



# Economic and environmental evaluation of heat pump-assisted pressure-swing distillation of maximum-boiling azeotropic mixture water-ethylenediamine



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## ABSTRACT

Different options to reduce the energy demand of a pressure-swing distillation process for separating the maximum-boiling azeotropic mixture water (A)-ethylenediamine (B) are studied by rigorous simulation. The total annualised cost (TAC) without any energy demand reduction option is minimised by a genetic algorithm coupled to a flow-sheet simulator, then the options partial (PHI) and full heat integration (FHI), and vapour recompression heat pumps (VRC) were studied. Heat pumps are applied either for only one (the high- or the low-pressure) or both columns. By optimising the flow rate of the working fluid of heat pumps, the compressor work, thus the energy demand and capital cost of the heat pump are considerably reduced. For the steam and electricity prices used, the optimised PHI is the most economical, reducing the TAC by 23.7%. The influence of these prices on the TAC of each configuration is also studied. The environmental evaluation is performed by calculating CO<sub>2</sub> emissions and Eco-indicator 99 values. Heat pump-assisted processes have lower values compared to the other configurations, especially with optimal working fluid flow rate. PHI or FHI leads to a reduction of both above indicators, but they are still higher than those of heat pump-assisted processes.

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## 1. Introduction

Distillation is the most frequently used technology for the separation of liquid mixtures. For the separation of azeotropic and close-boiling mixtures, special distillation methods such as extractive distillation (ED [1]), heterogeneous azeotropic distillation (HAD) or pressure-swing distillation (PSD) must be used. These special methods can also be combined with membrane separation in hybrid separation schemes [2]. In extractive distillation, a mass separating agent (called entrainer or solvent), which is often a new component, is continuously fed to the column and changes the

relative volatilities of the original components favourably. The entrainer is usually a heavy component forming no new azeotrope with the original components. Entrainer selection is important not only for the economics but also for the controllability of the process. These two aspects can be simultaneously considered by e.g. the framework proposed by Papadopoulos et al. [3]. In heterogeneous azeotropic distillation, the entrainer forms a heterogeneous azeotrope with one of the original components leading to the formation of two liquid phases that can be separated by decantation.

Pressure-swing distillation can be applied if the azeotrope is pressure-sensitive. As a rule of thumb, the application of pressure-swing distillation can be practical if the azeotropic composition changes at least 5 mol% over a pressure interval of 10 bars [4]. The main advantage of pressure-swing distillation over extractive and heterogeneous azeotropic ones is that no new component is added to the system. Binary azeotropic mixtures can be separated using PSD in two distillation columns operating at different pressures. In both columns, one of the components is obtained in the bottom product (in the case of minimum boiling azeotropes) or in the distillate (in the case of maximum boiling azeotropes). The other product of each column has a composition close to the azeotropic

*Abbreviations:* Az, azeotrope; bp, boiling point; EDA, ethylenediamine; EI99, Eco-indicator 99; FHI, full heat integration; GA, genetic algorithm; HP, heat pump; HPC, high-pressure column; LP, low pressure; LPC, low-pressure column; MP, medium pressure; NHI, non-heat integrated process; OF, objective function; OPHI, optimal partial heat integration; PHI, partial heat integration; PSD, pressure-swing distillation; TAC, total annualised cost; TCC, total capital cost; TEC, total energy cost; VRC, vapour recompression; WF, working fluid.

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one at the given pressure, and it is fed or recycled to the other column.

Water (A) and ethylenediamine (EDA, B) form a pressure-sensitive maximum-boiling azeotrope below ca. 4.5 bar [5]. The separation of these components by ED, HAD and PSD was studied in several papers. Yu et al. [6] investigated the application of ED with different heavy entrainers (1,2- and 1,3-propanediol, 1,4-butanediol) and that of HAD with different light entrainers (n-propyl acetate, 1,2-dichloroethane and diisopropyl ether). The lowest total annualised cost (TAC) was reached by ED with 1,4-butanediol. Methanol as a light entrainer for ED was applied by Rodríguez-Donis et al. [7], among others. The application of PSD in a double-column batch rectifier was proposed by Modla and Lang [8]. In their case study, the feed contained 40 mol% A, and the pressures applied were 0.1 and 8.0 bar. However, as pointed out by Fulgueras et al. [5], who studied the continuous PSD of the same mixture with the same composition, experimental data show that no azeotrope exists above ca. 4–4.5 bar. This highlights the importance of verifying the validity of the description of the phase equilibrium. Fulgueras et al. [5] used pressures of 0.13 and 6.55 bar and found that the energy demand of the system is lower if the mixture is fed to the high-pressure column (HPC) instead of the low-pressure column (LPC). Although no azeotrope exists at 6.55 bar, a tangent azeotrope is formed at low concentrations of A; thus, the application of PSD instead of conventional distillation is still recommended. Li et al. [9] studied the separation of a mixture water-ethylenediamine containing 60 mol% water by PSD using 0.1 and 2.0 bar as the column top pressures. The mixture was fed to the HPC. The process parameters were optimised with a sequential iterative optimisation procedure.

Since the energy demand of distillation is very high, it is important to apply options of energy recovery. In the case of PSD, a straightforward option is the heat integration (HI) of the columns. The reboiler of the LPC can be partially or totally heated by the condensation of the top vapour of the HPC, provided that a suitable temperature difference is present. In partial heat integration (PHI), the operational parameters of the process are not changed, and the heat duty of the condenser of the HPC ( $Q_c^{HPC}$ ) and that of the reboiler of the LPC ( $Q_r^{LPC}$ ) are not equal. Therefore, either an auxiliary condenser (if  $Q_c^{HPC} > Q_r^{LPC}$ ) or reboiler (if  $Q_c^{HPC} < Q_r^{LPC}$ ) is needed. By thermal coupling of the condenser of HPC and the reboiler of LPC, the heat duty of the reboiler-condenser ( $Q_{rc}$ ) will be the smaller one, that is, either  $Q_r^{LPC}$  or  $Q_c^{HPC}$ , respectively.

By modifying the values of the operational parameters, full heat integration (FHI) can be reached [10] where the two heat duties are equal:  $Q_c^{HPC} = Q_r^{LPC}$ , and there is no need for an auxiliary heat exchanger. FHI does not necessarily result in a lower energy demand than PHI, and an optimal partial heat integration (OPHI) exists, as demonstrated by You et al. [11] for an ED process, where the heat duty in the integrated reboiler-condenser is between that of PHI and FHI.

Another option to reduce the energy demand is the application of heat pumps (HP [12]). In the conventionally applied mechanical heat pumps, a working fluid is used to condense the top vapour of a column then it is compressed to heat the reboiler. The working fluid can be an external heat transfer medium (vapour compression, VC), the top vapour of the column (vapour recompression, VRC) compressed, or, less frequently, the bottom liquid (bottom flash, BF) expanded. Modla and Lang [13] proposed a new VRC heat pump where the working fluid expanded is not condensed completely (which is the conventional operation), but only partially. The vapour phase is then recycled to the compressor to increase the flow rate of the working fluid. By recycling the working fluid, they were able to reduce the compressor work by 45% for the separation

of i-butane and n-butane. To our best knowledge, the recycling of the working fluid was not studied by others for any distillation process.

The work of Shi et al. [14] was dedicated to investigating vapour recompression-assisted pressure-swing distillation of the equimolar mixture methanol-diethylamine forming a pressure-sensitive maximum azeotrope. The feed composition was between the azeotropic ones at the two pressures applied. They have investigated two alternative separation sequences, feeding into the low-pressure column (LPC) and feeding into the high-pressure column (HPC). For both sequences, separations with and without heat integration were studied, and in each case, they have studied the possibility of by-pass (where only a portion of the overhead vapour stream is compressed to provide the heat requirement in the reboiler). Moreover, the preheating of one or both feed streams (the fresh feed and the recycled stream) was also studied. All cases were compared based on economic (TAC) and environmental (CO<sub>2</sub> emission) indicators. The results have shown that self-heat recuperative process with preheating streams and without splitting the working fluid with the sequence LPC-to-HPC was the most economical and environment-friendly configuration.

Yang et al. [15] studied the separation of the mixture ethyl acetate-ethanol by heat pump-assisted PSD, where they applied by-pass in the heat pumps. For the HPC, the vapour by-passing the compressor was split into two, compressed in two additional, smaller compressors, and used to preheat the feeds of HPC to their dew points. For the LPC, the part of the vapour by-passing the compressor was condensed using cooling water.

