerably lower than  $Q_{r1}$ ,  $P_{out}$  can be reduced by recycling one part of the WF (VRC1b), thus increasing the heat that can be transferred by condensing WF. The flow rate of recycled WF ( $V_{rec} = (\beta - 1) \cdot V_{top}$ ) is determined by the heat duty of the after-cooler. By decreasing this heat duty, the amount of WF condensed in the after-cooler increases, and a higher amount of WF recycled. An upper limit of  $\beta$  thus exists where  $Q_{after-cooler}$  is zero:  $\beta$  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. [29], WF cannot be a saturated liquid and have the desired temperature (179.1 °C) simultaneously without additional

heating, and two cases arise:

1. The reboiler temperature difference is  $\Delta T_{rc} = 5$  °C, but WF is considerably (by 32.4 °C) subcooled.  $P_{out}$  is 19.55 bar ( $CR = 4.35$ ),  $\beta = 1.068$ ,  $W$  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:  $\beta = 1.141$ .

The compressor work is slightly lower in the second case. 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 15.4%). TEC is also lower by 18.4%. In consequence, the TAC is reduced by 17.6%; however, the application of the heat pump is still not economical.

##### 4.4.2. Heat pump for LPC only

The results of the VRC heat pump for LPC (VRC2a and VRC2b) are also shown in Table 6. With the conventional heat pump (VRC2a,  $\beta = 1$ ), 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 the total condensation of WF is performed in an after-cooler after the expansion. (The after-cooler is generally needed, even if WF is totally condensed in the reboiler-condenser since, during the expansion, partial flashing takes place.) Since  $Q_{r2}$  is much lower than  $Q_{r1}$ , the compressor work is also lower than for VRC1a. 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% than by NHI1b.

Since  $Q_{c2}$  is considerably higher than  $Q_{r2}$ , the compressor work can be reduced by by-passing the compressor with one part of  $V_{top}$  (VRC2b). Although  $P_{out}$  does not change (0.24 bar),  $V_{WF}$  is lower. The by-pass stream ( $V_{byp}$ ), which is 30.3% of  $V_{top}$ , is condensed in an auxiliary 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 5.7%). TEC is only slightly lower (by 2.7%). In consequence, TAC is slightly reduced (by 4.1%). The application of the heat pump is still not economical, but the difference in TAC is small (3.3% of the TAC of NHI1b).

##### 4.4.3. Heat pump for both columns

Applying two heat pumps simultaneously with  $\beta = 1$  (VRC3a) decreases TEC by 24.3%; however, the high cost of the compressors increases TAC by 51.1% (Table 6). By optimising  $V_{WF1}$  and  $V_{WF2}$  (VRC3b,  $\beta \neq 1$ ), TEC is further decreased by 24.4%, to a value that is 57.2% of the TEC of the optimal NHI. Though TAC is decreased by 18.2%, but it is still higher (by 23.5%) than that of NHI1b.

##### 4.4.4. Simultaneous optimisation of the PSD system and the heat pump for HPC only

By the simultaneous optimisation of the PSD system and the conventional heat pump ( $\beta = 1$ ) for HPC by GA (VRC1a\*), most of the optimisation variables have very similar results to those of NHI1b.

**Table 6**

Comparison of the results of heat pump-assisted PSD without and with recycling or by-pass.

Parameter	VRC1a	VRC1a*	VRC1b	VRC2a	VRC2b	VRC3a		VRC3b	
						HPC	LPC	HPC	LPC
$\beta$	1	1	1.141	1	0.697	1	1	1.141	0.697
W (kW)	637.0	628.8	485.9	76.1	53.3	637.0	76.1	485.9	53.3
$Q_{after-cooler}$ (MJ/h)	543.1	502.4	–	1343.4	76.21	543.1	1343.4	–	76.21
$Q_c$ (MJ/h)	–	–	–	–	1185	–	–	–	1185
TCC ( $10^5$ \$)	34.16	33.82	28.90	19.26	18.16	40.22	–	34.18	–
Steam cost ( $10^5$ \$/y)	1.83	1.96	1.83	7.36	7.36	–	–	–	–
Electricity cost ( $10^5$ \$/y)	6.22	6.12	4.74	0.74	0.52	6.96	6.96	5.26	–
TEC ( $10^5$ \$/y)	8.05	8.08	6.57	8.10	7.88	6.96	6.96	5.26	–
TAC ( $10^5$ \$/y)	19.43	19.36	16.21	14.52	13.93	20.37	–	16.66	–

Detailed results are given in Part 2 of the Supporting information. Only a minor reduction (0.36%) in TAC is achieved and even this can be attributed to a change in  $\Delta T_r$ . Therefore, a simultaneous optimisation is not necessary; it is sufficient to apply the heat pump to the optimised NHI process.

