A systematic selection and decision matrix for energy-efficient intensified distillation technologies

Li, Q.; Somoza Tornos, A.; Kiss, A.A.

DOI
10.1515/cppm-2024-0035

Publication date
2024

Document Version
Final published version

Published in
Chemical Product and Process Modeling

Citation (APA)
Li, Q., Somoza Tornos, A., & Kiss, A. A. (2024). A systematic selection and decision matrix for energy-efficient intensified distillation technologies. *Chemical Product and Process Modeling*. https://doi.org/10.1515/cppm-2024-0035

Qing Li, Ana Somoza-Tornos and Anton A. Kiss*

A systematic selection and decision matrix for energy-efficient intensified distillation technologies

https://doi.org/10.1515/cppm-2024-0035
Received May 12, 2024; accepted November 21, 2024; published online December 11, 2024

Abstract: Distillation is widely used for fluid separation in chemical industries, but accounts for a half of the operational cost and 40–50 % of the energy usage due to its low energy efficiency. Process intensification could effectively enhance the energy efficiency as well as improve the economic performance of distillation processes by integrating unit operations or functions. However, matching suitable intensified distillation techniques systematically with given separation tasks remains a challenge. This study is the first to generate a conceptual multi-step selection and decision approach by first going through several high level questions with corresponding suggested solutions for a separation task, then identifying the process bottlenecks and intensification targets via a list of evaluation criteria. Each of the technologies goes through a pre-filled process intensification (PI) matrix, and the most promising intensified technologies are recommended, and potential solutions are compared against the task specifications. The PI matrix proposed in this work yields a short list of appropriate solutions to be designed and economically assessed, proposing a screening framework for fluid separations in order to make a rapid selection at an early stage. Several binary, ternary, and multicomponent zeotropic and azeotropic mixture separations are carried out as case studies to illustrate the application of the proposed methodology, being validated using literature data. The proposed methodology can also help reduce the search space before carrying out rigorous optimization for the synthesis and design of the distillation.

Keywords: distillation; process intensification; energy efficiency; process synthesis; process systems engineering

1 Introduction

Separation processes are important operations in chemical industries, but also energy intensive, accounting for approximately 50 % of energy requirements [1]. Among the separation techniques, distillation remains the most widely used separation technology due to its simplicity and effectiveness, taking up 90–95 % of all separation processes and 40–60 % of the energy requirement in the chemical and refining industries [2]. However, because of its relatively low thermal efficiency, rethinking the energy use of distillation processes is essential [3, 4].

Process intensification (PI) technologies are considered to have great potential in reducing the high costs and energy requirements of the separation and purification step, enhancing productivity while improving process safety, reducing waste without sacrificing product quality in chemical industries [5–7]. Advanced distillation technologies based on PI principles in order to reduce the operational costs as well as the capital costs are considered highly competitive in terms of enhancing the energy efficiency and economic performance of distillation columns [4, 8]. It is reported that when introducing PI technologies, in some cases the thermal efficiency of distillation could be comparable to membranes. For example, heat pump assisted distillation might require the power lower than the membranes by a factor of 2–7 [9]. One focus of PI studies is on maximizing driving forces to improve the efficiency of distillation processes. Gani and Bek-Pedersen [10, 11] first developed a

---

***Corresponding author: Anton A. Kiss**, Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, 2629 HZ, Delft, The Netherlands, E-mail: a.a.kiss@tudelft.nl
Qing Li and Ana Somoza-Tornos, Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, 2629 HZ, Delft, The Netherlands. https://orcid.org/0000-0002-4715-204X (A. Somoza-Tornos)

driving-force-based approach for the design and synthesis of distillation systems given the number of stages of the distillation column and the product purity requirements, and further applied their driving-force-based method to the reactive distillation system [12], cyclic distillation [13], and bioprocess intensification [14]. There were also numerical approaches developed with the focus on applying a specific intensified distillation technology to a specific application. For example, a pilot-scale cyclic distillation was studied for ethanol/water separation and was compared to an existing industrial beer column used to concentrate ethanol, and about 30 % energy savings could be achieved as compared with the classic distillation process [15]. A review of internally heat-integrated distillation columns (HIDiC) reports case studies in which HIDiC was applied to reduce energy requirements of the processes, for example, 2-ethylbenzene/styrene separation, acetic acid dehydration, and methanol/water separation [16]. Another review focussed on the application of dividing wall columns in chemical industry [17]. However, no previous study looks at the selection of the PI technologies from a broader perspective, but focuses on the choice of specific intensification technologies on specific separation systems, without having a systematic method for finding out which typical characteristics led to which specific intensified solutions to enhance the process energy efficiency, which means that the above-mentioned methods also require the users to have extensive knowledge and experience in this field.

In order to develop more general methodologies to find the intensification possibilities in a process, Gooty et al. [18] proposed a mixed-integer nonlinear programming (MINLP)-based solution approach that identifies the promising energy-efficient distillation configuration sequence for a given separation. Baldea [19] presented a pinch-like targeting framework to systematically identify process intensification opportunities for a process flowsheet. In this approach, when three (or more) units are chosen to be combined, a thermal process intensification can take place in a single intensified device combining two or more heat sources and heat sinks, possibly along with a thermal utility stream. However, this method is still at an early conceptual design stage, with the assumption that the temperatures of heat sinks and heat sources are constant. Other groups carried out research to identify, generate and evaluate PI options at the flowsheet level: Lutze et al. [6] proposed a 6-step computer-aided decomposition approach with over 50 sub-steps to systematically find PI opportunities for a defined problem based on a model-based framework developed by Gernaey and Gani [20]. Later, they produced a similar study on synthesis processes incorporating PI but focussed more on phenomena-based design [21] – a database of phenomena was generated and combined to form phenomena building blocks, from which phenomena-based flowsheets are generated by a series of screening steps and connection rules. Demirel et al. [22, 23] used building blocks to represent fundamental phenomena where assembly of different types of blocks result in an intensified unit. However, these studies centred on the combination of reactors, separators and recycle systems including PI techniques were carried out using their software with a specific database which is not open access to all general users. Also since their focus was more about the overall flowsheet, the separation was not explored in detail and provided no systematic approach to designing the intensification of the separation processes in detail.

Therefore, developing a decision tool for the choice of best-available technologies from a holistic viewpoint of the overall separation process is important. Commenge and Falk [24] proposed a pre-filled connection matrix for a set of intensification strategies to match the intensified solutions with the process bottlenecks, which yielded a shortlist of technically designed appropriate solutions. However, this matrix is only applicable to reaction systems not to separation systems. Plesu et al. [25] developed a shortcut assessment of alternative distillation sequence schemes for process intensification, generating a quantitative criteria so-called *distillation sequence energy efficiency* to score and rank each distillation column configuration possibility based on feed composition and products boiling points before designing any processes, providing a shortcut assessment of alternative distillation sequences for both zeotropic and azeotropic mixtures. Process intensification opportunities are recommended if the product of column efficiency is low. Their work is a good starting point for the fast screening of the separation efficiency, but the advanced distillation techniques are not involved and need to be further explored. Our previous work showed a fast screening method to synthesize and design heat integrated and non-heat integrated distillation sequences by process optimization for multicomponent mixture separation, allowing the change of several operation variables [26]. However, only dividing wall columns and thermally coupled complex column configurations are involved in this research, and also screening the full search space is computationally challenging [27] and developing an approach to reduce the vast search space (and thus computational time) is also important.