Although the different options for the reduction of the energy demand of PSD were studied by many researchers, the comparison of PHI or FHI with heat-pump assisted PSD is less common. Xia et al. [16] compared FHI with the application of heat pumps for the separation of isopropanol and diisopropyl ether in terms of energy demand, TAC and CO<sub>2</sub> emissions. By the heat pump-assisted process, all of these values were lower, although the difference was small in TAC because of the high capital cost of the compressor. You et al. [17] compared the lifetime total cost and the environmental impacts of PHI, FHI and heat pump-assisted PSD for the same mixture. Once again, the application of heat pumps was the most favourable option. FHI had a slightly higher total cost than PHI. In contrast, Han and Chen [18] found that FHI was more economical and had a lower CO<sub>2</sub> emission than heat pump-assisted PSD for the separation of methanol and acetonitrile. Note that all three works studied the separation of minimum-boiling azeotropes.

The separation of maximum-boiling azeotropes by PSD is less studied. In terms of heat integration, the literature mostly studies PHI, with only a handful of works investigating the application of heat pumps [14,19]. For the water-ethylenediamine mixture, Li et al. [9] applied only PHI for the separation of the A-B mixture and reached a reduction of 19.8% of energy demand. The control issues of the partially heat-integrated pressure swing distillation separation of the mixture were studied for the conventional two-column system by Li et al. [20] and Zhang et al. [21]. Moreover, dynamic control analyses were made for partially heat-integrated side-stream pressure-swing distillation of this mixture without [22] and with the application of heat pump [19].

The environmental impact of pressure-swing distillation is usually expressed by the CO<sub>2</sub> emission of the process (e.g. Ref. [14]). The Eco-indicator 99 (EI99), which takes into account the damage to human health, the ecosystem quality, and resource consumption, was used for the evaluation of the environmental effects of pressure-swing distillation first by You et al. [17]. EI99 was used later by Sánchez-Ramírez et al. [23], who performed multi-objective optimisation of a PSD process for the separation of bio-butanol and water. The objective functions included the TAC, EI99,

the condition number and the individual risk index. However, they did not study heat integration possibilities.

The optimal design and operation of the PSD can greatly reduce its energy demand, cost and environmental impact. The most frequently applied objective function is the TAC. Several authors (e.g. Refs. [9,17,18]) use an optimisation method called sequential iterative optimisation, which consists of varying the optimisation variables one at a time in multiple iteration loops embedded in each other. The inner steps, where only continuous variables (such as reflux ratios, flow rates) are varied, can be performed using the built-in sequential quadratic programming tool of flow-sheet simulator [17]. The sequential iterative optimisation is inherently a local optimisation method, in contrast to metaheuristic methods such as genetic algorithm [24] or differential evolution [23] that are capable of finding the global optimum. In the papers discussed above, the different options to reduce the energy demand of the process are usually, but not always, applied to an optimised basic process.

In this work, the separation of a water(A)-ethylenediamine(B) mixture by a PSD process described by Li et al. [9] is studied. The research gaps addressed here are the following ones. A comparison of partially heat integrated, fully heat integrated and heat-pump assisted PSD processes for the separation of maximum-boiling azeotropes is not found in the literature. In particular, full heat integration was not studied for the water-ethylenediamine mixture. The process described by Li et al. [9] was optimised using the local, sequential iterative method; it is thus not certain that the authors have found the global optimum. The optimisation of the amount of working fluid was not performed for heat pump-assisted PSD.

The goals of this paper, therefore, are (1) to study whether it is possible to obtain a lower TAC by performing the optimisation with a global optimisation method (genetic algorithm) instead of the local one (sequential iterative optimisation) applied by Li et al. [9], (2) to investigate options for reducing the energy demand of the optimised system, such as partial and full heat integration as well as the application of VRC heat pumps, (3) to study if the compressor work of the heat pumps can be reduced by finding the optimal flow rate of the working fluid, and (4) to evaluate the environmental impact of the different configurations studied, (5) to investigate the influence of the utility prices on the economy of the different methods.

The procedure followed in the present work is outlined in Fig. 1. After the description of the vapour-liquid equilibrium (VLE), the results of the optimal, non-heat integrated (NHI) process obtained by Li et al. [9] using Aspen Plus are reproduced by using the professional flow-sheet simulator ChemCAD. Since distillation can be

accurately modelled by flow-sheet simulators, such a reproduction is possible provided all the necessary data are given. In the next step, the process is optimised using a genetic algorithm, with the hypothesis that a better solution can be obtained. This solution is then considered the base case to which PHI, FHI or heat pumps (without and with optimal working fluid flow rate) are applied to reduce the energy demand of the process. In the next steps, the TAC of PHI and FHI is minimised. The environmental impact (CO<sub>2</sub> emission and EI99 values) are then calculated for the configurations studied, and finally, the influence of utility (steam and electricity) prices on the TAC values is evaluated.

The article is structured in the following way: after the Introduction, Section 2 presents the VLE data, Section 3 describes the processes studied in a general way, and Section 4 contains the description of calculation methods, including the input data, details of the calculation and optimisation and the method of cost calculation and environmental evaluation. The results are presented in Section 5 in the following order: NHI, PHI, FHI, the application of heat pumps. This section is concluded by two subsections comparing the configurations from an economic and an environmental point of view, respectively. The article is finished with the conclusions drawn from the results.

### 2. Vapour-liquid equilibrium

To describe the vapour-liquid equilibrium (VLE) conditions, the UNIQUAC model is applied with the binary interaction parameters shown in Table 1. Fig. 2 shows the boiling point (T-x), dew point (T-y) and equilibrium (y-x) curves, the composition of the maximum-boiling azeotrope and the composition of the feed (z) at different pressures. The plots show that the concentration of water in the maximum azeotrope decreases with the increase of the pressure (Fig. 2a and b). It also shows that with the increase of the pressure, the equilibrium curve gets closer to the diagonal at both ends of the y-x diagram (Fig. 2b) (at high concentrations of water and at high concentration of EDA); therefore, the increase of pressure has a detrimental effect for the purification of water (and would have it for the purification of EDA, as well).

Fig. 3, presenting the boiling points of the components and the azeotrope, and the azeotropic composition as the function of pressure, shows that the azeotropic behaviour breaks with the increase of the pressure. The azeotrope disappears above ca. 4–4.5 bar, but above this pressure, a tangent azeotrope is still present at low water concentrations.

The azeotropic data at two different pressures are presented in Table 2.

### 3. Process description

The separation of a maximum-boiling azeotropic mixtures A-B is performed in two columns using a pressure-swing system. If the feed contains more A than either azeotrope and the A content of the azeotrope decreases on the increase of pressure ( $x_F > x_{az}^{LP} > x_{az}^{HP}$ ), the first column, where the fresh feed (F) and the steam recycled from the second column (W<sub>2</sub>) are introduced, operates at higher

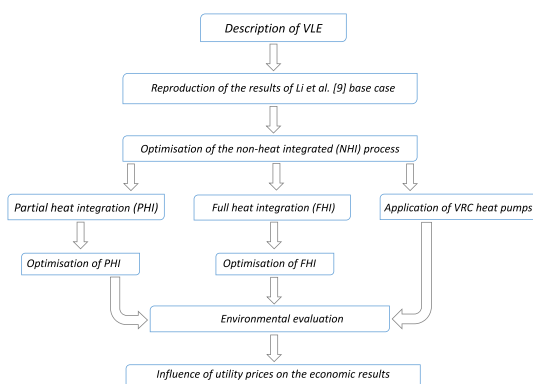


Fig. 1. The research procedure followed.

Table 1  
UNIQUAC binary interaction parameters.

