Available online at www.sciencedirect.com

ScienceDirect

Current Opinion in Chemical Engineering

Synthesis and design methods for energy-efficient distillation processes

Mirko Skiborowski

In order to achieve net-zero emissions until 2050, it is of utmost importance to improve the energy efficiency and thereby reduce the greenhouse gas emissions in the chemical industry. As distillation processes are accounting for the majority of all fluid separations, they are an important target for potential improvements. Although other separation technologies might be a favorable alternative, distillation is not generally an energy-intensive technology and advanced distillation process concepts, exploiting heat pumps, thermal coupling, as well as solvent- and membrane-assisted hybrid processes, may enable significant improvements regarding energy efficiency. The current article summarizes recent developments regarding the synthesis and design of energy-efficient distillation processes and points out future needs and directions for developments to foster the systematic evaluation and application of these advanced distillation process concepts.

Address
Hamburg University of Technology, Institute of Process Systems Engineering, Am Schwarzenberg-Campus 4, 21073 Hamburg, Germany

Corresponding author: Skiborowski, Mirko (mirko.skiborowski@tuhh.de)

Current Opinion in Chemical Engineering 2023, **42**:100985

This review comes from a themed issue on **model-based process design**

Edited by **Xiang Zhang** and **Kai Sundmacher**
For complete overview of the section, please refer to the article collection, "Model-based process design"

Available online 8 November 2023

https://doi.org/10.1016/j.coche.2023.100985

Introduction

Distillation is one of the oldest-known fluid separation technologies with continuous distillation columns being applied for more than 200 years [1]. Owing to its robustness and reliability, distillation has maintained its status as the most widely applied fluid separation process in industry, with ten thousands of distillation columns in operation, accounting for more than 90% of all fluid separations [2,3]. Besides the quantity of industrial applications, also the technological maturity of distillation is considered to be the highest in respect to other thermal separation processes, with especially the fundamentals of mass transfer and equipment design being very well-understood [4]. Yet, being the predominant fluid separation technology that is driven by thermal energy, distillation is accounting for a large fraction of the energy requirement in the chemical industry [5]. Being considered as a process that provides only limited thermodynamic efficiency, it is oftentimes conjured as outdated technology that provides little room for improvement and that could and should be replaced by less energy-intense technologies, such as membrane separations, in the near future [5].

However, as recently pointed out by Agrawal and Tumbalam Gooty [3], the growing belief that distillation processes are generally more energy-intense than other separation technologies and that research on distillation processes is no longer required is misleading researchers and decision-makers alike into a misconception that fundamentally builds on the focus on the heat of evaporation or the reboiler duty of distillation columns as indicative of the actual energy requirement. The latter should rather be analyzed by conceptualizing a distillation column as a heat engine, which transforms the heat duty of the reboiler into separation work, while simultaneously providing heat for further usage at the condenser temperature [6], which can and should be utilized to minimize the required energy. This can be accomplished in multiple ways, either utilizing it directly through heat integration with other equipment, or by application of heat pumps that effectively allow for electrification of distillation columns [7]. Equipment-integrated distillation processes, such as heat-integrated distillation columns (HIDiC) and dividing wall columns (DWC), as well as hybridization of distillation with other separation processes, are other means for process intensification that can lead to significant improvements in energy efficiency [8]. Following the definition of Franke and Górak [9], "hybrid separation processes are defined as combination of at least two different unit operations in different apparatus which contribute to the separation task," and as such include, for example, extraction–distillation and heteroazeotropic distillation processes.

While the design of simple distillation columns and simple column sequences is covered by a variety of classical textbooks [4,10], subject of lectures on

conceptual design and fluid separations, as well as easily commenced by established process flowsheeting software, more advanced concepts, such as heat-pump-assisted, heat-integrated and thermally coupled distillation, as well as hybrid distillation processes, oftentimes provide more sustainable solutions [11•]. Consequently, these options should be part of process synthesis and design, for the generation of feasible flowsheet variants and their optimization. The current article provides a concise overview and review of the recent efforts to support the synthesis and design of energy-efficient distillation processes, providing some perspective on future developments, needed to fill the remaining gaps. The need for such methods and advanced distillation concepts is highlighted by several recent review and perspective articles that discuss the various concepts for improving the energy efficiency of distillation processes [12,13]. The current review focusses on the efforts for providing the respective synthesis and design methods, confined to nonreactive separations and research articles published in the last five years. The interested reader is referred to the textbook on Reactive and Membrane-Assisted Separations [8] as well as the recent review papers on design and optimization of advanced reactive distillation processes [14,15].

Energy-efficient distillation for single splits

When analyzing the energy efficiency of separation processes, it is important to compare them on a common basis. This can be done best by relating the minimum (reversible) work for the separation ($\dot{W}_{\min}$) to the actual separation work ($\dot{W}_{sep}$) in order to compute a thermodynamic efficiency