Overall, two research gaps are identified: (1) there is no clear basis to identify the promising intensification technologies especially in the early stages when numerous processing options need to be rapidly evaluated; (2) there is no systematic method to identify the attractive sequences and intensification technologies before doing any detailed designs.

Invited for this special issue of CPPM, this original work aims to address this decision-making problem, and match suitable intensified distillation techniques with the separation tasks. This is done by developing a knowledge-based methodology that provides a list of most promising intensified distillation techniques for given separation tasks via a novel PI matrix based on the same set of high-level questions and evaluation criteria. The PI matrix proposed in this work yields a short list of appropriate solutions to be designed and economically assessed, proposing a screening framework for separating binary and ternary mixtures in order to make a rapid selection at an early stage, applying to both ideal and non-ideal separation systems. A few case studies are carried out to illustrate the application of the proposed methodology. The proposed methodology can also help reduce the search space before carrying out rigorous optimization for the synthesis and design of the distillation, as once the search region is narrowed, methods with more detailed considerations can be applied.

2 Problem statement

The implementation of promising intensified distillation techniques among possibilities (i.e., heat pump assisted distillation (HPAD), heat integrated distillation (HIDiC), membrane assisted distillation, high gravity (HiGee) distillation, cyclic distillation (CyDist), thermally coupled distillation systems (TCD), dividing wall column (DWC), extractive distillation and azeotropic distillation) would have the potential to replace conventional energy-intensive technologies, yet is also challenging for given tasks (e.g., variety of mixtures, a wide range of feed flowrates and concentrations, and different products purities). It is unclear which PI technologies are more suitable for different types of processes, and screening PI opportunities for process design is challenging. This work starts from the separation of binary and ternary zeotropes and azeotropes, develops a decision matrix based on several criteria, to select promising intensified distillation technologies before carrying out detailed process design or optimization, based on the different separation bottlenecks and intensified targets, aiming to provide a general user-friendly and easy-to-understand selection method.

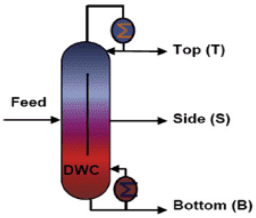
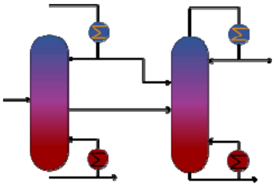
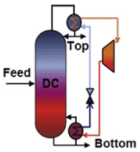
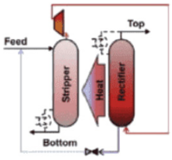
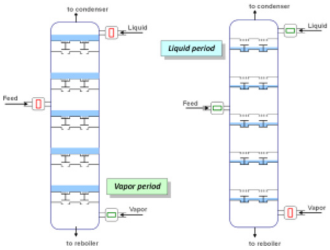
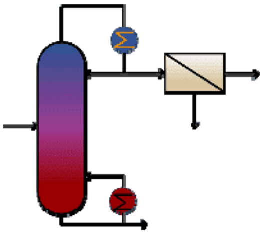
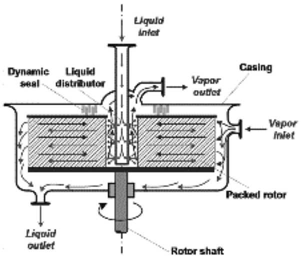
3 Methodology

In this section, the developed methodology is demonstrated in detail. Section 3.1 lists all the intensified distillation technologies covered in this study, and also the potential benefits of using these technologies. However, every technology has its drawbacks, which is the reason why it is necessary to choose the right technology for different separation systems. Therefore the advantages and disadvantages of each technology are listed as well in this section. Section 3.2, 3.3 and 3.4 explain individually in detail the distillation sequence efficiency, high-level questions and the potential solutions, as well as the PI matrix. After these, Section 3.5 summarizes the overall approach, and a flowsheet of the methodology is proposed.

3.1 Overview of intensified distillation technologies

Intensified distillation technologies have the potential to enhance the process performance in terms of energy requirement and capital cost reduction. However, each technology has its advantages and disadvantages. Table 1 lists seven intensified distillation techniques considered in this study, including intensification targets, features, and the summarized main key advantages and disadvantages of each technology [3, 28]. Some technologies (e.g.,

Table 1: Features and performances of intensified distillation technologies.

Type	Key feature	Remarks on design and performance
Ternary		**Dividing wall column (DWC)** + Low re-mixing effects + Highly purified side products + CAPEX reduction (>25 %) + Reduced energy demands (20–40 %) - Fewer degrees of freedom on pressure - Complex column structure and control
Ternary		**Thermally coupled distillation (TCD)** + Low re-mixing effects + Highly purified side products + Reduced energy demands - Operation complexity - Complex control
Binary		**Heat pumps assisted distillation (HPAD)** + Upgrading energy level + Reduced energy demands (40–80 %) - High CapEx of large heat pumps - High CapEx of large temperature lifts
Binary		**Heat integrated distillation columns (HIDiC)** + High energy savings (60–90 %) - Vacuum column not applicable - Operation and design complexity - Complex integrated process and control
Binary		**Cyclic distillation (CyDist)** + No liquid remixing or flooding on the stage + High product purities + High mass transfer efficiency + Reduced energy demands (~35 %) + Adjustable residence time - Operation complexity - Vacuum operation not applicable - Complex column structure and control
Binary/Ternary		**Membrane assisted distillation (MAD)** + Size reduction + Reduced energy demands + Facilitated separation process + Enhanced product purities - Higher equipment cost - Membrane limitations (short lifetime)
Binary		**HiGee** + High mass transfer efficiency + Reduced energy demands + Size reduction (6–8 times) - Difficult to scale up (use numbering up) - Rotational device needing more energy - Aversion to long-periodic operation

cyclic distillation, HiGee) might be less well known than others, but they are all applied at industrial scale (TRL9). The readers are guided to relevant review papers for more information about cyclic distillation [29] or HiGee distillation [30, 31]. Binary and ternary separations are defined based on the number of products instead of the number of components.

3.2 Distillation sequence efficiency

Distillation sequence efficiency (DSE) is a parameter used to evaluate the energy efficiency of each alternative distillation sequence [25]. It enables advantages derived from process intensification for a given feed composition to be quantified, and does not rely on heuristics. Equations (1) and (2) illustrate the calculation of the DSE value.

$$\eta = \frac{T_B - T_D}{T_B} \tag{1}$$

$$DSE = \sum_{i=1}^{O} \left(X_i \prod_{C=1}^{N} \eta_C \right) \tag{2}$$

where η denotes Carnot efficiency, T_B is the temperature (Kelvin) of the bottom product (reboiler), T_D is the temperature (in K) of the distillate product (condenser). x_i is the liquid composition of component i, C represents distillation columns.

The higher the DSE number, the higher the efficiency of the distillation sequence; while the lower the DSE number, the more advisable process intensification technologies are. Therefore it is a useful tool to gain an idea of the energy efficiency of the process, and whether there is intensification potential for the process.