Parameter	Value
U <sub>AB</sub> -U <sub>BB</sub>	-2690.424 cal/mol (-11,256.73 J/mol)
U <sub>BA</sub> -U <sub>AA</sub>	449.932 cal/mol (1882.52 J/mol)
A <sub>AB</sub>	-3.4831 (1)
A <sub>BA</sub>	1.5662 (1)

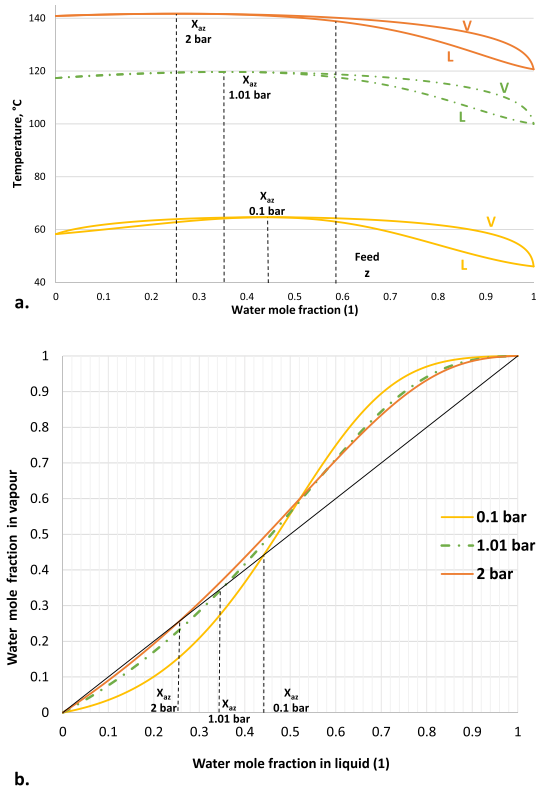


Fig. 2. a. Boiling and dew point (T-xy) and b. Equilibrium (y-x) diagrams of the water-EDA mixture at different pressures.

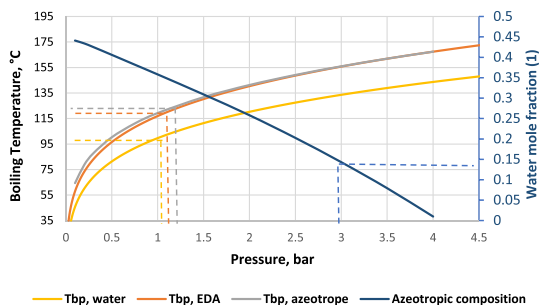


Fig. 3. The boiling points of the components and the azeotrope, and the azeotropic composition as the function of pressure.

Table 2  
Azeotropic data at different pressures.

Parameter	0.101 bar	1.013 bar	2.03 bar
$x_{Az,water}$ (mol%)	44.1	35.7	25.6
$T_{Az}$ (°C)	64.7	119.7	141.7
$T_{bp,A}$ (°C)	46.0	100.0	120.7
$T_{bp,B}$ (°C)	58.2	117.4	140.9

pressure (HPC) (Fig. 4). HPC contains  $NT_1-2$  theoretical trays, while the reboiler provides an additional theoretical tray, and the condenser is considered as the first tray. The fresh feed enters onto tray  $NF_1$ , while the recycled stream onto  $NR$ . Since the A content of the feed is higher than that of the recycled stream,  $NR > NF_1$ . Component A is collected as the distillate of HPC ( $D_1$ ). The bottom product of HPC ( $W_1$ ), whose composition is near to the azeotropic one at the pressure of the HPC, is fed into the second, low-pressure

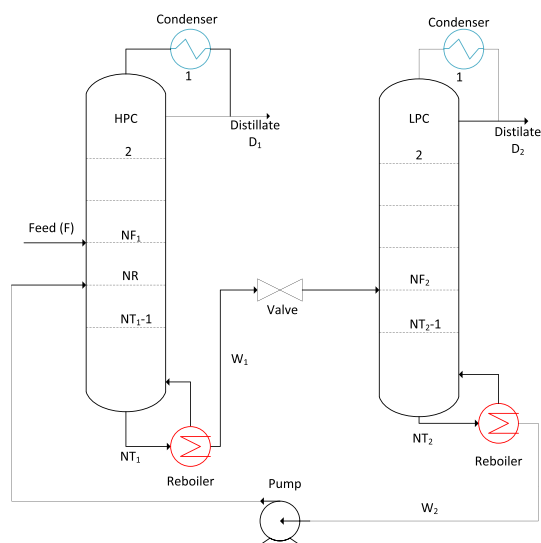


Fig. 4. Pressure-swing flow-sheet for maximum-boiling azeotrope separation.

column (LPC) onto tray  $NF_2$ . The total tray number of LPC (including the reboiler and the condenser) is  $NT_2$ . High purity B is collected as the distillate of LPC ( $D_2$ ), and the bottom product ( $W_2$ ), whose composition is near the azeotropic one at the pressure of LPC, is recycled to HPC.

### 3.1. Partial heat integration (PHI)

The PHI consists of heating the reboiler of the LPC with the condensing top vapour of HPC (Fig. 5, modified streams and heat exchangers are shown in green) without modifying the operational parameters and thus the heat duties of the columns. Due to the difference in the pressures of HPC and LPC, the temperature difference in the new reboiler-condenser is high enough to enable sufficient heat transfer. If the heat duty of the condenser of HPC is higher than that of the reboiler of LPC ( $Q_c^{HPC} > Q_r^{LPC}$ ), LPC does not need external heating, while an additional condenser is required to condense the top vapour of HPC completely.

By changing the operational parameters of the columns, an optimal level of heat integration can be found. If the geometrical parameters of the columns (number of trays, feeding locations) are

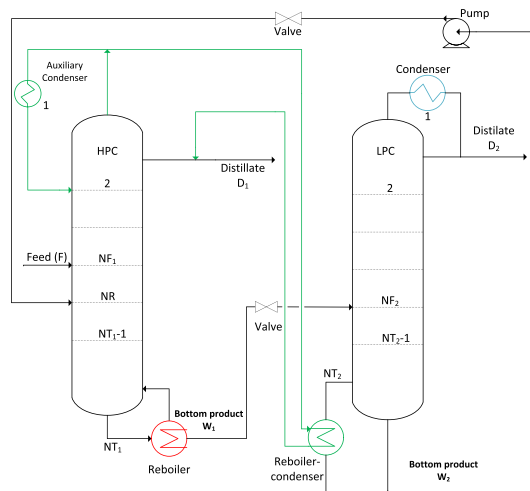


Fig. 5. Flow-sheet of the partially heat-integrated pressure-swing distillation process.

changed, as well, the optimal partial heat integration (OPHI) system is obtained.

### 3.2. Full heat integration (FHI)

For the FHI process, the whole heat duty of the condenser of HPC is used to heat LPC. As the heat duty of the condenser of HPC is equal to that of the reboiler of LPC, LPC does not need external heating ( $Q_{rc} = Q_c^{HPC} = Q_r^{LPC}$ ). The flow-sheet of the FHI process is identical to the one shown in Fig. 5 with the exception of the auxiliary condenser that is not needed in this case. In order to model the FHI process, some parameters such as the reflux ratios of both columns and the reboiler heat duty of HPC have to be varied. A controller was added to the model between the two columns to ensure that the heat duty of the condenser of HPC is equal to that of the reboiler of LPC.

### 3.3. Application of heat pumps

Beside heat integration, heat pump-assisted PSD might help to reduce the total energy cost of the PSD process, as well. In the vapour recompression (VRC) heat pump (HP) technique, the top vapour of a column (whose flow rate is  $V_{top}$ ) is the working fluid (WF) used to heat the reboiler of the same column. After leaving the column, the top vapour is compressed to pressure  $P_{out}$ ; its temperature increases and leaves the compressor as a superheated vapour. The WF is then used to partially vaporise the bottom liquid of the LPC in the reboiler-condenser. Meanwhile, the WF:

- cools down to its dew point (transferring its (small) heat of superheating  $\Delta h_{sup}$ ),
- condenses (transferring its (large) latent heat of condensation  $\lambda$ ) and
- eventually cools further below its boiling point (transferring its (small) heat of subcooling  $\Delta h_{sub}$ )

After the reboiler-condenser, the pressure of the working fluid is reduced onto the top pressure of the column in an expander, which leads to the partial evaporation of the working fluid.

In vapour recompression heat pumps (Fig. 6), three different cases can be distinguished based on the value of the ratio of the flow rate of working fluid compressed ( $V_{WF}$ ) to the flow rate of top

vapour leaving the column ( $V_{top}$ ) introduced by Modla and Lang [13]:  $\beta = V_{WF}/V_{top}$ .

In the conventional case,  $\beta = 1$  ( $V_{WF}=V_{top}$ ), that is, the flow rate of the working fluid is fixed. In this case, after the expansion, the vapour part of the working fluid is condensed totally in an after-cooler, then it is divided into distillate and reflux. The literature almost exclusively deals with this case.