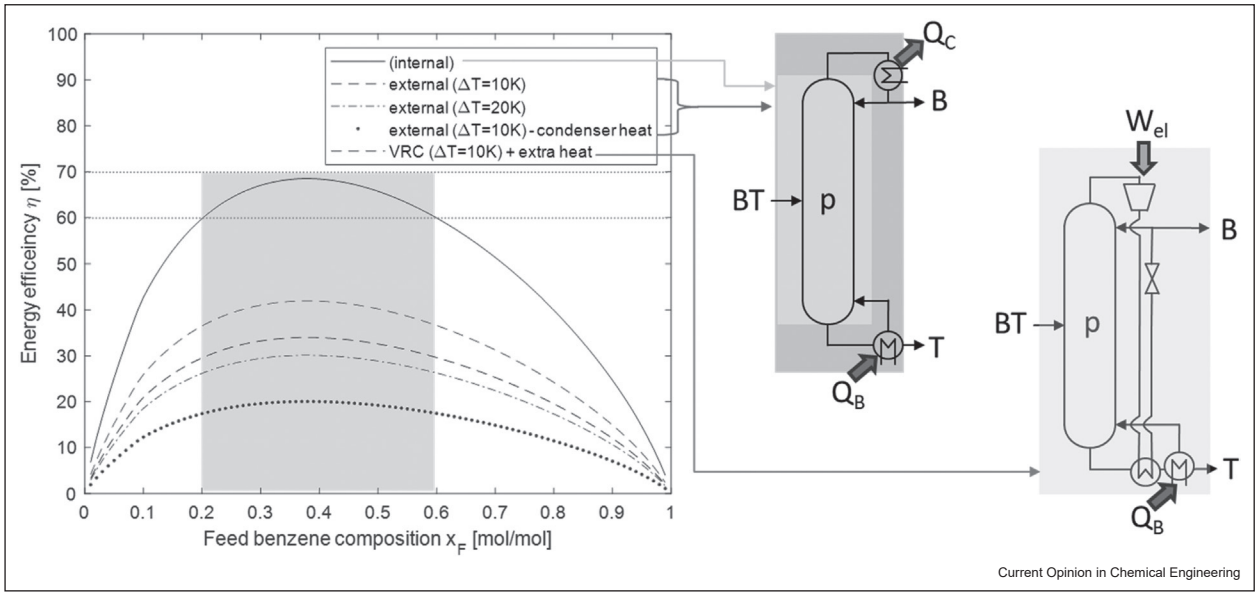
$$\eta = \frac{\dot{W}_{\min}}{\dot{W}_{sep}}. \tag{1}$$

The difference between the real separation work and the minimum work contributes the exergy loss, which summarizes all inefficiencies inside the actual separation equipment (internal loss) and in any auxiliary equipment (external loss), such as heat exchangers, pumps, compressors, and valves. Tumbalam Gooty et al. [16••] recently presented a thorough analysis of the energy efficiency and possible improvements for distillation of (nearly) ideal binary mixtures. They provide a rough guideline for designing energy-efficient distillation units, pointing out various means to reduce internal losses (e.g. feed conditioning and intermediate heat exchangers) and external losses (e.g. multi-effect distillation [MED] and heat pumps). Figure 1 illustrates some of the major results of the analysis for the separation of a benzene–toluene mixture, for which the results illustrated in the figure indicate that distillation can reach internal efficiencies in the range of 60–70% for feed compositions with 20–60 mol% benzene.

When utilizing the heat from the condensation and keeping approach temperatures in the heat exchangers at $\Delta T \approx 10K$ external efficiencies exceeding 40% can be realized. These do, however, drop below 20% for dilute feed streams or in general, in case of larger ΔT and wasting the condenser heat duty to the environment. In case of high internal efficiencies, heat-pump-assisted distillation, in the form of mechanical vapor recompression (VRC), is an extremely promising option for direct heat integration, resulting in efficiencies of more than 30%, assuming a $\Delta T \approx 10K$ and a compressor efficiency of 85%. The analysis of Tumbalam Gooty et al. [16••] is in line with and extends previous results presented by Cussler and Dutta [17] and Blahusiak et al. [18], who also provided some comparison with alternative separation processes, such as extraction, absorption, and membrane separations.

The application of heat pumps provides large potential for reducing the energy requirement in the chemical industry in general and distillation processes in specific [19]. The recent study of Chavez-Valesco et al. [20•] performed a systematic comparison of heat-pump-assisted distillation configurations with multistage membrane separation processes, showcasing a superior energy efficiency of the distillation processes for separations with high product recovery and (moderately) high purities. The large improvement potential by means of heat-pump-assisted distillation is also shown by industrial simulation studies [21•], indicating severe energy savings, but also highlighting the economic burdon of large-scale heat pumps. Practical limitations, which still limit the application ranges of large-scale heat pumps [22], as well as operability and safety considerations, should always be considered in addition to the evaluation of energy efficiency, which has to be combined with an economic evaluation to warrant relevant designs. The latter especially becomes evident for the HIDiC concept, in which a compressor is integrated between the rectifying and stripping section, in order to operate the stripping section at elevated pressure and allow for heat transfer between both sections along the individual section height. Thereby, the HIDiC provides even further potential for energy efficiency improvements by combining heat-pump-assisted distillation with diabatic distillation. The review paper of Fang et al. [23] provides a thorough overview of the research status, technical issues, and simulation and optimization studies for the HIDiC, for which so far only a single industrial implementation has been reported [24]. Notably, the latter is not an equipment-integrated, but a discretely heat-integrated setup, for which the design methodology was reported by Wakabayashi et al. [25]. Despite the potential benefits of the highly integrated HIDiC, there

Figure 1



Energy efficiency for the distillation-based separation of a binary benzene–toluene mixture, at ambient pressure, for different feed compositions, assuming an ideal heat exchange between the feed and product streams, following Tumbalam Gooty et al. [16••]. The individual curves present the internal efficiency of the distillation column, as well as external efficiencies with approach temperatures of 10 K or 20 K in the reboiler and condenser, as well as the use of mechanical VRC with an approach temperature of 10 K and extra heat transfer to compensate for different heat duties for condensation and evaporation.

are important limitations that need to be considered in design and evaluation, such as balancing heat and mass transfer and changing vapor loads along the column height. The basic requisite of an appropriate alignment of the internal temperature profiles has further been pointed out by Shenvi et al. [26].