4.5. Effect of the optimisation of pressure of HPC on TAC

The effects of optimising  $P_1$  can be evaluated by comparing the optimal results obtained in this work with those of Ferchichi et al. [29] (Table 7), where  $P_{HPC}$  was fixed (to 2.02 bar). The greatest reduction on TAC is obtained by NHI, primarily due to the very important decrease of TEC. For PHI and FHI, the results are similar to each other. The decrease of TEC, and thus that of TAC is lower, but still considerable. For VRC3b, the reduction of TAC is similar to those in the heat integrated cases; however, the decrease of TCC contributes to it to a greater extent. Approximately half of the decrease of TCC is caused by the reduction of the cost of compressor.

4.6. Economic comparison of the cases studied

The total capital, energy, and annual costs are summarised in Table 8 for the optimal case of each option. The lowest TCC is obtained with PHI, while TEC is the lowest if heat pumps (with optimal  $V_{WF}$ ) are applied for 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.

To study the influence of utility prices, which vary even in the same country from site to site, a map (Fig. 4) is constructed that shows which energy demand reduction options are more economical as a function of the prices of steam and electricity. (The cases shown in Table 7 are considered). The ratio of the price of MP and LP steam is kept constant. By considering the two most economical options at each point, four domains (Table 9) can be distinguished.

The prices used in this work lie in Domain A, where PHI3 is the most economical option, followed by FHI3. In the very narrow Domain B, VRC3b is already better than FHI3 but worse than PHI3. In Domains C and D, VRC3b is the most economical, followed by either PHI3 (Domain C) or VRC1b (Domain D). On the increase of  $p_{st}$  under constant  $p_{el}$ , Domain B is reached (by a 70% increase of  $p_{st}$  to 13.21 \$/GJ). Domain C is reached at  $p_{st} = 13.46$  \$/GJ (corresponding to  $p_{el}/p_{st} = 2.3$ ), while Domain D at  $p_{st} = 14.71$  \$/GJ, which corresponds to an increase of 89%. By keeping  $p_{el}/p_{st}$  constant at 4.0 (dashed line), Domain B is reached, but only at a  $p_{st}$  more than three times higher (26.88 \$/GJ). The application of heat pumps becomes more economical with the decrease of the ratio  $p_{el}/p_{st}$ , as expected.

4.7. Environmental evaluation

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

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

Table 7  
Decrease of costs due to the optimisation of  $P_1$  comparing with the results of Ferchichi et al. [29].

Case	NHI		PHI		FHI		VRC3b	
	Value	Decrease, %	Value	Decrease, %	Value	Decrease, %	Value	Decrease, %
TCC ( $10^5$ \$/y)	14.64	12.0	13.41	11.4	13.72	9.0	44.01	22.4
TEC ( $10^5$ \$/y)	14.52	37.7	10.34	29.1	10.39	29.3	5.92	11.1
TAC ( $10^5$ \$/y)	19.40	30.5	14.81	23.6	14.97	23.1	20.59	19.1

Table 8  
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

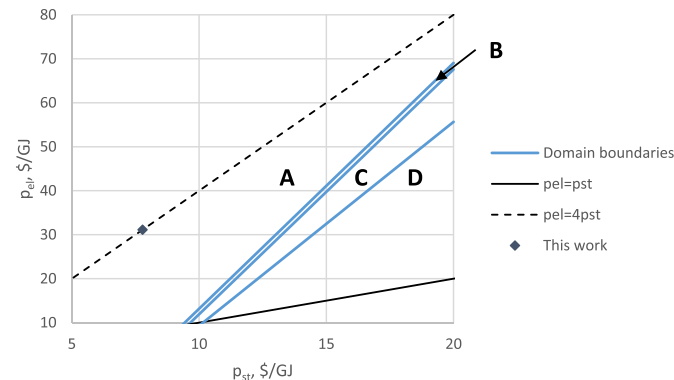


Fig. 4. Map of utility price domains determined by the two most economical configurations.

Table 9  
Utility price domains.

Domain	Most economical configuration	Second most economical configuration
A	PHI3	FHI3
B	PHI3	VRC3b
C	VRC3b	PHI3
D	VRC3b	VRC1b

Table 10  
 $CO_2$  emissions and EI99 values of the different configurations.