In the second case,  $\beta > 1$  ( $V_{WF} > V_{top}$ ). After the expansion, the vapour of the working fluid is only partially condensed. The part of the working fluid not condensed ( $V_{rec}$ ) is then recycled and mixed with the top vapour in order to increase the quantity of the working fluid compressed:  $V_{WF}=V_{top} + V_{rec}$ . Here  $\beta$  is a variable that must be optimised. As it was demonstrated by Modla and Lang [13], by increasing  $V_{WF}$  in this way, the outlet pressure of the compressor can be decreased, resulting in lower operating and investment costs.

In the third case,  $\beta < 1$  ( $V_{WF} < V_{top}$ ). The top vapour leaving the column is divided into two parts. One part of the top vapour ( $V_{WF} = \beta V_{top}$ ) is compressed and used for heating the reboiler-condenser. The other part of the top vapour ( $V_{BYP}=(1-\beta)V_{top}$ ) bypasses the compressor and the expander and is condensed in an auxiliary condenser. The working fluid leaving the expander is totally condensed in an after-cooler and is mixed with the condensate of  $V_{BYP}$ , and then the mixture is divided into distillate and reflux. Here  $\beta$  is again a variable that must be optimised. The reduced  $V_{WF}$  leads to a decrease in compressor work and investment cost. This case was also investigated by Shi et al. [14] and Yang et al. [15].

In this work, three different VRC HP-PSD configurations are investigated: VRC-assisted HPC, VRC-assisted LPC and VRC-assisted HPC + LPC, where a VRC heat pump is applied for both columns. The compressor(s) used are single-stage centrifugal compressors.

## 4. Calculation method

Calculations are performed with the ChemCAD 7.1 professional flow-sheet simulator [25]. The columns are modelled with SCDS units that perform tray-by-tray calculations using a rigorous, proprietary simultaneous correction method (a general description is available in Kister [26]). The following assumptions are used in the present work: theoretical trays, boiling-point reflux, constant pressure drop per plate.

First, the results of Li et al. [9] are reproduced by using the same geometrical and operational parameters. This is considered as the base case. The top pressure of HPC is 2.0 atm (2.02 bar), and the number of theoretical trays in the base case is  $NT_1 = 90$  (1) (counted from top, including the total condenser and the partial reboiler), while for LPC, the top pressure is 0.1 atm (0.101 bar) and the number of trays is  $NT_2 = 22$  (1). The feeding locations are  $NF_1 = 6$  (1) for the feed,  $NR = 20$  (1) for the recycle stream  $W_2$  and  $NF_2 = 11$  (1) for the bottom product of HPC ( $W_1$ ). The pressure drop of HPC is 0.2407 bar and of LPC is 0.0492 bar. The feed is subcooled liquid at 2.02 bar with a temperature of 46.85 °C. Its flow rate is 100 kmol/h, and it has a composition of 60 mol% A. Both A and B must be obtained in a purity of 99.5%.

Subsequently, the optimisation of the non-heat integrated process (NHI) is performed. The objective function (OF) to be minimised is the total annualised cost (TAC, \$/y) of the two columns:

$$OF = TAC = \frac{TCC}{\text{payback period}} + TEC \tag{1}$$

where TCC is the total capital cost (\$), and TEC is the total energy cost.

The optimisation of NHI is performed by an elitist, real-coded

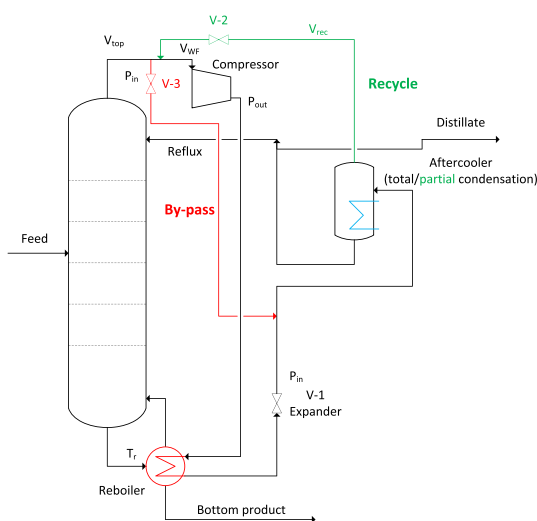


Fig. 6. Vapour recompression heat pump with  $\beta = 1$  (1) (conventional),  $\beta > 1$  (1) (recycle, green),  $\beta < 1$  (1) (by-pass, red). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

genetic algorithm (GA) written in VBA under Excel. The parameters of the GA: mutation probability: 5%, crossover probability: 70%, population size: 30, number of generations: 100. The algorithm handles discrete variables (e.g. tray numbers) by rounding their values to the nearest integer. For each individual in a population, Excel transfers the values of the optimisation variables to ChemCAD using its Data Map feature. The simulation is run with ChemCAD, and its results are transferred to Excel, where the value of OF is calculated. The convergence of the simulation is checked, and in the case of non-convergence, a penalty function of  $10^8$  \$ is used as OF. Further details of the algorithm can be found in Modla and Lang [27].

Preliminary sensitivity studies were performed to determine suitable ranges (Range 1, Table 3) of the optimisation variables. The optimal values of NR and  $Q_{r1}$  of the first optimisation run were close to their lower bounds; therefore, a second run was performed with modified ranges (Range 2, Table 3).

The TAC of the non-optimised PHI process is calculated by using the results of the optimised NHI process. PHI is then optimised to obtain the OPHI process, and the optimisation of FHI is performed, as well. In order to study the influence of geometrical and operational optimisation variables, two optimisations are performed with different sets of variables.

By the first optimisation, only the reboiler heat duties are varied in order to reduce the total energy cost and, as a result, the TAC. For PHI, both  $Q_{r1}$ ,  $Q_{r2}$  are varied, but for FHI, only  $Q_{r1}$  is varied as we only have one reboiler with external heat duty.

The second optimisation of PHI (OPHI) and FHI is performed by the same GA applied for the optimisation of NHI, where the optimisation variables are the tray numbers (HPC: NT<sub>1</sub>, LPC: NT<sub>2</sub>), the feeding locations (HPC: NF<sub>1</sub>, NR, LPC: NF<sub>2</sub>) and the reboiler duties ( $Q_{r1}$ ,  $Q_{r2}$  for PHI and  $Q_{r1}$  only for FHI). For OPHI, the ranges were modified after the 24th generation from Range 3 to Range 4 (Table 3). For FHI, Range 5 was applied.

The heat pumps are applied to the optimised NHI process. The compressor is assumed to be adiabatic. The calculation method consists of optimising  $P_{out}$  for the case of  $\beta = 1$  (1) and both  $P_{out}$  and  $\beta$  for the case where  $\beta \neq 1$  (1). If  $\beta = 1$  (1),  $P_{out}$  is chosen so that the temperature of WF ( $T_{WF}$ ) is higher than the temperature of the bottom liquid ( $T_r$ ) by the minimum approach temperature  $\Delta T_{min}$ , which is chosen here as 5 °C (a typical value for VRC heat pumps [12,28]). 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.

If  $\beta \neq 1$  (1), the minimum values of  $P_{out}$  and  $\beta$  must be determined while fulfilling the following requirements:

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

The method and data for cost calculation are taken from Li et al. [9]. Exceptions are the value of the annual working hours (not given in Li et al. [9]) and the data related to the heat pumps. The total capital cost (TCC) consists of the cost of the column vessels, heat

exchangers and compressors and the payback period is equal to 3 y.

The heat exchanger cost ( $C_{HE}$ , \$) consists of the cost of condenser, reboiler, and integrated heat exchanger cost.

$$C_{HE} = 7,296 \cdot A^{0.65} \tag{2}$$

where A is the heat transfer area (m<sup>2</sup>):

$$A = \frac{1.1Q}{k\Delta T} \tag{3}$$

where Q is the heat duty (kW),  $\Delta T$  the temperature difference (K), and k the overall heat transfer coefficient (kW/m<sup>2</sup>K). The value of k is 0.852 kW/m<sup>2</sup>K for the condenser, 0.568 kW/m<sup>2</sup>K for the reboiler and the reboiler-condenser [9], and 0.28 kW/m<sup>2</sup>K [12] between superheated vapour and boiling liquid.