Shortcut-based screening methods for process and molecular design

While some of the previously described studies on the energy efficiency are based on rigorous simulations, most of them build on shortcut calculations, especially the well-known Underwood equations [16••,18,20•,27]. Although these rely on assumptions of constant relative volatility (CRV) and constant molar overflow (CMO), which limit their applicability to mixtures with (almost) ideal vapor-liquid equilibria, they do allow for an extensive screening of alternative process configurations, which mandate computationally efficient calculations, especially for multicomponent separations. This is illustrated in the comparative study of Ramapriya et al. [28], who evaluate accuracy and computational effort for a shortcut screening and a detailed simulation-based optimization for the separation of a quaternary mixture.

Even for binary splits, a variety of alternatives can be evaluated, as, for example, illustrated by Cui et al. [29], who present an enumeration-based framework for the evaluation of various MED processes. For multicomponent distillation for the separation of zeotropic mixtures, much progress was made in recent years in the group of Rakesh Agrawal, resulting, for example, in an enumeration-based global optimization method for the determination of the best-possible thermally coupled process configuration with minimum heat duty [30] or total exergy loss [31]. The nonlinear programming approach was further extended to include pressure variation and heat integration between reboilers and condensers of the different columns in the evaluation of the configuration with the lowest heat duty [32•]. Such methods enable a systematic and efficient screening of a vast number of process options, and do furthermore support initialization and optimization of rigorous design models, as, for example, illustrated in the work of Li et al. [33].

Another promising application area of shortcut models is in computer-aided molecular and process design (CAMPD) of solvents for chemical separations. Such solvent-assisted distillation processes are important alternatives for narrow-boiling and azeotropic distillation processes [18]. The recent reviews of Gertig et al. [34] and Chai et al. [35] provide an excellent overview of CAMPD methods for separation solvent design. As illustrated in Figure 2, CAMPD methods build on an integrated approach, which applies property prediction methods to evaluate candidate molecules, for example, from a predefined database, by evaluating some metric

Figure 2

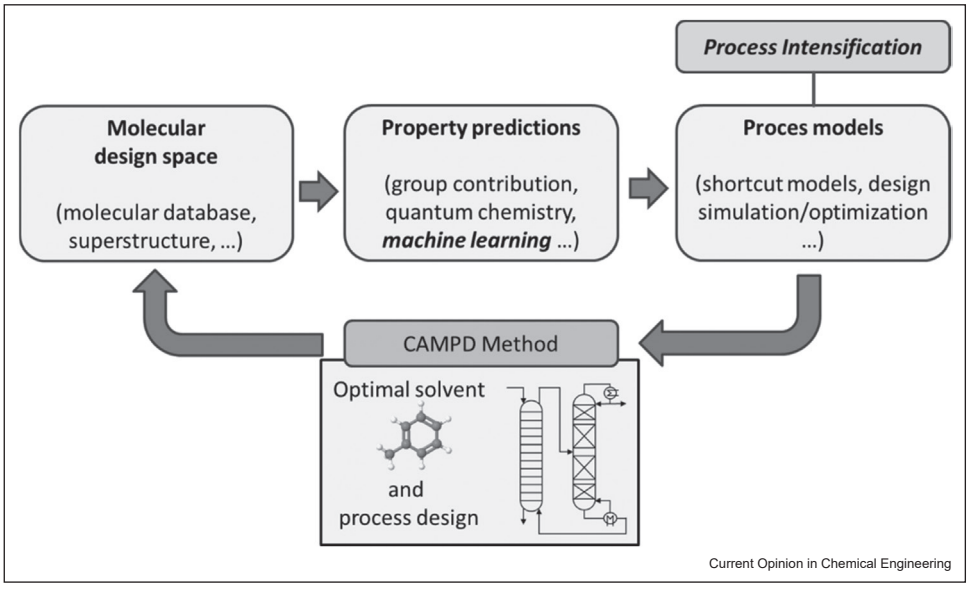


Illustration of the interplay of the individual aspects of CAMPD.

quantifying process performance, such as solvent or energy requirements, seeking the optimal solvent and process. So far, process intensification and advanced distillation processes have received little attention as an integral part of CAMPD, especially for the screening of large-solvent databases or the optimization of a molecular design.

The application of computationally efficient shortcut methods allows for the screening of several thousand molecules, but requires accurate property predictions, as well as thermodynamically sound shortcut models, which avoid CMO and CRV assumptions for distillation. The development of property prediction methods, which as illustrated in Figure 2 is an essential element of CAMPD, has recently gained significant traction due to the impact of machine learning [36]. One of several interesting developments in this research area allows for the prediction of thermodynamically consistent activity coefficients and the respective Non-Random-Two-Liquid-Modell (NRTL) parameters based on a natural language processing model [37•]. On such a basis, a variety of pinch-based shortcut methods can be applied for the evaluation of distillation-based separation processes, such as extraction–distillation, extractive, or heteroazeotropic distillation processes [38]. As illustrated by Skiborowski [39,40] these shortcut methods can also be used to screen heat-pump-assisted, heat-integrated, and thermally coupled distillation configurations for the separation of nonideal mixtures, enabling the consideration of process intensification, as illustrated in Figure 2. For extraction–distillation processes, the group of Andre Bardow has demonstrated the applicability of such a combination, including predictive life cycle assessment [41] and basic heat integration [42•]. For extractive distillation processes, so far, only iterative CAMPD strategies are applied, using structural and property constraints to narrow down the search space, while finally applying rigorous simulation or optimization to evaluate the process performance of few remaining molecules [43,44]. To the best of the author's knowledge, heteroazeotropic and membrane-assisted distillation processes have so far not been considered in CAMPD at all, despite their prospect for energy-efficient separations.