To evaluate the reliability of this criteria, we calculated the DSE for the optimization results from our previous work [26] about the zeotropic multicomponent C2–C5+ separation using simple columns, and apply the DSE calculation on these 14 possible sequences. As shown in Figure 1, the optimization results show that sequences S1, S2, S4, S6, S7 are the most economically attractive sequence family in terms of total operating cost, followed by S5 and S3 - the direct sequences are more energy efficient in this case. Based on the DSE numbers calculated for the 14 sequences, the above-mentioned sequences are all pre-selected within the first sequence family (S1, S2, S3, S4, S5, S6, S7), with a clear gap compared to the rest of the sequences in terms of DSE numbers. Note that the fast calculation is a simplified screening criteria assuming that the products are at 100 % purity and recovery, and the change of operating conditions for example column pressures are not considered, yet it requires only the feed composition and their normal boiling points which are very simple to use. Therefore, helping reduce the second half of the design or search space (S8–S14) safely by calculating the DSE numbers dramatically saves on design and computational input, and showing that the DSE numbers is a reliable pre-selection tool.

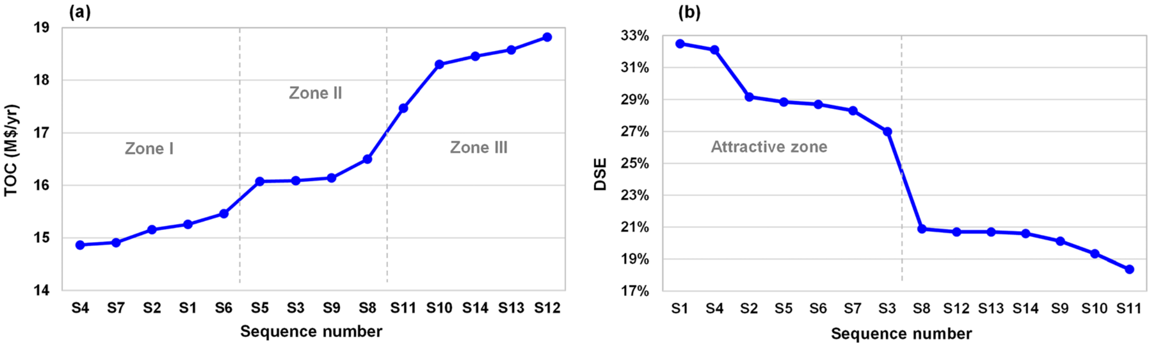


Figure 1: DSE evaluation based on the optimization results (a) Li et al. [26], and (b) DSE calculation.

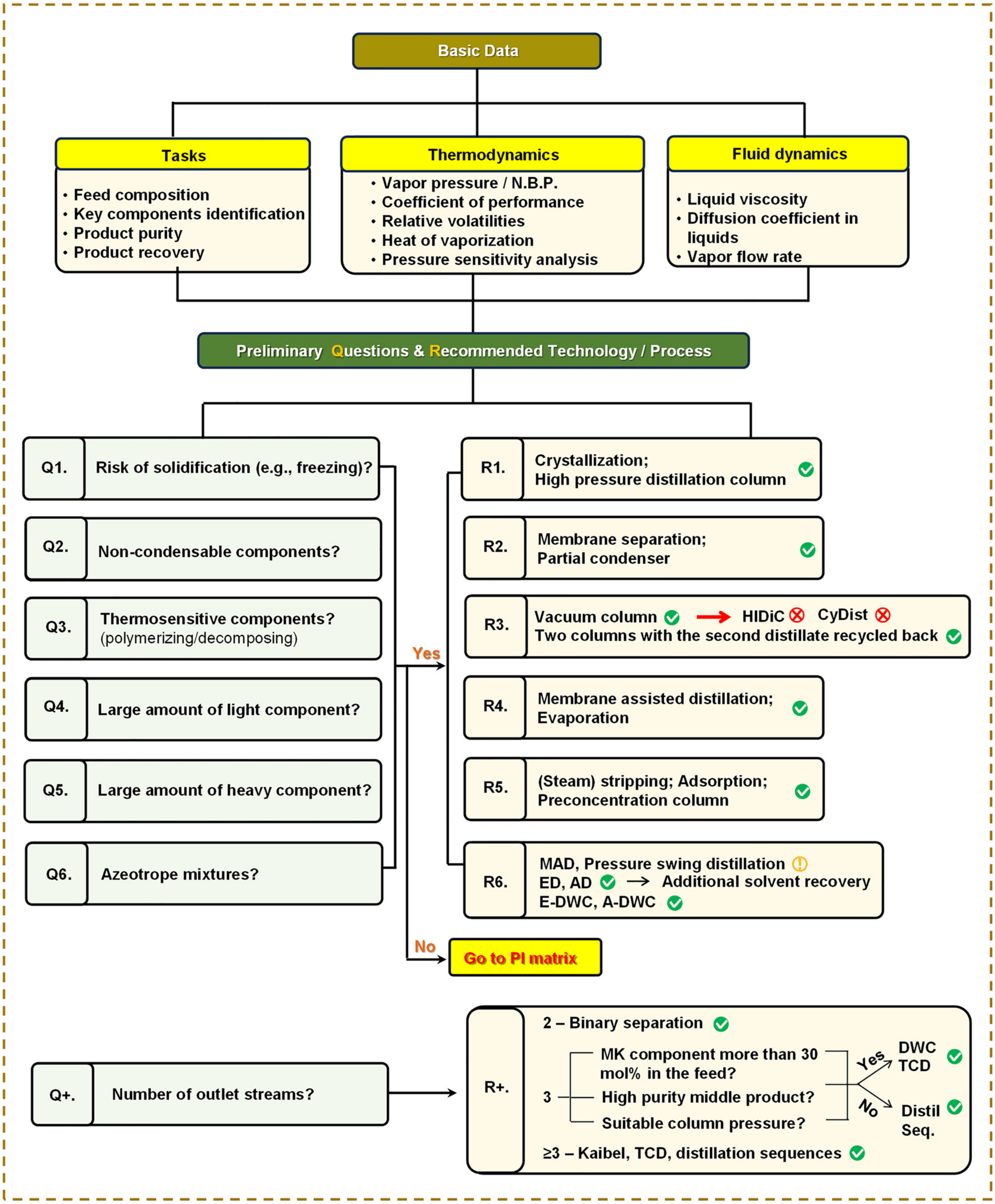


Figure 2: High-level questions and potential solutions.

3.3 High-level questions and potential solutions

Before evaluating process intensification possibilities, the limitations of the processes need to be identified. In addition to the restrictions of phase equilibrium (e.g., low relative volatility) or mass transfer (high viscosity), six high-level questions are made to identify the special components in the separation which might make the separation difficult, as shown in Figure 2, and six corresponding solutions are provided in order to overcome the separation difficulties. This step is performed prior to using the process intensification (PI) matrix.

Q1: Are there any components at risk of solidification (e.g., freezing) during the separation? If so, high pressure distillation column is needed in order to increase the temperature of the column to avoid the solidification. In this case crystallization is also a good choice for this separation as compared to distillation if the solidification temperature is higher than the standard room temperature, as no cooling will be needed.