Case	$CO_2$ emissions (kg/h)	Specific $CO_2$ emissions		EI99 (point/y)
		(kg $CO_2$ /kg feed)	(kmol $CO_2$ /kmol feed)	
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	5517
VRC3b	99.18	0.028	0.023	4171

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  $\beta$ , 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<sub>2</sub> emission is 55.7%, its EI99 value is only 4.88% of that of the optimal NHI1b process.

Considering both TAC and the CO<sub>2</sub> emissions, three options are non-dominated, that is, meaning other configuration having both lower TAC and CO<sub>2</sub> emission do not exist: PHI3, VRC1b and VRC3b (connected by a line in Fig. 5). The VRC configurations with optimal  $\beta$  have both lower TAC and CO<sub>2</sub> emission than those with  $\beta = 1$ . With regards to TAC and EI99, in addition of the three configurations mentioned above, FHI1 is also non-dominated.

## 5. Conclusions

A pressure-swing distillation process to separate the maximum-boiling azeotropic mixture water-EDA was studied by simulation and optimisation. The influence of varying the top pressure ( $P_1$ ) of the high-pressure column (HPC) was investigated. First, the total annual cost (TAC) of the separation process was minimised without applying heat integration (NHI) by using different optimisation approaches. By NHI1b, only the operational parameters ( $P_1$ , the flow rate of recycling ( $F_{rec} = W_2$ ), 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, which were 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.

Partial (PHI1) and full Heat Integration (FHI1) were applied to the optimal NHI process and further optimised by varying either the operational parameters ( $F_{rec}$  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), and 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 working fluid (WF) flow rate of the heat pumps was optimised to minimise the compressor power (VRC1b, 2 b, 3 b), and thus its cost by either partially recycling WF or by-passing the compressor with one part of the top vapour. Applying heat pumps reduced the total energy cost (TEC) considerably; however, it was not economical as a result 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. The compression ratio decreased to a lesser extent than the increase of  $P_1$ . By optimising the flow rate of WF (VRC1b), this value was reduced to 18.0 bar, resulting in a 18% decrease in TAC. This highlights the importance of optimising the amount of the WF.

TAC of the different configurations was studied as a function of steam and electricity prices. For most price combinations, PHI3 was the most economical configuration; however, when the price of steam was relatively high and that of electricity low, VRC3b became more economical.

By comparing the results to those obtained by constant  $P_1 = 2.02$  bar, the effect of including  $P_1$  as optimisation variable on TAC was evaluated. In case of NHI, a decrease of 31% was reached, while for PHI, FHI and VRC3b, it was between 19 and 24%. The decrease is primarily due to the reduction of TEC, except for VRC3b where the contribution of TCC decrease is more important.

The CO<sub>2</sub> emission and Eco-indicator 99 (EI99) values of the different options were calculated to evaluate their environmental impact. By optimising NHI, both values were considerably reduced (by 35 and 37%, respectively). By either PHI or FHI, the CO<sub>2</sub> emissions can be further reduced by ca. 12%, while EI99 by 20%. While applying heat pumps was uneconomical, it was very favourable from the environmental point of view, particularly for the HPC. For example, the CO<sub>2</sub> emission and EI99 values of VRC3b (with optimal flow rate of WF) are lower than those of

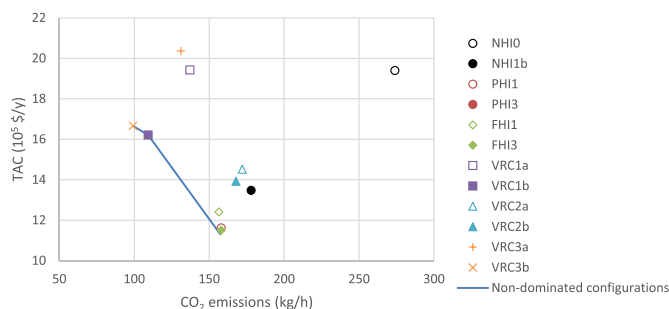


Fig. 5. TAC of the different configurations as a function of their CO<sub>2</sub> emissions.

the optimal NHI process by 44 and 95%, respectively. Considering both TAC and environmental impact, PHI3, VRC1b and VRC3b are non-dominated; that is, no other configuration exists having both lower TAC and CO<sub>2</sub> emission simultaneously.

Future works might include 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.

## Credit author statement

Laszlo Hegely: Conceptualization, Methodology, Investigation, Writing – original draft, Visualization, Software, Funding acquisition, Validation. Peter Lang: Conceptualization, Writing – review & editing, Funding acquisition, Validation.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.energy.2023.126939>.

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