Design and optimization of energy-efficient distillation-based processes

According to Scopus, the number of publications on process design and optimization for distillation-based processes shows an increasing trend (average annual publications for a 5- year period from 1998, 2008, and 2018) for heat-pump-assisted (1→3→24), thermally coupled (5→11→35), and hybrid distillation processes (16→28→90) alike in recent years. While the number of publications exceeds the scope of the current review, most of these publications focus on a specific application and the analysis of few selected process configurations. These do however extend to highly integrated process configurations, such as heat-pump-assisted 4-product DWC [45] or heat-pump-assisted extractive DWC [46].

As indicated in the recent review on extractive DWC by Czarnecki et al. [47], most studies apply a simulation-based optimization that either builds on an iterative approach or the use of a metaheuristic, especially

Figure 3

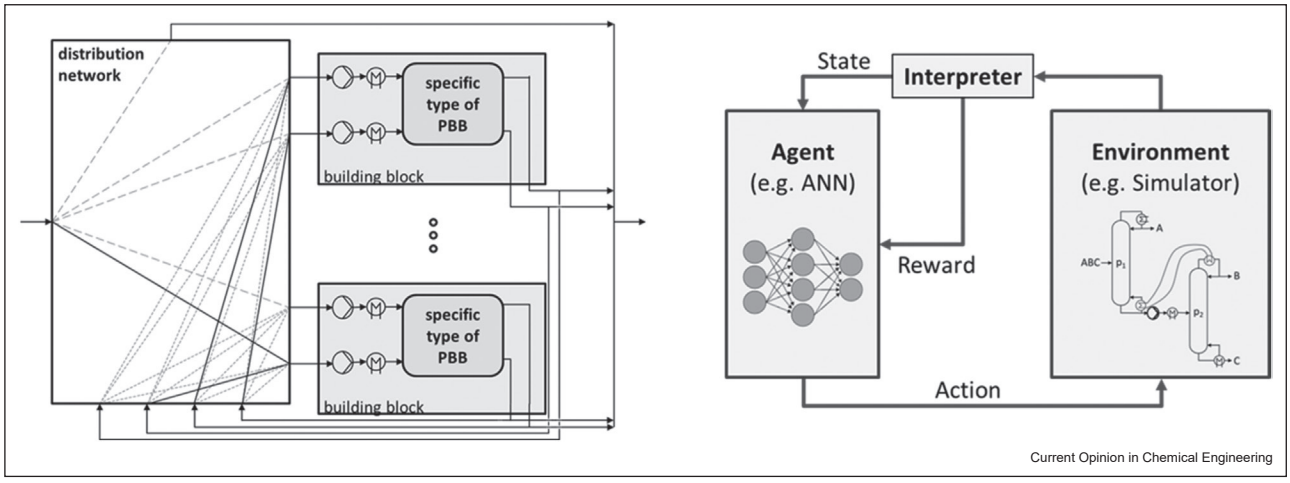


Illustration of a superstructure for phenomena-based process synthesis with a general distribution network and a number of specific types of building blocks in accordance with Kuhlmann et al. [64] (left) and reinforcement learning approach for process synthesis using an artificial neural network (ANN) as agent and a process simulator as learning environment, as, for example, illustrated by Göttl et al. [68].

evolutionary algorithms. Despite the different methods for process optimization, there have been little efforts for a comparative evaluation on a common basis so far. A comparison of a shortcut-based evaluation, as well as an iterative simulation-based optimization and a simultaneous optimization-based design of a superstructure model for a DWC, is reported in the article of Waltermann and Skiborowski [48]. A very interesting approach that combines an iterative approach for DWC optimization with a genetic algorithm for the optimization of a superstructure of heat-pump-assisted distillation was recently presented by Miao et al. [49]. The design of arbitrary DWC for 3- and 4-product separations can also be performed efficiently by means of mathematical programming methods, as, for example, illustrated by Waltermann et al. [50]. This also enables the comparative evaluation of energy-integrated extractive and heteroazeotropic distillation processes [51]. For the latter, topology-based initialization [52] concepts can effectively overcome challenges in the initialization of the complex process configurations and the highly nonlinear models.

Among the different membrane processes, especially vapor permeation and pervaporation have received considerable attention in distillation-based hybrid processes. The recent review paper of Liu et al. [53] provides a concise overview of recent advances for these hybrid processes, which due to the absence of membrane models in most process simulators, require tailored models for process design and optimization. These membrane-assisted distillation processes do however bear the potential to improve the energy efficiency while reducing the need for heat integration [54•]. Yet, as pointed out for heat-pump-assisted distillation [21], energy efficiency needs to be aligned with a techno-economical assessment for membrane-assisted distillation processes [54]. Similar to other azeotropic distillation processes, such techno-economic optimization can be performed effectively by means of superstructure optimization in combination with metaheuristics, as, for example, illustrated by Chia et al. for different hybrid configurations [55] and a comparison with extractive distillation [56]. Such hybrid optimization methods are also of particular interest for a final evaluation of potential solvents from CAMPD, for which solvent selection and energy integration can be evaluated simultaneously [57].