Q2: Are there any non-condensable components? Condensing (near) non-condensable components results in low condenser temperature, which may require refrigerant as the cooling utility. Partial condensers could be used to enable the non-condensable components to be removed in the vapor phase without being condensed. Non-condensable gases can be separated by membrane separation.

Q3: Are there any thermo-sensitive components, e.g., thermal denaturation, polymerizing or decomposing? Vacuum column is suggested for the separation of thermo-sensitive components in order to lower the temperature of the column. Alternatively, two-column configurations can be applied. The feed is fed into a normal pressure column to separate the non-thermo-sensitive component, and the thermos-sensitive component is fed into the second column which in this case is a smaller vacuum column, and the second distillate can be recycled back to the feed of the first column.

Q4: Is there a large amount of light component in the feed? Evaporation of a large amount of the light component results in high reboiler duties in the column, therefore, separating the light component by membranes before feeding the mixture into the column can reduce the energy requirement. Evaporation can also be used to replace distillation when there is a large amount of light component in the feed.

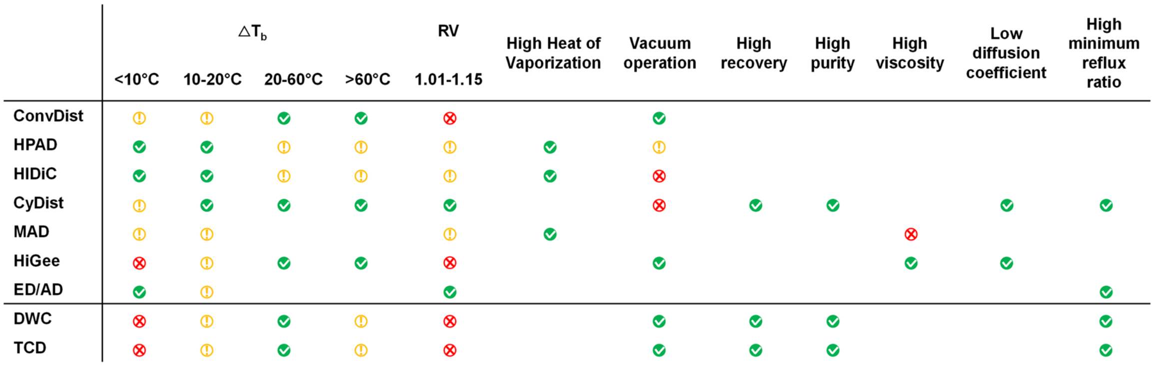
Q5: Is there a large amount of heavy component in the feed? Similarly, condensing a large amount of heavy component results in high condenser duties of the column. (Steam) stripping, adsorption or preconcentration columns can be used in this case.

Q6: Are there any azeotropic mixtures in the feed? Azeotropes need to be identified before process design or intensification. If it is a heterogenous azeotrope, a heterogeneous azeotropic distillation configuration can be applied. If it is a homogeneous azeotrope, membrane separation can be considered. If the azeotrope is pressure sensitive, pressure swing distillation can be used to separate the azeotrope effectively. By adding additional solvent, extractive distillation or azeotropic distillation can be used for separating homogeneous azeotropes, and additional solvent recovery is needed.

Q7: The number of outlet streams need to be identified beforehand. DWC, thermal coupled distillation columns, and distillation sequences are typically used for ternary or multicomponent mixture separations. Whereas other technologies (e.g., cyclic distillation, HiGee) are more commonly applied to binary separations.

3.4 Process intensification matrix

After identifying all special components by going through the high-level questions, a PI matrix has been developed to find out the intensification potentials of the separation system, and to match different intensified distillation technologies based on the evaluation criteria defined in this study, as shown in Figure 3. The columns represent the intensified distillation technologies, and the rows list the criteria relevant to phase equilibrium and mass transfer limitation of a separation task:



	$\triangle T_b$				RV	High Heat of Vaporization	Vacuum operation	High recovery	High purity	High viscosity	Low diffusion coefficient	High minimum reflux ratio
	<10°C	10-20°C	20-60°C	>60°C	1.01-1.15							
ConvDist	!	!	✓	✓	⊗		✓					
HPAD	✓	✓	!	!	!	✓	!					
HIDiC	✓	✓	!	!	!	✓	⊗					
CyDist	!	✓	✓	✓	✓		⊗	✓	✓		✓	✓
MAD	!	!			!	✓				⊗		
HiGee	⊗	!	✓	✓	⊗		✓			✓	✓	
ED/AD	✓	!			✓							✓
DWC	⊗	!	✓	!	⊗		✓	✓	✓			✓
TCD	⊗	!	✓	!	⊗		✓	✓	✓			✓

Figure 3: Process intensification matrix for advanced distillation technologies.

- *Phase equilibrium limitation identification:* separations are categorized as azeotropic mixture and very close boiling point mixture separation (ΔTb≤10 °C); close boiling point mixture separation (10 °C<ΔTb<20 °C); and (near)ideal mixture separation (ΔTb≥20 °C) based on the normal boiling point difference (ΔTb) and relative volatilities (RV). High minimum reflux ratio, high heat of vaporization, high recovery or high purity products can also lead to high energy requirements even for (near-)ideal mixture separations.
- *Mass transfer limitation identification:* Mass transfer could be limited by high viscosity (dimensionless correlating to Reynolds number), which causes difficulties by creating turbulence and achieving high gas/liquid interface; low liquid phase diffusion coefficient leads to inefficient vapor liquid mass transfer.

In addition to the above mentioned criteria, vacuum operation is also an important criterion to be considered, as for example, it is very widely used in the separation of biochemicals.

These criteria are presented in an intensification matrix for advanced distillation technologies. The check mark indicates the specific technology is recommended when meeting the criteria; the exclamation mark represents the technologies which can be considered, but furthers are needed; while a cross mark represents technologies not suitable for use, according to that specific criterion. No mark indicates that the criteria is not relevant to the decision of the specific technology. Taking the first column as an example, if ΔTb≤10 °C, conventional column could be used to achieve the separation requirement, however, high reflux ratio and energy requirements might result. HPAD and HIDiC are recommended, because the temperature lift between the top and the bottom of the column in this case will be small, cyclic distillation is not applicable in this case because the pressure drop will be too large if cyclic distillation is used for very difficult separations (ΔTb≤10 °C). All the marks for the matrix are pre-filled and for a separation task the users need to go through the intensified technologies (row by row) to find the right recommendations. Taking the first row as an example, HPAD is highly recommended if ΔTb is lower than 10 °C or is between 10 °C and 20 °C, or if there is a component with high heat of vaporization to be separated. If ΔTb is higher than 20 °C, further of the coefficient of performance (COP) of heat pumps is needed for HPAD. For low relative volatilities (between 1.01 and 1.15), the mixture could have close boiling points (e.g., 50 °C and 55 °C) when the temperature is not very high, and HPAD is not applicable in this case, or there might be still over 20 °C difference in boiling points (e.g., 200 °C and 220 °C), which HPAD is applicable. So, further checks are needed if the mixture has low relative volatility. For vacuum operation conditions, different heat pump configurations can be considered [3]. The rest of the criteria are not relevant to the decision making of HPAD.

With this intensification matrix, both the relevance (i.e., whether the criteria have an influence on the selection of a specific technique), and recommendations of the PI techniques are suggested.