For the heat pump application, after the compressor, the working fluid is superheated, so the heat duty of the reboiler-condenser (integrated heat exchanger) is divided into the heat of superheating ( $Q_{sup}$ ) and latent heat ( $Q_{lat}$ ), with their corresponding temperature differences  $\Delta T_{sup}$  and  $\Delta T_{lat}$ . As a result, the reboiler cost (\$) in this case is modified to:

$$C_{r,HP} = 7,296 \left( \frac{1.1Q_{sup}}{0.28\Delta T_{sup}} + \frac{1.1Q_{lat}}{0.568\Delta T_{lat}} \right)^{0.65} \tag{4}$$

The cost of a single-stage centrifugal compressor (\$) is [29]:

$$C_C = \frac{M\&S}{280} \cdot 517.5 \cdot (1.34 \cdot W)^{0.82} \cdot (2.11 + F_d) \tag{5}$$

where M&S is the Marshall & Swift Index: 1638.2 (1) (2018), and W the compressor motor power (kW), while  $F_d = 1$  (1).

The compressor work is [25]:

$$W = z \cdot \frac{\mu}{\mu - 1} \cdot V_{WF} \cdot P_{in} \cdot \left[ \left( \frac{P_{out}}{P_{in}} \right)^{\frac{\mu-1}{\mu}} - 1 \right] \tag{6}$$

where: z is the compressibility factor,  $P_{in}$  the inlet pressure of the compressor, and

$$\frac{\mu}{\mu - 1} = \frac{k - 1}{\eta} \tag{7}$$

where:  $\eta = 0.8$  (1) is the polytropic efficiency of the compressor, and k is the ratio of the heat capacities:

$$k = \frac{C_p}{C_v} \tag{8}$$

The column vessel cost (\$) for each column:

$$C_{CV} = 17,640 \cdot Di^{1.066} H^{0.802} \tag{9}$$

where Di is the column (inner) diameter (m), and H denotes the height of the column (m) calculated from the number of theoretical trays (NT) as  $H = 1.2 \cdot 0.61 \cdot (NT-2)$  by taking into account tray

**Table 3**  
Ranges of optimisation variables used with the genetic algorithm.

	NT <sub>1</sub> (1)	NF <sub>1</sub> (1)	NR (1)	NT <sub>2</sub> (1)	NF <sub>2</sub> (1)	$Q_{r1}$ (MJ/h)	$Q_{r2}$ (MJ/h)
Range 1	50–100	3–10	13–30	20–30	7–17	15,594–19,000	4390–6000
Range 2			10–25			12,000–17,000	
Range 3			13–45	10–30	3–9	14,135–19,000	5300–12,165
Range 4		2–10				14,000–19,000	
Range 5	20–75		10–20	10–30	2–10	14,137–19,000	–

spacing (0.61 m) and average tray efficiency (0.833 (1)). The column diameter is calculated by ChemCAD, assuming valve trays with V-1 type valves and a vapour velocity of 80% of the flooding one (calculated by the Glitsch flooding correlation).

The total capital cost (TCC, \$) is:

$$TCC = C_{HE} + C_C + C_{CV,HP} + C_{CV,LP} \quad (10)$$

The total energy cost (TEC) includes the cost of heating steam and (when a heat pump is applied) electricity. The cost of cooling water is neglected. The annual cost of saturated heating steam ( $C_{HS}$ , \$) and the annual cost of electricity ( $C_E$ , \$) are:

$$C_{HS} = Q \cdot p_{st} \cdot t \quad (11)$$

$$C_E = W \cdot p_{el} \cdot t \quad (12)$$

where  $Q$  is the heat duty (GJ/h);  $t$  the annual working hours (8712 h) and  $p_{st}$  is the price of either LP steam (4 bar): 7.78 \$/GJ used for heating LPC, or MP steam (11 bar): 8.22 \$/GJ used for heating HPC [9]. The price of electricity is taken as four times the price of LP steam:  $p_{el} = 4 \cdot 7.78 = 31.12$  \$/GJ.

The total energy cost (TEC, \$/y) is:

$$TEC = C_{HS} + C_E \quad (13)$$

In order to evaluate the impact on the environment and fuel consumption rate of the different processes, the CO<sub>2</sub> emissions and the Eco-indicator 99 (EI99) values are calculated.

The equation for evaluating CO<sub>2</sub> emissions (CO<sub>2,HS</sub>, kg/h) via fuel combustion to produce heating steam is shown below [30]:

$$CO_{2,HS} = \frac{\alpha}{NHV} \cdot \frac{C\%}{100} \cdot \frac{Q_{proc}}{\lambda_{proc}} \cdot (h_{proc} - (-15,544.59)) \cdot \frac{T_{FTB} - T_0}{T_{FTB} - T_{stack}} \quad (14)$$

where NHV, C% and  $\alpha$  (3.67 (1)) are net heating value, the carbon content of fuel and the ratio of the molar masses of CO<sub>2</sub> and C, respectively. In this study, the NHV and C% are 39,771 kJ/kg and 86.5 mass% by assuming that heavy oil is used as fuel. The  $Q_{proc}$ ,  $\lambda_{proc}$  and  $h_{proc}$  are the reboiler heat duty of the column, the latent heat and enthalpy of the steam, respectively. The temperatures of the flame ( $T_{FTB}$ ), stack ( $T_{stack}$ ) and the ambient temperature ( $T_0$ ) are assumed as 2073.15 K, 333.15 K and 298.15 K. The value  $-15,544.59$  kJ/kg is the enthalpy of feed water at 100 °C. The CO<sub>2</sub> emission corresponding to the electricity consumption of the compressor is taken as 51.1 kg CO<sub>2</sub>/GJ [11].

For the EI99 calculation, which was proposed by Goedkoop and Priensma [31], the main factors contributing to EI99 are the steam used to provide the heat duty of reboiler, the steel used to build the columns, and electricity utilised by compressors.

The mathematical expression of EI99 is as follows:

$$EI99 = \sum_j \omega_j C_{j,as} as + \sum_j \omega_j C_{j,asl} asl + \sum_j \omega_j C_{j,ael} ael \quad (15)$$

where  $\omega_j$  ( $j = 1-3$ ) is the weighting factor of the damage to human health, the ecosystem quality, and resource consumption. According to the study by Contreras-Zarazúa et al. [32], the suggested values of  $\omega_1 = \omega_2 = 0.4$  (1) and  $\omega_3 = 0.2$  (1) are used in this study. The coefficients  $C_{j,as}$ ,  $C_{j,asl}$ ,  $C_{j,ael}$  represents the value of damage for category  $j$  associated with the steam, carbon steel, and electricity, respectively [32]. The weighted sum of the damage coefficients ( $\sum_j \omega_j C_{j,i}$ ,  $i \in \{as, asl, ael\}$ ) are:

- Steam:  $3.48 \cdot 10^{-3}$  (point/kg).
- Steel:  $9.63 \cdot 10^{-5}$  (point/kg).
- Electricity:  $4.44 \cdot 10^{-3}$  (point/kWh).

The damage values include the following impact categories: carcinogenicity, climate change, ionising radiation, ozone depletion, respiratory effects, acidification, ecotoxicity, land occupation, fossil fuels, mineral extraction [32].

The notations as, asl, and ael refer to the amount of steam (kg), carbon steel (kg), and electricity (kWh) required by the process. In this study, a 10-year lifetime of the shells is employed in this work, so the weight of steel was divided by 10 y.

## 5. Results

### 5.1. No heat integration (NHI)

The results of the conventional PSD without heat integration are presented in Table 4. Compared to the results of Li et al. [9], with the same variables used (base case), the total energy cost (TEC) and the total capital cost (TCC) values were close, and as a result, the TAC values were close as well, the difference in TAC is only to 1.14%.

By optimisation, the number of theoretical trays of HPC considerably decreased (from 90 to 69 (1)) whilst that of LPC increased (from 22 to 27 (1)), respectively. The flow rate of the recycle ( $W_2$ ) increased compared to the base case and to Li et al. [9]; however, its water content ( $x_{w2}$ ) remained constant. The condenser and reboiler heat duties of both columns decreased, which led to the decrease of the total energy cost by 22.9% compared to that of the base case. As a result of the optimisation, the TAC was reduced by 20.8%.