Generative process synthesis tools

The previously addressed screening and process design methods all build on the definition of a suitable process configuration or a unit operation-based superstructure that allows for certain structural variations. However, in recent years, several generative methods for the synthesis of intensified processes have been proposed, which show interesting prospects to support engineers in process synthesis [58]. These methods either build on a general structured workflow supported by different specialized tools [59], or utilize superstructure-based process synthesis combined with a certain level of abstraction. Especially, the Generalized Modular Framework [60••], which was recently illustrated for the synthesis of DWC [61] and extractive distillation processes [62], as well as building block-based process synthesis methods on the individual phase-level [63,64] bear the potential to automatically generate energy-efficient intensified distillation processes. The latter was

also illustrated for the synthesis of work–heat exchanger networks [65]. An illustration of a general state-space superstructure for a phenomena-building block-based process synthesis is illustrated in Figure 3 (left). Note that the more general superstructure models either require special initialization and solution strategies [64], or the application of global deterministic optimization [63,65], in order to solve the complex optimization problems. Both require additional effort and a considerably larger computational load, when compared with individual process optimization problems referred to in the previous section.

Another promising effort for process synthesis are superstructure-free methods that apply concepts from machine learning. Besides the generation of process flowsheets by means of genetic programming [66], very interesting results have recently been presented for flowsheet generation by different approaches for hierarchical reinforcement learning [67•–69]. Similar to established metaheuristics for process optimization, these methods mostly build on a process simulator as learning environment for the evaluation of proposed process designs, as illustrated in Figure 3 (right). So far, these methods have only been demonstrated for the generation of rather conventional configurations of classical unit operations. However, they may as well be extended to intensified processes in the near future and may potentially be further integrated with the aforementioned CAMPD methods. In that case, it is important to note that as for the application of metaheuristics, convergence of the process simulation and the consideration of constraint violations are important aspects to obtain (at least locally) optimal solutions.

Conclusion and look ahead

As the recent work of Agrawal et al. [3,16] highlighted, distillation is not necessarily inefficient and should not be considered as an outdated technology. The rich history has rather provided a variety of options for process intensification, especially in respect to mass and energy integration, which have to be considered for a fair comparison with alternative technologies that can also be combined with distillation in hybrid separation processes [8]. In order to design the most advanced and energy-efficient distillation processes, process engineers should

- be able to analyze the (internal and external) energy efficiency of distillation and separation processes in general,
- be aware of the various advanced distillation process concepts, including heat-pump- assisted distillation, thermally coupled distillation, and hybrid distillation processes,
- be aware and able to apply CAMPD methods for solvent-assisted distillation-based processes,
- be able to apply optimization-based design methods for a computationally efficient design of the resulting integrated process configurations,
- considering them in the scope of an overall process-wide integration.

The effective design of such advanced distillation processes mandates advanced integrated knowledge in thermodynamics, fluid separations, process intensification, and systems engineering alike. While a variety of publications illustrate the possibility to design such processes by the help of flowsheet simulators in combination with iterative methods or metaheuristics, equation-oriented superstructure models and gradient-based optimization methods are still less frequently applied, as they require dedicated model formulation and initialization strategies that cannot easily be implemented in established modeling, simulation, and optimization software. These limitations may in the future be overcome by open-source projects such as the IDEAS (Institute for the Design of Advacned Energy Systems) process modeling framework and PYOMO (Python Optimization Modeling Objects) [70•]. Nevertheless, numerically robust optimization of highly non-convex and large-scale problems remains a challenge that either requires sophisticated initialization and modeling strategies or further advances in deterministic global optimization, which is currently not directly applicable for such problems.

In order to harvest the full potential of the advanced distillation process concepts, design methods for process evaluation and optimization have to be extended to the aforementioned generic process synthesis approaches, enabling the identification of suitable process configurations without prespecification. Integrating these methods with the astonishing recent advances in property prediction, a completely new class of CAMPD methods could be generated, which allows for the simultaneous design and synthesis of solvents and processes.

While these processes should be optimized for energy efficiency, process economics have to be included in the evaluation and should be aligned by further metrics for sustainability, controllability, and safety. Especially, the operability of highly integrated processes can become a challenge due to a reduced number of manipulated variables and should be considered as an important criterion during conceptual process design. Yet, the results for DWC indicate that even highly integrated processes can be properly controlled, given that a suitable control structure is implemented, for which there are however no easily applicable general rules available [71] Besides the need for efficient tools that enable process engineers to navigate the vast and complex space of process design

alternatives, many of the highly integrated, but energy-efficient options also still require experimental evidence, which is severely lacking in open literature, as also highlighted for the operation of DWC [71]. While Toyo has built the first industrially applied (external) HIDIC just a few years ago [25], a first multi-DWC pilot plant was only built two years ago at a research facility at the University of Ulm [72] and it was just announced that a first industrial plant has been commissioned by DWC Innovations in a refinery in Mumbai (⟨https://www.dwcinnovations.com/press-release/successful-commissioning-of-dual-dividing-wall-column-at-bpcl-mumbai/⟩ [accessed 23.11.2023]). Thus, although distillation is by no means a young technology, there is still much room for innovation and research to foster the implementation of energy-efficient distillation processes, which bear large potential to decrease the energy requirement in the chemical industry and support the effort to reach climate neutrality until 2050.

Data Availability

Data will be made available on request.

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.

Acknowledgements

Gefördert durch die Deutsche Forschungsgemeinschaft (DFG) — 523327609/funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) — 523327609.