3.5 Description of the overall approach

The overall approach of the decision making procedure is illustrated in Figure 4. For binary separations, high level questions are considered first in order to find the special components which may cause high energy requirements of the separation. Three sets of data are first extracted from the separation task, including the basis of the tasks, thermodynamics data and fluid dynamics data. The basic data shows the feed composition, key components and separation requirements; thermodynamic data includes the vapor pressure of each component, relative volatilities, heat of vaporization and the pressure sensitivity analysis (via y-x diagram) for the separation mixture; and fluid dynamics includes the liquid viscosity, diffusion coefficient in liquids, and the estimated vapor flow rate if needed. As discussed before, there are seven high-level questions to go through. If the answer to any of the questions is YES, the suggested separation technologies are provided accordingly, until the answer to all of the questions is NO, then go to the next step to the PI matrix.

For ternary and multicomponent mixture separations, DSE evaluation is carried out first for the prescreening of the distillation sequence alternatives. The intermediate results (i.e., η values) provide additional useful information. For instance, the Carnot efficiency of each column indicates when a heat pump or enhanced distillation would be useful. The recovery efficiency for each particular compound allows an easy comparison

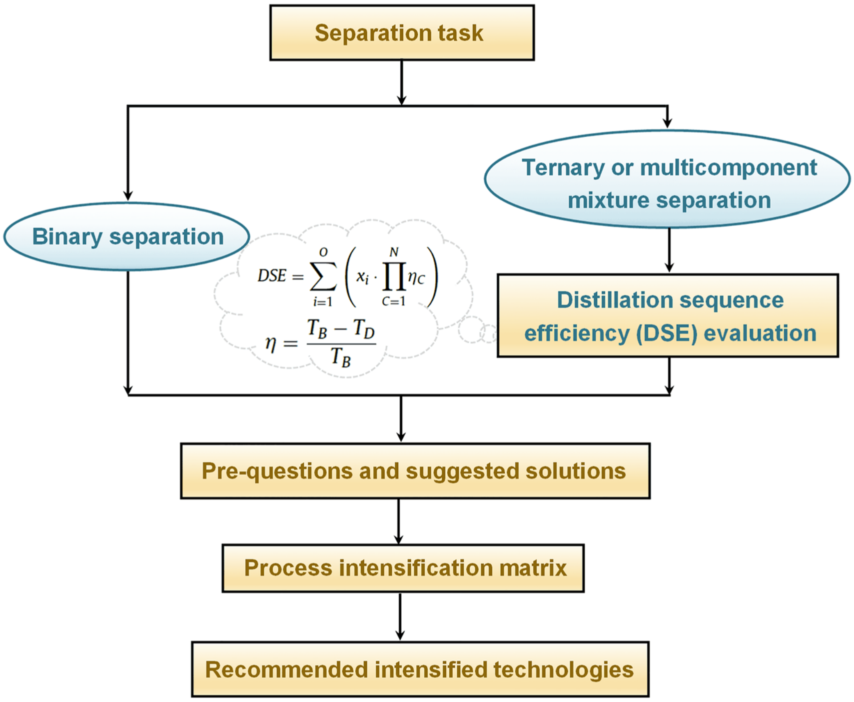


Figure 4: Fast-screening approach for the intensified distillation processes.

between alternatives, considering variations in the feed composition. After the DSE evaluation, the procedure is then the same as for binary separation. Finally, the recommended PI technologies are listed and further design and intensification can be carried out based on the recommendations.

Overall, this methodology consists of analyzing the given separation task in terms of selection criteria (e.g., volatile difference between key components, the type of separation tasks, feed and product flow, product specifications at different target purity levels, operating pressure, reboiler duty and its temperature level, reflux ratio, heat of vaporization). Subsequently, the methodology relates the selection criteria to process bottlenecks and promising intensified distillation techniques, through a connection matrix, to effectively address the identified bottlenecks. Finally, potential solutions are compared against the task specifications.

4 Case studies

Four case studies of industrial relevance are used to demonstrate the application of our new approach: a non-ideal zeotropic binary separation (methanol/water), an azeotropic binary separation (ethanol/water; acetonitrile/water), and a ternary mixture (benzene/toluene/xylene).

4.1 Binary zeotropic mixtures separation – methanol/water

Methanol-water separation is a large scale separation with the capacity of 1,100 ktpy feed. Feed consists of 69.81 mol% methanol and 30.19 mol% water [32], normal boiling point (N.B.P.) difference of 35.5 °C (N.B.P water 100 °C, methanol 64.5 °C), relative volatility (RV) is 2.98, heat of vaporization of methanol 1,273.4 kJ/kg and water 2,265.6 kJ/kg. The desired methanol product purity is 99.99 mol%, with a 99.98 % recovery, requiring a minimum reflux ratio (RRmin) of 0.87 (under atmospheric pressure).

4.2 Binary azeotropic mixtures separation – (1) ethanol/water, (2) acetonitrile/water

The ethanol/water separation is needed when producing food grade alcohol or producing hydrated ethyl alcohol fuel. For example, when producing hydrated ethyl alcohol fuel, the capacity of the design is 700,000 l/day of hydrated ethyl alcohol fuel, with a minimum top concentration of 92.6 wt% ethanol from an initial ethanol/water mixture of 8 wt% ethanol. Binary azeotrope (95.63 wt % ethanol) can also be formed between ethanol and water. The normal boiling point difference of ethanol and water is 22 °C. Heat of vaporization of ethanol 851.1 kJ/kg and water 2,265.6 kJ/kg.

Acetonitrile (ACN) recovery from wastewater is an important process, as ACN is an essential solvent in the pharmaceutical industry with an excellent ability to dissolve a wide range of chemicals and its strong C–C bonding makes it difficult to hydrolyze for use as a reaction solvent. The widely investigated waste ACN effluent contains 500 kmol/h feed, with the composition of 20 mol% ACN and 80 mol% water. The product specifications of ACN and water are set at 99.9 mol%. Acetonitrile and water forms an azeotropic mixture having a boiling point of 76.5 °C and containing about 82.2 wt % ACN at atmospheric pressure.

4.3 Ternary zeotropic mixtures separation – benzene (B)/toluene (T)/xylene (X)

For the near ideal mixture separation of BTX, the feed consists of 33.3 mol% benzene, 33.4 mol% toluene and 33.3 mol% m-xylene [33], $\Delta Tb = 59.0$ °C (N.B.P.: benzene 80.1 °C; toluene 110.7 °C and xylene 138.4 °C), $RV_{B/T}=2.39$, $RV_{T/X}=2.19$. Heat of vaporization: benzene 395.9 kJ/kg; toluene 365.1 kJ/kg; xylene 347.0 kJ/kg. The purities of BTX products are 99.0 mol%, and the recoveries are 99.8 %, 98.0 %, and 99.1 %, respectively. The RRmin of B/TX separation is ~1.90, and 1.92 for T/X separation. The viscosity values (expressed in cP at 20 °C) are 0.652, 0.590 and 0.620, respectively.