### 5.2. Partial heat integration

The results of PHI are presented in Table 5. For the non-optimised case, all parameters are the same as in the optimised NHI one, except  $Q_c$  of HPC, decreased by  $Q_r$  of LPC, and the external  $Q_r$  of LPC decreased to zero. Compared to NHI, due to the heat integration, the total energy cost of the non-optimised PHI was lower by 24.7% and the TAC by 19.0%.

By the first optimisation, the reboiler heat duty of HPC was reduced by 6.02% (918 MJ/h). The heat duty of the reboiler-condenser was higher by 30.8% (1634 MJ/h).  $W_2$  increased by 12.1%, and  $x_{w2}$  slightly increased, as well. TCC increased by only 0.27% as the trays numbers were unchanged; only  $Q_{rc}$  was slightly

**Table 4**  
Comparison of results of different cases without heat integration (NHI).

Parameter	Results of Li et al. [9]		Base case		Optimised case	
	HPC	LPC	HPC	LPC	HPC	LPC
NT (1)	90	22	90	22	69	27
NF (1)	6	11	6	11	5	10
NR (1)	20	–	20	–	17	–
Di (m)	1.50	1.97	1.52	1.98	1.37	1.98
$W_2$ (kmol/h)	49.77		49.69		68.89	
$x_{w2}$ (mole fraction)	0.434		0.434		0.434	
$T_c$ (°C)	120.8	58.4	120.9	58.3	120.8	58.3
$T_r$ (°C)	146.2	75.6	145.6	72.6	145.6	72.6
R (1)	7.12	2.80	7.16	2.80	4.65	2.79
$Q_c$ (MJ/h)	18,396	7039	19,535	6651	13,475	6666
$Q_r$ (MJ/h)	21,099	5504	21,099	5504	15,258	5301
TCC ( $10^5$ \$)	15.79		16.97		14.64	
TEC ( $10^5$ \$/y)	18.95		18.84		14.52	
TAC ( $10^5$ \$/y)	24.21		24.49		19.40	

higher, resulting in a slight increase in the cost of the heat exchanger. The heat duty of the auxiliary condenser ( $Q_{aux}$ ) decreased considerably. The reflux ratio of HPC ( $R_1$ ) decreased, but that of LPC ( $R_2$ ) increased. TEC slightly decreased by 6.03% and the TAC by 4.13% compared to the non-optimised case.

By the second optimisation (OPHI), the number of trays of HPC and LPC columns were reduced to 60 and 19 (1), respectively. As in the previous case,  $R_1$  slightly decreased, while  $R_2$  increased even more.  $W_2$  increased by 15.0% compared to the first optimisation, and  $x_{w2}$  slightly decreased.  $Q_{aux}$  decreased even further. The total energy cost was slightly higher than by the first optimisation. However, the TCC was lower by 6.75% compared to the non-optimised case and by 7.00% compared to the first optimised case due to the decrease of the tray numbers of both columns. The second optimisation gave a further reduction of 1.73% in the TAC (compared to the first optimisation). This is less by 5.78% than in the non-optimised case.

### 5.3. Full heat integration (FHI)

The results of FHI are presented in Table 6. For the non-optimised case, the number of trays and the feed locations are the same as in the optimised NHI. To perform FHI,  $Q_{r2}$  had to be increased in order to make it equal to  $Q_{c1}$ . Compared to NHI, without changing the values of other optimisation variables (non-optimised case), by changing  $Q_{r2}$ , the values of  $Q_{c1}$ ,  $Q_{c2}$ ,  $R_1$  and  $R_2$  changed, as well.  $R_1$  slightly decreased, but  $R_2$  increased due to the increase of  $Q_{r2}$ . The increase of  $W_2$  was negligible, and there was no change in  $x_{w2}$ . The total energy cost was lower by 24.7% and the TAC by 11.3%.

By the first optimisation, the reboiler heat duty of HPC was reduced by 7.35%, and as a result, the heat duty of the reboiler-condenser was lower by 10.2%. This led to a slight decrease of the total energy cost by 7.41% and the TAC by 6.02% compared to the non-optimised case, but the TAC was still higher by 6.34% than that of the first optimised PHI.

By the second optimisation, the number of trays of HPC and LPC columns were reduced to 61 and 16 (1), respectively.  $W_2$  increased by 26.2% compared to the first optimised case, and  $x_{w2}$  slightly decreased. The total energy cost was slightly higher than that of the first optimisation, but the TCC was lower by 26.20% compared to the non-optimised case and by 23.5% compared to the first optimisation due to the decrease of the number of trays of both

**Table 5**  
Comparison of results of different cases with partial heat integration.

Parameter	Non-optimised PHI		First optimisation		Second optimisation (OPHI)	
	HPC	LPC	HPC	LPC	HPC	LPC
NT (1)	69	27	69	27	60	19
NF (1)	5	10	5	10	3	6
NR (1)	17	–	17	–	23	–
Di (m)	1.37	1.98	1.22	2.29	1.22	2.59
$W_2$ (kmol/h)	68.89	–	78.33	–	92.20	–
$x_{w2}$ (mole fraction)	0.434	–	0.437	–	0.434	–
$T_c$ (°C)	120.8	58.3	120.8	58.3	120.8	58.4
$T_r$ (°C)	145.6	72.6	145.6	72.6	145.5	75.6
R (1)	4.65	2.79	4.23	3.79	4.21	5.53
$Q_c$ (MJ/h)	–	6666	–	8343	–	11,361
$Q_r$ (MJ/h)	15,258	–	14,340	–	14,441	–
$Q_{aux}$ (MJ/h)	8175	–	5488	–	2662	–
$Q_{rc}$ (MJ/h)	–	5300.9	–	6935	–	9832
TCC ( $10^5$ \$)	14.38	–	14.42	–	13.41	–
TEC ( $10^5$ \$/y)	10.93	–	10.27	–	10.34	–
TAC ( $10^5$ \$/y)	15.72	–	15.07	–	14.81	–

**Table 6**  
Comparison of results of different cases with full heat integration.

Parameter	Non-optimised FHI		First optimisation		Second optimisation	
	HPC	LPC	HPC	LPC	HPC	LPC
NT (1)	69	27	69	27	61	16
NF (1)	5	10	5	10	5	6
NR (1)	17	–	17	–	16	–
Di (m)	1.52	3.05	1.52	2.89	1.22	2.89
$W_2$ (kmol/h)	65.25	–	65.35	–	88.57	–
$x_{w2}$ (mole fraction)	0.438	–	0.438	–	0.434	–
$T_c$ (°C)	120.8	58.3	120.8	58.3	120.8	58.3
$T_r$ (°C)	145.6	72.6	145.6	72.6	145.6	72.6
R (1)	4.66	7.52	4.12	6.87	4.26	7.11
$Q_c$ (MJ/h)	–	14,840	–	13,719	–	14,104
$Q_r$ (MJ/h)	15,258	–	14,137	–	14,522	–
$Q_{rc}$ (MJ/h)	–	13,553	–	12,166	–	12,604
TCC ( $10^5$ \$)	18.59	–	17.93	–	13.72	–
TEC ( $10^5$ \$/y)	10.93	–	10.12	–	10.39	–
TAC ( $10^5$ \$/y)	17.12	–	16.09	–	14.97	–

columns. The second optimisation led to a further reduction of TAC by 6.96% (compared to the first optimisation). The TAC is less by 12.6% compared to the non-optimised case.

### 5.4. Application of heat pumps

First, the application of a single heat pump for HPC or LPC, then the simultaneous application of the two heat pumps is studied. The total number of trays and the feed locations are always the same as in the optimised NHI case. First, the amount of the working fluid is optimised, then the TAC of the optimised heat pump configuration is compared with that of the above optimised options.

#### 5.4.1. Heat pump in the high-pressure column (VRC-HPC)

Table 7 presents the results of the VRC-assisted HPC without ( $\beta = 1$  (1)) and with ( $\beta > 1$  (1)) recycling. For  $\beta = 1$  (1), which is the conventional operation of heat pumps, the outlet pressure of the compressor is  $P = 9.73$  bar (corresponding to a compression ratio of  $CR = 4.82$  (1)). This is the pressure where WF leaving the reboiler is at the desired temperature  $T_{WF} = T_{r1} + 5$  (150.5 °C). In this case, WF is subcooled in the reboiler by 28.0 °C. In order to reduce the outlet pressure and thus the compressor work, the quantity of WF is increased by adding a recycled part from the flash. In this case,  $\beta$  is greater than 1.0 (1). The value of  $\beta$  can be adjusted by the cooling duty of the flash: the lower the heat duty, the more WF is recycled. This also gives an upper limit for  $\beta$ , where the heat duty is zero. Further increase of  $\beta$  is only possible by heating in the flash instead of cooling, which would require the use of external heating energy.