References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- • of special interest
- •• of outstanding interest

1. Kockmann N: **200 Years in innovation of continuous distillation**. *ChemBioEng Rev* 2014, **1**:40-49, https://doi.org/10.1002/cben.201300003
2. Wankat PC: Separation Process Engineering: Includes Mass Transfer Analysis. 3rd ed., Prentice Hall; 2012.
3. Agrawal R, Tumbalam Gooty R: **Misconceptions about efficiency and maturity of distillation**. *AIChE J* 2020, **66**:e16294, https://doi.org/10.1002/aic.16294
4. Goedecke R: **Fluidverfahrenstechnik**. Wiley-VCH; 2008.
5. Sholl DS, Lively RP: **Seven chemical separations to change the world**. *Nature* 2016, **532**:435-437, https://doi.org/10.1038/532435a
6. Blahušiak M, Kiss AA, Kersten S, Schuur B: **Quick assessment of binary distillation efficiency using a heat engine perspective**. *Energy* 2016, **116**:20-31, https://doi.org/10.1016/j.energy.2016.09.097
7. Kiss AA, Ferreira CAI: Heat Pumps in the Chemical Process Industry. CRC Press Taylor & Francis Group; 2017.
8. Skiborowski M, Górak A: Reactive and Membrane-Assisted Separations: Process Intensification; by Rotating Packed Beds. 2nd ed., De Gruyter; 2022.
9. Franke M, Górak A, Strube J: **Auslegung und Optimierung von hybriden Trennverfahren: design and optimization of hybrid separation processes**. *Chem Ing Techn* 2004, **76**:199-210.
10. Douglas JM: Conceptual Design of Chemical Processes. McGraw-Hill; 1988.
11. • Skiborowski M, Kruber KF, Waltermann T: **Sustainable distillation processes**. In *Sustainable Separation Engineering: Materials, Techniques and Process Development*. Edited by Szekely G, Zhao D. John Wiley & Sons Ltd; 2022:431-481.

Elaborate overview on sustainable distillation processes, covering advanced distillation process concepts for single splits. Multi-product distillation processes and the separation of close-boiling and azeotropic mixtures.

12. Kiss AA, Smith R: **Rethinking energy use in distillation processes for a more sustainable chemical industry**. *Energy* 2020, **203**:117788, https://doi.org/10.1016/j.energy.2020.117788
13. Kooijman HA, Sorensen E: **Recent advances and future perspectives on more sustainable and energy efficient distillation processes**. *Chem Eng Res Des* 2022, **188**:473-482, https://doi.org/10.1016/j.cherd.2022.10.005
14. Kiss AA, Jobson M, Gao X: **Reactive distillation: stepping up to the next level of process intensification**. *Ind Eng Chem Res* 2019, **58**:5909-5918, https://doi.org/10.1021/acs.iecr.8b05450
15. Shu C, Li X, Li H, Gao X: **Design and optimization of reactive distillation: a review**. *Front Chem Sci Eng* 2022, **16**:799-818, https://doi.org/10.1007/s11705-021-2128-9
16. •• Tumbalam Gooty R, Chavez Velasco JA, Agrawal R: **Methods to assess numerous distillation schemes for binary mixtures**. *Chem Eng Res Des* 2021, **172**:1-20, https://doi.org/10.1016/j.cherd.2021.05.022.

Excellent analysis oft he energy efficiency of distillation for binary splits, covering various options to improve the internal and external efficiency of distillation columns.

17. Cussler EL, Dutta BK: **On separation efficiency**. *AIChE J* 2012, **58**:3825-3831, https://doi.org/10.1002/aic.13779
18. 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**:301-318, https://doi.org/10.1016/j.seppur.2017.10.026
19. Schultz T, Nagel M, Engenhorst T, Nymand-Andersen A, Kunze E, Stenner P, *et al*.: **Electrifying chemistry: a company strategy perspective**. *Curr Opin Chem Eng* 2023, **40**:100916, https://doi.org/10.1016/j.coche.2023.100916
20. • Chavez Velasco JA, Tawarmalani M, Agrawal R: **Which separation scenarios are advantageous for membranes or distillations?** *AIChE J* 2022, **68**:e17839, https://doi.org/10.1002/aic.17839.

A thorough comparison of heat pump-assisted distillation and multi-stage membrane separation processes for a wide range of separation problems, highlighting the separation problems, for which either of the separation processes is likely to be preffered from an energy efficiency perspective.

21. • Rix A, Schröder M, Paul N: **Vapor recompression: an interesting option for vacuum columns?** *Chem Eng Res Des* 2023, **191**:226-235, https://doi.org/10.1016/j.cherd.2023.01.030.

Very interesting analysis of the potential of open and closed-cycle heat pump-assisted distillation for vacuum distillation from an industrial perspective.

22. Schlosser F, Jesper M, Vogelsang J, Walmsley TG, Arpagaus C, Hesselbach J: **Large-scale heat pumps: applications, performance, economic feasibility and industrial integration**. *Renew Sustain Energy Rev* 2020, **133**:110219, https://doi.org/10.1016/j.rser.2020.110219
23. Fang J, Cheng X, Li Z, Li H, Li C: **A review of internally heat integrated distillation column**. *Chin J Chem Eng* 2019, **27**:1272-1281, https://doi.org/10.1016/j.cjche.2018.08.021
24. Wakabayashi T, Yoshitani K, Takahashi H, Hasebe S: **Verification of energy conservation for discretely heat integrated**

distillation column through commercial operation. *Chem Eng Res Des* 2019, **142**:1-12, https://doi.org/10.1016/j.cherd.2018.11.031

25. Wakabayashi T, Ferrari A, Hasebe S: **Design and commercial operation of a discretely heat-integrated distillation column**. *Chem Eng Res Des* 2019, **147**:214-221, https://doi.org/10.1016/j.cherd.2019.04.036

26. Shenvi AA, Herron DM, Agrawal R: **Energy efficiency limitations of the conventional heat integrated distillation column (HIDiC) configuration for binary distillation**. *Ind Eng Chem Res* 2011, **50**:119-130, https://doi.org/10.1021/ie101698f

27. Chavez Velasco JA, Tawarmalani M, Agrawal R: **Systematic analysis reveals thermal separations are not necessarily most energy intensive**. *Joule* 2021, **5**:330-343, https://doi.org/10.1016/j.joule.2020.12.002