5 Results and discussion

5.1 Binary zeotropic mixtures separation – methanol/water

As indicated in Figure 4, this binary separation goes to the pre-question step. As for methanol water separation, there is no risk of solidification, non-condensable components or thermosensitive components, the ratio of the amount of light component and heavy component in this case is not large, and no azeotropes are formed. The next step is to go to the PI matrix. The boiling point difference is within the range of 20–60 °C, conventional distillation column is applicable, the application of HPAD and HIDiC requires a further of the COP, while cyclic distillation and HiGee distillation are recommended. Water has high heat of vaporization, therefore HPAD, HIDiC and membrane assisted distillation are recommended. Methanol products require high purity, so cyclic distillation is recommended.

These steps are summarized in Figure 5. In summary, conventional distillation columns can achieve the separation target of this task, yet the energy requirement is not optimized. As for the intensification techniques, bying the COP, heat pumps and HIDiC (an internally heat integrated distillation column) are recommended for methanol/water separation, while cyclic distillation and membrane assisted distillation are also promising. These recommendations are also in line with the reports from literature on different intensification techniques for the separation of methanol/water, e.g., HPAD [32], MAD [34], and cyclic distillation [35]. However, note that although HiGee distillation is also recommended and there is research supporting this [36], HiGee is limited by the difficulty of manufacturing large-size high-speed rotators. The annual production capacity per HiGee unit is usually smaller than 10 ktons, and in practice the annual production capacity is less than 5 ktons in most cases [31].

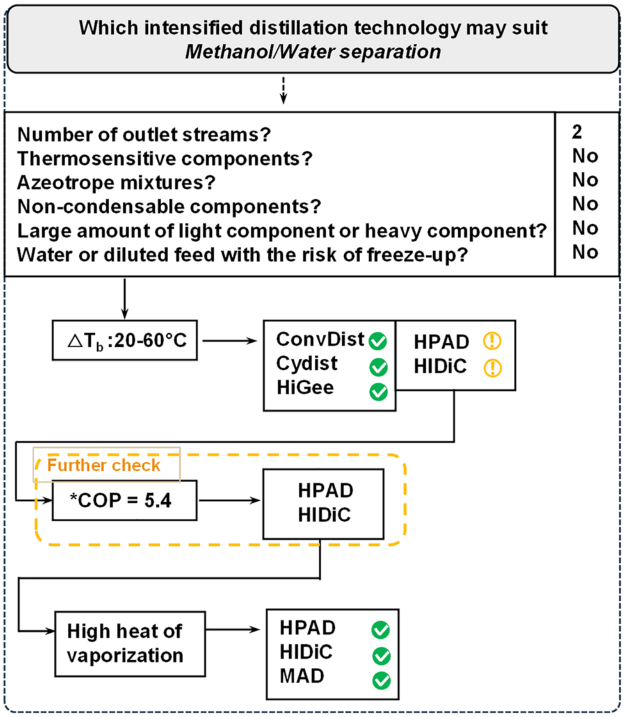


Figure 5: Case study on the methanol/water separation.

5.2 Binary azeotropic mixtures separation – (1) ethanol/water, (2) acetonitrile/water

For ethanol/water separation, there is a binary azeotrope (95.63 wt % ethanol) that must be taken into account. For Q6, the answer is yes, thus membrane separation, extractive distillation, azeotropic distillation and pressure swing distillation could possibly break the azeotrope. However, based on the y-x diagram, ethanol-water is not a pressure sensitive mixture, so pressure swing distillation is not recommended in this case. Due to the additional solvent that may be needed (leading to a ternary system) E-DWC and A-DWC are also recommended. HPAD and HIDiC can also be considered upon furthers, as using different entrainers lead to different temperatures thus the COP is different. Luo et al. [37] and Ponce et al. [38] reported two designs of using HPAD and HIDiC for separating ethanol and water.

For acetonitrile/water separation, assume that the industrial wastewater contains 20 mol% ACN. According to Q5 and R5, a preconcentration column is first needed to remove part of the large amount of water as heavy component. Figure 6 illustrates the use of the developed methodology. Acetonitrile and water forms an azeotropic mixture having a boiling point of 76.5 °C and containing approximately 82.2 wt% acetonitrile under atmospheric pressure. PSD, MAD, ED are recommended for acetonitrile/water separation, and HPAD could be applied, while the detailed configuration needs to beed based on the specific temperature lift. According to Liu et al. [39]; molecular sieve membrane assisted distillation is built for a 10 kt/a acetonitrile separation plant in Shandong Huihai Company, China. Zhai et al. [40] developed a heat-pump assisted extractive-azeotropic dividing wall column (DWC) for the acetonitrile/water separation.

5.3 Ternary zeotropic mixtures separation – benzene (B)/toluene (T)/xylene (X)

Since this is a ternary separation, DSE evaluation is carried out first. Figure 7 shows the η of each stream calculated based on equation (1), and the DSE is over 35 % which means that the separation is relatively easy. The DSE for direct sequence (38.33 %) is higher than that of indirect sequence (37.42 %), meaning that direct sequence is more favorable than indirect sequence for the BTX separation.