While optimising  $\beta$ , two requirements have to be fulfilled, WF leaving the reboiler should be saturated liquid, and its temperature should be equal to  $T_{r1} + 5$  (150.5 °C). In our case, these two criteria cannot be fulfilled at the same time without heating in the flash and

**Table 7**  
Comparison of results of VRC-HPC with and without recycling of the working fluid.

Parameter	$\beta = 1$ (1)	$\beta > 1$ (1)
	HPC	HPC
$W_{compressor}$ (kW)	720.8	500.1
$Q_{after-cooler}$ (MJ/h)	648.6	–
TCC ( $10^5$ \$)	41.23	35.29
Steam cost ( $10^5$ \$/y)	3.59	3.59
Electricity cost ( $10^5$ \$/y)	7.04	4.88
TEC ( $10^5$ \$/y)	10.63	8.47
TAC ( $10^5$ \$/y)	24.37	20.24



two cases can be distinguished:

- $T_{WF} = 150.5 \text{ }^\circ\text{C}$  but WF is subcooled; in this case, the outlet pressure of the compressor is  $P = 6.02 \text{ bar}$  ( $CR = 2.98$  (1)) and  $\beta = 1.061$  (1). The compressor work is 500.8 kW.
- WF is saturated liquid, but  $T_{WF}$  is higher than  $150.5 \text{ }^\circ\text{C}$  ( $158.4 \text{ }^\circ\text{C}$ ); in this case, the outlet pressure of the compressor is  $P = 5.92 \text{ bar}$  ( $CR = 2.93$  (1)) and  $\beta = 1.081$  (1). The compressor work is 500.1 kW.

The aim is to reduce the total energy cost and, as a result, the TAC, as well. Therefore, the second case is chosen where, even though the flow rate of WF is slightly higher, the compressor work is lower.

As it can be seen, in this case study,  $\beta$  is limited by the fact that no heating should be applied in the flash. Note that this was not observed by Modla and Lang [13] where at the optimal value of  $\beta$ , WF was cooled in the flash, and it was possible to fulfil simultaneously the two conditions mentioned above.

For both cases, as the recycled stream has a slightly lower temperature than that of the top vapour, a part of the WF is condensed, and there is liquid in the compressor inlet. Because of this, the WF must be very slightly heated before the compressor (in the order of 1 MJ/h).

Due to the recycling, the compressor work and the electricity cost is reduced by 30.7%, the TEC by 20.3% and the TAC by 16.9%, respectively. Compared to NHI and PHI processes, the application of VRC-HPC is not economical because of its considerably higher TAC as a result of the high investment cost of the compressor.

#### 5.4.2. Heat pump in the low-pressure column (VRC-LPC)

Table 8 presents the results of the VRC assisted LPC without ( $\beta = 1$  (1)) and with ( $\beta < 1$  (1)) by-pass. For  $\beta = 1$ , the outlet pressure of the compressor is  $P = 0.24 \text{ bar}$  (corresponding to  $CR = 2.38$  (1)), which is the pressure at which the bubble point of the top vapour is ca.  $T_{i2}+5 \text{ }^\circ\text{C}$  ( $73.1 \text{ }^\circ\text{C}$ ). In this case, the WF leaving the reboiler is only partially condensed; thus, an auxiliary condenser is needed. The partial condensation of WF also shows that in order to reduce the compressor work, the quantity of WF can be decreased by dividing the top vapour into two parts. One of them is sent as WF to the compressor; the other one by-passes it. In this case  $\beta$  is lower than 1.0 (1).  $\beta$  was varied between 0 and 1 (1) in order to find its optimal value, which gives the lowest compressor duty, the optimal value of  $\beta$  is equal to 0.8 (1), and the outlet pressure of the compressor is unchanged ( $P = 0.24 \text{ bar}$ ). Contrary to the previous case, the WF is always saturated vapour, and it does not need heating before the compressor.

Due to the by-pass, the compressor work and the electricity cost is reduced by 20.0%, TEC by 2.05% and the TAC by 2.95%.

The application of VRC-LPC is not economical either; however, compared to VRC-HPC, the energy cost of VRC-LPC is higher by

**Table 8**  
Comparison of results of VRC-LPC with and without by-pass of the working fluid.

Parameter	$\beta = 1$ (1)	$\beta < 1$ (1)
	LPC	LPC
$W_{\text{compressor}}$ (kW)	133.4	106.7
$Q_{\text{after-cooler}}$ (MJ/h)	1363	279.7
$Q_c$ (MJ/h)	343.4	1334
TCC ( $10^5$ \$)	24.36	23.36
Steam cost ( $10^5$ \$/y)	10.93	10.93
Electricity cost ( $10^5$ \$/y)	1.30	1.04
TEC ( $10^5$ \$/y)	12.22	11.97
TAC ( $10^5$ \$/y)	20.35	19.75

29.2%, while the TAC is lower by 2.42%. The higher energy cost of VRC-LPC can be explained by the fact that the reboiler duty of HPC is much higher; thus, the potential to reduce its energy cost by the application of a heat pump is higher, as well.

#### 5.4.3. Heat pump in both columns (VRC-HPC + LPC)

Table 9 presents the results of the simultaneous application of the two heat pumps with either  $\beta = 1$  (1) or  $\beta \neq 1$  (1) in both heat pumps. By using recycling for HPC and by-pass for LPC, the energy cost was reduced by 29.0% and the TAC by 18.7% (compared to the case  $\beta_1 = \beta_2 = 1$  (1)). As expected, the VRC-assisted HPC + LPC ( $\beta_1 = \beta_2 = 1$  (1)) has the highest TCC and electricity cost due to the compressors compared to all previous cases.

#### 5.5. Economic comparison of different configurations

Table 10 presents the total capital, the total energy and the total annualised costs for all the studied configurations.

Both partial and full heat integration reduced the TAC of the PSD process considerably. The lowest TAC is obtained for the OPHI. The optimal FHI process has a TAC value close to that of OPHI since the optimisation resulted in a greater decrease in the TAC than for PHI. With the application of heat pumps, the TAC could not be decreased. VRC-LPC with and without by-pass, VRC-HPC with recycling and VRC-HPC + LPC with recycling and by-pass have TAC values close to the optimised NHI case (the conventional PSD).

In this case study, the (partial or full) heat integration of the column is economical, but the application of heat pumps is not. However, such conclusions depend strongly on the ratio of the prices of steam and electricity, which vary widely not only from country to country but also from site to site. The sequence of the configurations by the total energy cost depends only on the ratio of the prices, but their sequence by TAC on their absolute values, as well. Therefore, a map is constructed (Fig. 7) that shows which configuration is more economical at different combinations of steam and electricity prices. (The ratio of MP and LP steam prices is assumed to be the same as used earlier.) Only the PHI and FHI configurations optimised by GA are considered here. (Heat pump assisted configurations with  $\beta = 1$  (1) are not shown either.) Here, the map is divided into domains considering not only the most but also the second most economical configuration. Four different domains can be distinguished (Table 11).

The prices used in this study lie in domain A, where the application of heat pumps is not recommended. In domain B, the simultaneous application of the two heat pumps becomes more economical than FHI but less than OPHI. At relatively high steam and low electricity prices (domain C), VRC-HPC + LPC becomes the most economical configuration. FHI and NHI are inferior to OPHI in every domain.