28. Ramapriya GM, Selvarajah A, Jimenez Cucaita LE, Huff J, Tawarmalani M, Agrawal R: **Short-cut methods versus rigorous methods for performance-evaluation of distillation configurations**. *Ind Eng Chem Res* 2018, **57**:7726-7731, https://doi.org/10.1021/acs.iecr.7b05214

29. Cui C, Xi Z, Liu S, Sun J: **An enumeration-based synthesis framework for multi-effect distillation processes**. *Chem Eng Res Des* 2019, **144**:216-227, https://doi.org/10.1016/j.cherd.2019.02.018

30. Nallasivam U, Shah VH, Shenvi AA, Huff J, Tawarmalani M, Agrawal R: **Global optimization of multicomponent distillation configurations: 2. Enumeration based global minimization algorithm**. *AIChE J* 2016, **62**:2071-2086, https://doi.org/10.1002/aic.15204

31. Jiang Z, Chen Z, Huff J, Shenvi AA, Tawarmalani M, Agrawal R: **Global minimization of total exergy loss of multicomponent distillation configurations**. *AIChE J* 2019, **65**:e16737, https://doi.org/10.1002/aic.16737

32. • Nogaja AS, Mathew TJ, Tawarmalani M, Agrawal R: **Identifying heat-integrated energy-efficient multicomponent distillation configurations**. *Ind Eng Chem Res* 2022, **61**:13984-13995, https://doi.org/10.1021/acs.iecr.2c00870.
Optimization-based shortcut screening for thermally-coupled and heat-integrated distillation processes for multicomponent, multi-product separations, based on constant relative volatilities.

33. 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, https://doi.org/10.1016/j.seppur.2023.123717

34. Gertig C, Leonhard K, Bardow A: **Computer-aided molecular and processes design based on quantum chemistry: current status and future prospects**. *Curr Opin Chem Eng* 2020, **27**:89-97, https://doi.org/10.1016/j.coche.2019.11.007

35. Chai S, Song Z, Zhou T, Zhang L, Qi Z: **Computer-aided molecular design of solvents for chemical separation processes**. *Curr Opin Chem Eng* 2022, **35**:100732, https://doi.org/10.1016/j.coche.2021.100732

36. Alshehri AS, You F: **Machine learning for multiscale modeling in computational molecular design**. *Curr Opin Chem Eng* 2022, **36**:100752, https://doi.org/10.1016/j.coche.2021.100752

37. • Winter B, Winter C, Esper T, Schilling J, Bardow A: **SPT-NRTL: a physics-guided machine learning model to predict thermodynamically consistent activity coefficients**. *Fluid Phase Equilibria* 2023, **568**:113731, https://doi.org/10.1016/j.fluid.2023.113731.
Very impressive approach for the generation of a massive NRTL parameter set for 100.000.000 mixtures, by means of a SMILESToPropertyTransformer model, providing the foundation of massive solvent screening and distillation process evaluations.

38. Skiborowski M, Harwardt A, Marquardt W: **Conceptual design of azeotropic distillation processes**. Distillation. Elsevier; 2014:305-355, https://doi.org/10.1016/B978-0-12-386547-2.00008-9

39. Skiborowski M: **Fast screening of energy and cost efficient intensified distillation processes**. *Chem Eng Trans* 2018, **69**:199-204, https://doi.org/10.3303/CET1869034

40. Skiborowski M: **Energy efficient distillation by combination of thermal coupling and heat integration**. *Comput Aided Chem Eng* 2020, **48**:991-996, https://doi.org/10.1016/B978-0-12-823377-1.50166-X

41. Fleitmann L, Kleinekorte J, Leonhard K, Bardow A: **COSMO-susCAMPD: sustainable solvents from combining computer-aided molecular and process design with predictive life cycle assessment**. *Chem Eng Sci* 2021, **245**:116863, https://doi.org/10.1016/j.ces.2021.116863

42. • Fleitmann L, Gertig C, Scheffczyk J, Schilling J, Leonhard K, Bardow A: **From molecules to heat-integrated processes: computer-aided design of solvents and processes using quantum chemistry**. *Chem Ing Tech* 2023, **95**:368-380, https://doi.org/10.1002/cite.202200098.
First ever CAMPD approach accounting for heat integration, providing the basis for future developts for more advanced process evaluations and a process-wide energy demand evaluation.

43. Zhang J, Wang Q, Eden M, Shen W: **A deep learning-based framework towards inverse green solvent design for extractive distillation with multi-index constraints**. *Comp Chem Eng* 2023, **177**:108335, https://doi.org/10.1016/j.compchemeng.2023.108335

44. Zhou T, Song Z, Zhang X, Gani R, Sundmacher K: **Optimal solvent design for extractive distillation processes: a multiobjective optimization-based hierarchical framework**. *Ind Eng Chem Res* 2019, **58**:5777-5786, https://doi.org/10.1021/acs.iecr.8b04245

45. Ge G, Han S, Huang K, Fan C, Chen H, Zhang L, *et al.*: **An effective procedure for the development of vapor recompressed Kaibel dividing-wall distillation columns**. *Sep Purif Technol* 2023, **310**:123171, https://doi.org/10.1016/j.seppur.2023.123171

46. Zhai J, Chen X, Xie H, Sun X, Zhao P, Liu Y: **Improving the economic saving, environmental sustainability, and energy efficiency of separating acetone/n-heptane mixture via heat pump-assisted extractive dividing wall column with heat exchanger network**. *Chem Eng Process* 2023, **187**:109354, https://doi.org/10.1016/j.cep.2023.109354

47. • Czarnecki NJ, Owens SA, Eldridge RB: **Extractive dividing wall column for separating azeotropic systems: a review**. *Ind Eng Chem Res* 2023, **62**:5750-5770, https://doi.org/10.1021/acs.iecr.3c00302.
Up-to-date review on case studies, design methods and control analysis for extractive DWC.