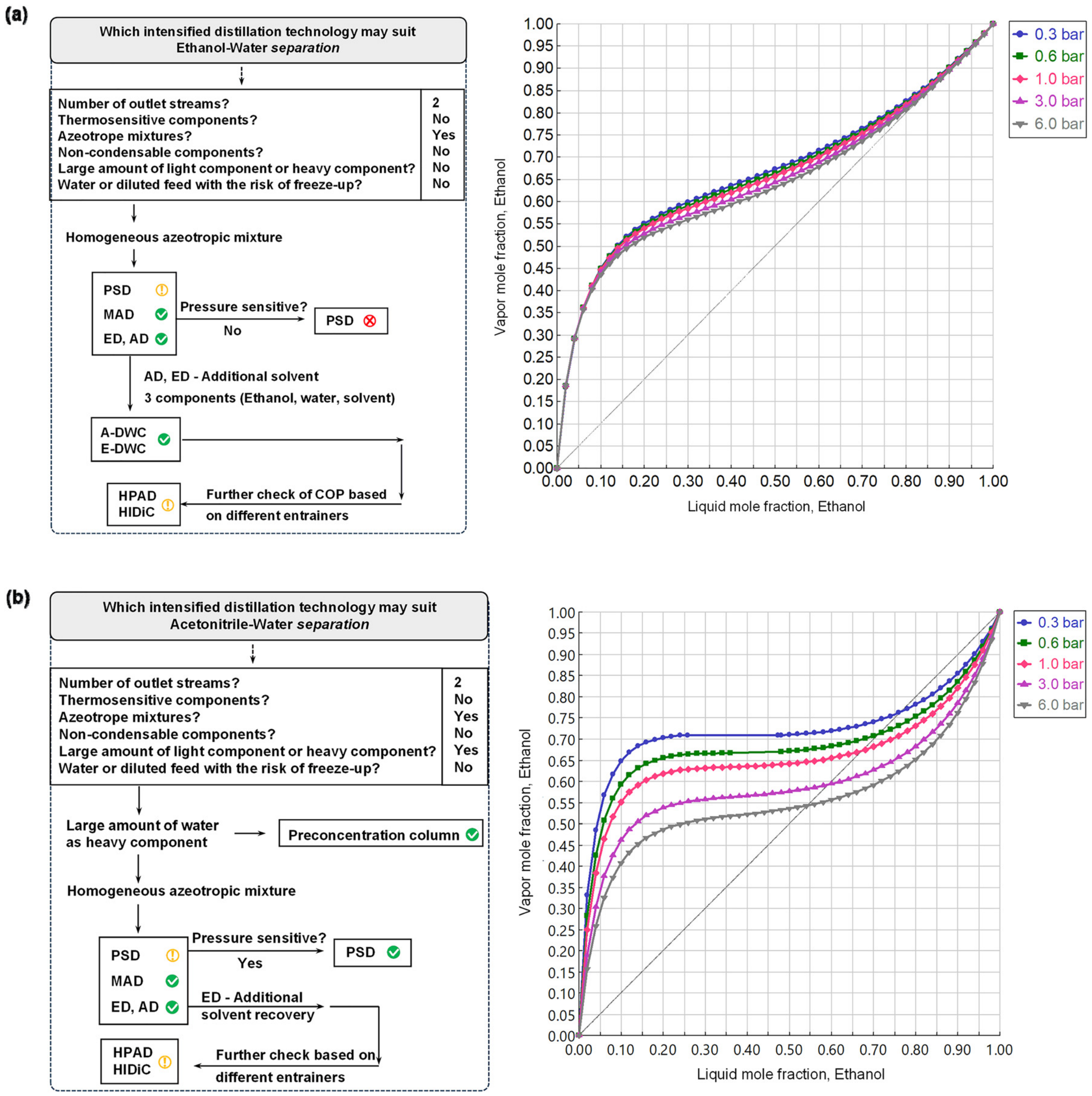


Figure 6: Case studies on (a) ethanol/water and (b) acetonitrile/water separation.

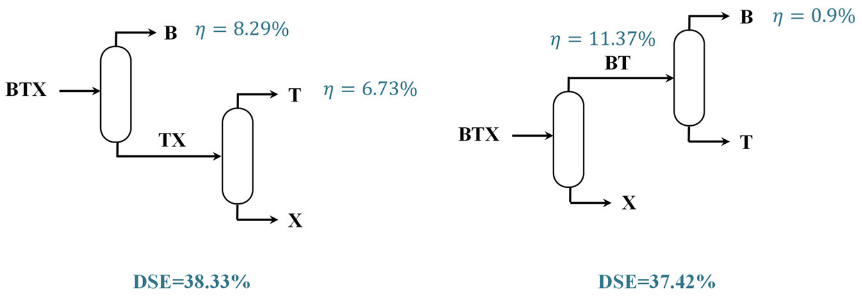


Figure 7: DSE evaluation of direct sequence (left) and indirect sequence (right).

The next steps go to high-level questions and the PI matrix, Figure 8 shows the results for the BTX separation. According to the evaluation procedure, the use of dividing wall column is recommended for BTX separation, and bying the coefficient of performance, heat pumps could also be applied additionally or

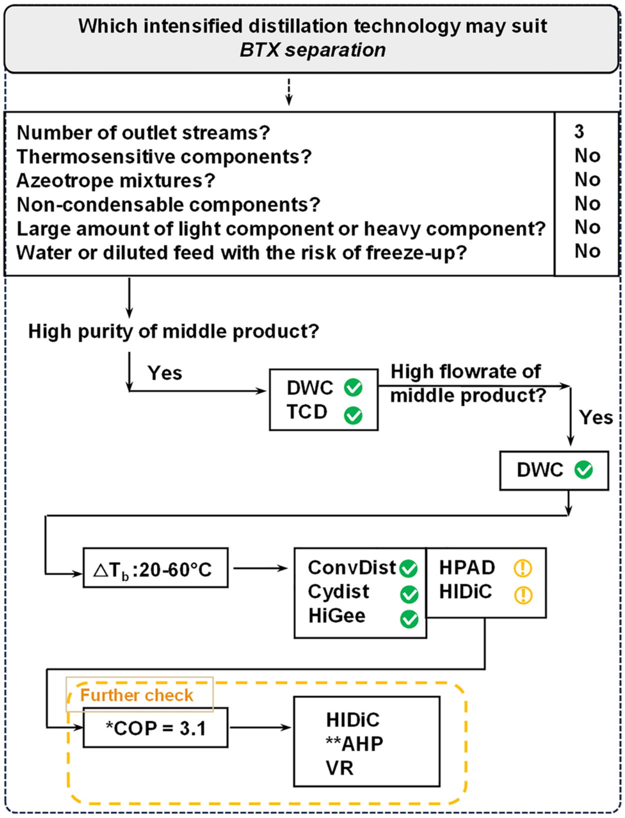


Figure 8: Case study on the benzene/toluene/xylene separation. Note: *Assume compressor efficiency 0.7, minimum temperature difference 5 °C, pressure drop 50 kPa. **AHP, absorption heat pump; VR, vapor recompression.

alternatively. These recommendations are supported with the studies on DWC [33], HIDiC [41], and heat pump assisted DWC [42].

6 Conclusions

This work proposed and successfully validated a new decision making framework, matching promising intensified distillation technologies for specific fluid separation tasks at an early stage. This methodology consisting of high-level questions and process intensification matrix, and the features and performances of intensified distillation technologies were assessed and exploited to support the intensification matrix, allowing for rapid and reliable selections of the most promising distillation techniques. A short list of promising technologies is obtained as outcome of the developed methodology.

Four industrially relevant case studies including binary and ternary zeotropic and azeotropic mixtures successfully demonstrate the use of the proposed methodology. The list of the promising intensification technologies gained from the developed approach are approved by the PI techniques reported in the literature, yet without carrying out any simulations or designs. Therefore, this methodology contributes to integrate a wide range of evaluation criteria, provide a basis for the selection of technologies at an early design stage. This screening can also act as a decision making tool in the pre-selection step for synthesis or optimization methodologies to help dramatically reduce the search space.

Further research should be carried out to understand the interplay of intensification technologies and the degrees of freedom of distillation sequences for multicomponent mixture separations. Heat integration criteria is a good point to be considered at this early design stage, to get an idea of what is the energy saving potential for each process, although the detailed heat exchanger network can be carried out later after the design. Other criteria, for example, separation driving force could be considered so that more separation technologies can be included in the PI matrix (e.g., decanter, membrane, absorption), and sustainability metrics can also be integrated into the matrix in order to evaluate the sustainability of the processes.

Research ethics: Not applicable.
Informed consent: Not applicable.
Author contributions: Qing Li: Conceptualization, Methodology, Software, Data Curation, Validation, Visualization, Writing - Original Draft, Writing - Review & Editing. Ana Somoza-Tornos: Conceptualization, Methodology, Formal analysis, Validation, Supervision, Writing - Review & Editing. Anton A. Kiss: Conceptualization, Methodology, Formal analysis, Investigation, Resources, Validation, Supervision, Project administration, Writing - Original Draft, Writing - Review & Editing.
Use of Large Language Models, AI and Machine Learning Tools: None declared.
Conflict of interests: The authors state no conflict of interest.
Research funding: None declared.
Data availability: The data supporting this article can be obtained on reasonable request from the corresponding author.