Starting from the point representing this work, domain B can be

**Table 9**  
Comparison of results of VRC-HPC + LPC with and without by-pass and recycling of the working fluid.

Parameter	$\beta_1 = \beta_2 = 1$ (1)		$\beta_1 = 1.081$ (1); $\beta_2 = 0.8$ (1)	
	HPC	LPC	HPC	LPC
$W_{\text{compressor}}$ (kW)	720.8	133.4	500.1	106.7
$Q_{\text{after-cooler}}$ (MJ/h)	648.6	1363	–	279.7
$Q_c$ (MJ/h)	–	343.4	–	1334
TCC ( $10^5$ \$)	50.95	–	44.01	–
Electricity cost ( $10^5$ \$/y)	8.34	–	5.92	–
TEC ( $10^5$ \$/y)	8.34	–	5.92	–
TAC ( $10^5$ \$/y)	25.32	–	20.59	–

**Table 10**  
Economic comparison of the cases studied.

	TCC (10 <sup>5</sup> \$)	TEC (10 <sup>5</sup> \$/y)	TAC (10 <sup>5</sup> \$/y)
NHI optimised	14.64	14.52	19.40
Second optimisation PHI (OPHI)	13.41	10.34	14.81
Second optimisation FHI	13.72	10.39	14.97
VRC-HPC β ≠ 1	35.29	8.47	20.24
VRC-LPC β ≠ 1	23.36	11.97	19.75
VRC-HPC + LPC β ≠ 1	44.01	5.92	20.59

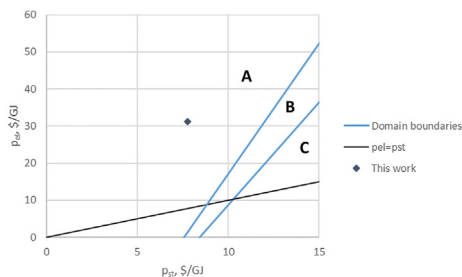


Fig. 7. Map of domains determined by the two most economical configurations.

**Table 11**  
The two most economical configurations in each domain.

Domain	Most economical configuration	Second most economical configuration
A	OPHI	FHI (optimised)
B	OPHI	VRC-HPC + LPC (β ≠ 1)
C	VRC-HPC + LPC (β ≠ 1)	OPHI

reached with a moderate increase of steam price (at  $p_{st} = 11.94$  \$/GJ), and then domain C is reached at  $p_{st} = 12.1$  \$/GJ (under constant electricity price). If the prices increase with a constant ratio of electricity and steam price (4.0 (1)), domain B is only reached at  $p_{st} = 17.55$  \$/GJ.

5.6. Environmental evaluation

Table 12 presents the results of CO<sub>2</sub> emissions, the specific CO<sub>2</sub> emissions and the Eco-indicator 99 (EI99) for all configurations. The three aspects contributing to EI99 are the steam used to provide the heat duty of reboiler, electricity utilised by compressors, and the steel used to build the columns; however, it is the consumption of steam that influences the most the EI99 indicator. From an

**Table 12**  
The CO<sub>2</sub> emissions and EI99 values for all configurations.

Process	CO <sub>2</sub> emissions (kg CO <sub>2</sub> /h)	Specific CO <sub>2</sub> emissions		EI99 (point/y)
		(kg CO <sub>2</sub> /kg feed)	(kmol CO <sub>2</sub> /kmol feed)	
NHI base case	329.6	0.095	0.075	160,127
NHI optimised	273.9	0.079	0.062	135,038
Non optimised PHI	234.7	0.067	0.053	101,910
First optimisation PHI	220.6	0.063	0.050	95,778
Second optimisation (OPHI)	222.1	0.064	0.051	96,452
Non optimised FHI	234.7	0.067	0.053	101,911
First optimisation FHI	217.5	0.062	0.049	94,423
Second optimisation FHI	223.4	0.064	0.051	96,993
VRC-HPC β = 1	171.8	0.049	0.039	38,305
VRC-HPC β ≠ 1	131.2	0.038	0.029	36,998
VRC-LPC β = 1	259.2	0.074	0.059	102,942
VRC-LPC β ≠ 1	254.3	0.073	0.058	102,736
VRC-HPC + LPC β = 1	157.1	0.045	0.036	6608
VRC-HPC + LPC β ≠ 1	111.6	0.032	0.025	4494

environmental point of view, the most advantageous configuration is VRC-HPC + LPC with by-pass and recycling, as it has the lowest CO<sub>2</sub> emission and EI99 values. The NHI configurations are not recommended in this case, as they have the highest values of CO<sub>2</sub> emissions and EI99.

By comparing the first optimised PHI and FHI to NHI, the results show that performing heat integration decreased the CO<sub>2</sub> emissions by 19.5% using PHI and by 20.6% using FHI, both compared to the optimised NHI process. The situation is similar for EI99; performing PHI led to a decrease 20.1% of the EI99 value compared to optimised NHI, while performing FHI led to a 30.1% decrease.

However, performing the second optimisation both for PHI and FHI increases slightly both environmental indicators due to the increase of  $Q_{r1}$ .

Moreover, applying heat pumps is highly recommended from an environmental point of view, especially with optimising β. By applying VRC-HPC with β = 1, both the CO<sub>2</sub> emission and EI99 were reduced by 37.3% and 71.6%, respectively. However, by optimising β, both values were further reduced by 23.6% and 3.41% compared to the VRC-HPC β = 1. VRC-LPC (even with) by-pass is not recommended as its CO<sub>2</sub> emissions and EI99 values were very high and close to those of NHI optimised process.

Considering both economic and environmental indicators, only three configurations are non-dominated, meaning that no other configuration exists having both lower TAC and lower environmental impact. These configurations are OPHI, VRC-HPC β ≠ 1 and VRC-HPC + LPC β ≠ 1.

6. Conclusions

The separation of the maximum-boiling azeotropic mixture water-EDA was performed using pressure-swing distillation. In order to reduce the total annualised cost (TAC), first an optimisation by a genetic algorithm coupled to the flow-sheet simulator was performed, then a reduction of the energy demand was achieved through the application of partial (PHI) and full heat integration (FHI) or vapour recompression (VRC) heat pumps. The optimisation of PHI and FHI was also performed, first by optimising operational variables only, then the geometrical ones, as well. Heat pumps were applied for the high-pressure column (VRC-HPC), for the low-pressure column (VRC-LPC) and for both columns (VRC-HPC + LPC) with considering the possibility of recycling part of the working fluid to the compressor or by-passing the compressor by part of the working fluid.

For the steam and electricity prices used in this study, the lowest TAC is obtained for the optimised (including geometrical variables)

partial heat integration (OPHI), which was by 23.7% lower than that of the optimised non-heat integrated (NHI) process. The second-lowest value of TAC was achieved by optimised (including geometrical variables) FHI, which was by 22.8% lower than that of the optimised NHI.

By optimising the flow rate of the working fluid of the heat pumps, the compressor work, and consequently, the energy demand and TAC were considerably reduced: e.g. by VRC + HPC, TAC was reduced by 16.9% by recycling part of the working fluid to the compressor. With the same prices, the results have shown that VRC-HPC without recycling and VRC-HPC + LPC without recycling and by-pass are not recommended.

In the following step, the influence of the steam and electricity prices on the TAC of each configuration was studied. For the majority of combinations of the prices, OPHI was the most economical configuration. However, VRC-HPC + LPC had the lowest TAC at relatively high steam and low electricity prices. However, equipment prices are estimated values that might vary in a real situation. This uncertainty can affect TAC, and as a result, the price domains, where a certain configuration is the most economical one, might vary, as well.

To perform an environmental evaluation of the different configurations studied, CO<sub>2</sub> emissions and Eco-indicator 99 (EI99) values were calculated. VRC-HPC + LPC with by-pass and recycling has the lowest values compared to all configurations. NHI is not recommended as it has the highest value of CO<sub>2</sub> and EI99. Performing partial and full heat integration decreased CO<sub>2</sub> emissions by 19.5% using PHI and by 20.6% using FHI compared to the optimised NHI. The EI99 value decreased by 20.1% using PHI and by 30.1% using FHI. Although the application of heat pumps is not economical, it is very favourable from an environmental point of view, especially with optimal working fluid flow rate.

To summarise the key findings of the present work: (1) the energy demand, TAC and environmental impact of the separation process studied can be considerably reduced by optimisation and the application of partial heat integration; (2) the application of VRC heat pumps greatly reduces the energy demand and the environmental impact, but it is not economical in this case; (3) the optimisation of the flow rate of the working fluid has the potential to reduce the energy demand and cost of heat pumps considerably. The optimisation of the amount of the working fluid has a general significance for more energy-efficient heat-pump assisted distillation since it is independent of the distillation process in question.

The main limitations of the study, which could be addressed in future research work, are the following ones. The pressures of columns were not included as optimisation parameters, although changing them can lead to further reductions in the energy demand and TAC of the processes studied. It would be worthwhile to study the influence of feed composition, as well. The interplay between economic and environmental aspects could be more thoroughly studied by performing multi-objective optimisation with one or more environmental objective functions.

#### Credit author statement

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

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