References

1. Blahušiak M, Kiss AA, Babic K, Kersten SR, Bargeman G, Schuur B. Insights into the selection and design of fluid separation processes. Sep Purif Technol 2018;194:301–18.
2. Kong ZY, Sánchez-Ramírez E, Yang A, Shen W, Segovia-Hernández JG, Sunarso J. Process intensification from conventional to advanced distillations: past, present, and future. Chem Eng Res Des 2022;188:378–92.
3. Kiss AA. Distillation technology still young and full of breakthrough opportunities. J Chem Tech Biotechnol 2014;89:479–98.
4. Kiss AA, Smith R. Rethinking energy use in distillation processes for a more sustainable chemical industry. Energy 2020;203:117788.
5. Abdulrahman I, Máša V, Teng SY. Process intensification in the oil and gas industry: a technological framework. Chem Eng Process 2021; 159:108208.
6. Lutze P, Román-Martinez A, Woodley JM, Gani R. A systematic synthesis and design methodology to achieve process intensification in (bio) chemical processes. Comput Chem Eng 2012;36:189–207.
7. Tian Y, Demirel SE, Hasan MF, Pistikopoulos EN. An overview of process systems engineering approaches for process intensification: state of the art. Chem Eng Proc 2018;133:160–210.
8. Skiborowski M. Process synthesis and design methods for process intensification. Curr Opin Chem Eng 2018;22:216–25.
9. Chavez Velasco JA, Tawarmalani M, Agrawal R. Which separation scenarios are advantageous for membranes or distillations? AIChE J 2022;68:17839.
10. Bek-Pedersen E, Gani R. Design and synthesis of distillation systems using a driving-force-based approach. Chem Eng Process: Process Intensif 2004;43:251–62.
11. Gani R, Bek-Pedersen E. Simple new algorithm for distillation column design. AIChE J 2000;46:1271–4.
12. Mansouri SS, Huusom JK, Gani R, Sales-Cruz M. Systematic integrated process design and control of binary element reactive distillation processes. AIChE J 2016;62:3137–54.
13. Nielsen RF, Huusom JK, Abildskov J. Driving force based design of cyclic distillation. Ind Eng Chem Res 2017;56:10833–44.
14. Van der Wielen LA, Mussatto SI, van Breugel J. Bioprocess intensification: cases that (don't) work. New Biotechnol 2021;61:108–15.
15. Maleta BV, Shevchenko A, Bedryk O, Kiss AA. Pilot-scale studies of process intensification by cyclic distillation. AIChE J 2015;61:2581–91.
16. Kiss AA, Olujić Ž. A review on process intensification in internally heat-integrated distillation columns. Chem Eng Process 2014;86:125–44.
17. Yildirim Ö, Kiss AA, Kenig EY. Dividing wall columns in chemical process industry: a review on current activities. Sep Purif Technol 2011;80: 403–17.
18. Gooty RT, Agrawal R, Tawarmalani M. Advances in MINLP to identify energy-efficient distillation configurations. Oper Res 2024;72: 639–59.
19. Baldea M. A pinch-like targeting framework for systematic thermal process intensification. AIChE J 2017;64:877–85.
20. Gernaey KV, Gani R. A model-based systems approach to pharmaceutical product-process design and analysis. Chem Eng Sci 2010;65: 5757–69.
21. Lutze P, Babi DK, Woodley JM, Gani R. Phenomena based methodology for process synthesis incorporating process intensification. Ind Eng Chem Res 2013;52:7127–44.
22. Demirel SE, Li J, Hasan MF. Systematic process intensification using building blocks. Comput Chem Eng 2017;105:2–38.
23. Demirel SE, Li J, El-Halwagi M, Hasan MF. Sustainable process intensification using building blocks. ACS Sustainable Chem Eng 2020;8: 17664–79.

24. Commenge JM, Falk L. Methodological framework for choice of intensified equipment and development of innovative technologies. Chem Eng Process 2014;84:109–27.
25. Pleşu V, Ruiz AEB, Bonet J, Llorens J, Iancu P. Shortcut assessment of alternative distillation sequence schemes for process intensification. Comput Chem Eng 2015;83:58–71.
26. Li Q, Finn AJ, Doyle SJ, Smith R, Kiss AA. Synthesis and optimization of energy integrated advanced distillation sequences. Sep Purif Technol 2023;315:123717.
27. Li Q, Somoza-Tornos A, Grievink J, Kiss AA. Challenges and opportunities for process intensification in Europe from a process systems engineering perspective. Front Energy Res 2024;12:1340635.
28. Stankiewicz A, Van Gerven T, Stefanidis G. The fundamentals of process intensification. Weinheim, Germany: John Wiley & Sons; 2019.
29. Bîldea CS, Pătruţ C, Jørgensen SB, Abildskov J, Kiss AA. Cyclic distillation technology- a mini-review. J Chem Tech Biotechnol 2016;91: 1215–23.
30. Cortes Garcia GE, van der Schaaf J, Kiss AA. A review on process intensification in HiGee distillation. J Chem Tech Biotechnol 2017;92: 1136–56.
31. Pazmiño-Mayorga I, Li Q, Kiss AA. Recent developments of high-gravity (reactive) distillation in rotating packed beds. Curr Opin Chem Eng 2024, in press. https://doi.org/10.1016/j.coche.2024.101071.
32. Shahandeh H, Jafari M, Kasiri N, Ivakpour J. Economic optimization of heat pump-assisted distillation columns in methanol-water separation. Energy 2015;80:496–508.
33. Gupta R, Kaistha N. Role of nonlinear effects in benzene-toluene-xylene dividing wall column control system design. Ind Eng Chem Res 2015;54:9407–20.
34. Pribic P, Roza M, Zuber L. How to improve the energy savings in distillation and hybrid distillation-pervaporation systems. Sep Sci Technol 2006;41:2581–602.
35. Pătruţ C, Bîldea CS, Liţă I, Kiss AA. Cyclic distillation–Design, control and applications. Sep Purif Technol 2014;125:326–36.
36. Wang GQ, Xu ZC, Ji JB. Progress on Higee distillation—introduction to a new device and its industrial applications. Chem Eng Res Des 2011; 89:1434–42.
37. Luo H, Bildea CS, Kiss AA. Novel heat-pump-assisted extractive distillation for bioethanol purification. Ind Eng Chem Res 2015;54:2208–13.
38. Ponce GHSF, Alves M, Miranda JC, Maciel Filho R, Maciel MRW. Using an internally heat-integrated distillation column for ethanol–water separation for fuel applications. Chem Eng Res Des 2015;95:55–63.
39. Liu S, Li H, Kruber B, Skiborowski M, Gao X. Process intensification by integration of distillation and vapor permeation or pervaporation-an academic and industrial perspective. Res Eng 2022;15:100527.
40. Zhai J, Chen X, Xie H, Sun X, Hu M, Dang M, et al. Energy-saving heat pump-assisted extractive-azeotropic dividing wall column with heat exchanger network for separating acetonitrile and water: a techno-economic and inherent safety investigation. Process Saf Environ Protect 2023;173:178–90.
41. Iwakabe K, Nakaiwa M, Huang K, Nakanishi T, Røsjorde A, Ohmori T, et al. Energy saving in multicomponent separation using an internally heat-integrated distillation column (HIDiC). Appl Therm Eng 2006;26:1362–8.
42. Chew JM, Reddy CCS, Rangaiah GP. Improving energy efficiency of dividing-wall columns using heat pumps, organic Rankine cycle and Kalina cycle. Chem Eng Process2014;76:45–59.