48. Waltermann T, Skiborowski M: **Conceptual design of highly integrated processes - optimization of dividing wall columns**. *Chem Ing Tech* 2017, **89**:562-581, https://doi.org/10.1002/cite.201600128

49. Miao G, Ma Y, Yang C, Tong B, Li G, Xiao J: **The effective synthesis of heat-pump assisted distillation process with multiple columns for light hydrocarbon separation**. *Chem Eng Sci* 2023, **269**:118449, https://doi.org/10.1016/j.ces.2023.118449

50. Waltermann T, Sibbing S, Skiborowski M: **Optimization-based design of dividing wall columns with extended and multiple dividing walls for three- and four-product separations**. *Chem Eng Process Process Intensif* 2019, **146**:107688, https://doi.org/10.1016/j.cep.2019.107688

51. Waltermann T, Grueters T, Muenchrath D, Skiborowski M: **Efficient optimization-based design of energy-integrated azeotropic distillation processes**. *Comp Chem Eng* 2020, **133**:106676, https://doi.org/10.1016/j.compchemeng.2019.106676

52. • Kruber KF, Skiborowski M: **Topology-based initialization for the optimization-based design of heteroazeotropic distillation processes**. *Processes* 2022, **10**:1482, https://doi.org/10.3390/pr10081482.
Analysis of membrane, distillation and hybrid membrane-assisted distillation processes in respect to energy efficiency and techno-economic performance.

53. 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**. *Results Eng* 2022, **15**:100527, https://doi.org/10.1016/j.rineng.2022.100527

54. Kruber B, Droste K, Skiborowski M: **Thermodynamic efficiency of membrane-assisted distillation processes**. *AIChE J* 2023, **69**:e18015, https://doi.org/10.1002/aic.18015

55. Chia DN, Duanmu F, Sorensen E: **Single- and multi-objective optimisation of hybrid distillation-pervaporation and dividing wall column structures**. *Chem Eng Res Des* 2023, **194**:280-305, https://doi.org/10.1016/j.cherd.2023.04.041

56. Chia DN, Sorensen E: **Optimal design of hybrid distillation-membrane processes based on a superstructure approach**. *Chem Eng Res Des* 2023, **194**:256-279, https://doi.org/10.1016/j.cherd.2023.04.014

57. Kruber KF, Grüters T, Skiborowski M: **Advanced hybrid optimization methods for the design of complex separation processes**. *Comp Chem Eng* 2021, **147**:107257, https://doi.org/10.1016/j.compchemeng.2021.107257

58. Mencarelli L, Chen Q, Pagot A, Grossmann IE: **A review on superstructure optimization approaches in process system engineering**. *Comp Chem Eng* 2020, **136**:106808, https://doi.org/10.1016/j.compchemeng.2020.106808

59. Garg N, Kontogeorgis GM, Gani R, Woodley JM: **A process synthesis-intensification method for generation of novel and intensified solutions**. *Chem Eng Process* 2020, **156**:108103, https://doi.org/10.1016/j.cep.2020.108103

60. Pistikopoulos, Tian Y: Synthesis and Operability Strategies for Computer-Aided Modular Process Intensification. Elsevier; 2022.
••Extensive presentation of the Generalized Modular Framework in form of a textbook that covers various applications for process design and operability analysis.

61. Tian Y, Meduri V, Bindlish R, Pistikopoulos EN: **A Process Intensification synthesis framework for the design of dividing wall column systems**. *Comp Chem Eng* 2022, **160**:107679, https://doi.org/10.1016/j.compchemeng.2022.107679

62. Tian Y, Pistikopoulos EN: **A process intensification synthesis framework for the design of extractive separation systems with material selection**. *J Adv Manuf Process* (4) 2021, **3**:1-17, https://doi.org/10.1002/amp2.10097

63. Demirel SE, Li J, Hasan MMF: **A general framework for process synthesis, integration, and intensification**. *Ind Eng Chem Res* 2019, **58**:5950-5967, https://doi.org/10.1021/acs.iecr.8b05961

64. Kuhlmann H, Skiborowski M: **Optimization-based approach to process synthesis for process intensification: general approach and application to ethanol dehydration**. *Ind Eng Chem Res* 2017, **56**:13461-13481, https://doi.org/10.1021/acs.iecr.7b02226

65. Li J, Demirel SE, Hasan MMF: **Building block-based synthesis and intensification of work-heat exchanger networks (WHENS)**. *Processes* 2019, **7**:23, https://doi.org/10.3390/pr7010023

66. Neveux T: **Ab-initio process synthesis using evolutionary programming**. *Chem Eng Sci* 2018, **185**:209-221, https://doi.org/10.1016/j.ces.2018.04.015

67. Stops L, Leenhouts R, Gao Q, Schweidtmann AM: **Flowsheet generation through hierarchical reinforcement learning and graph neural networks**. *AIChE J* 2023, **69**:e17938, https://doi.org/10.1002/aic.17938.
•Interesting process synthesis approach nbased on hierarchical reinforcement learning and graph neural networks, which also provides an up-to-date overview of conceptually similar methods.

68. Göttl Q, Grimm DG, Burger J: **Automated synthesis of steady-state continuous processes using reinforcement learning**. *Front Chem Sci Eng* 2021, **16**:288-302, https://doi.org/10.1007/s11705-021-2055-9

69. Khan AA, Lapkin AA: **Designing the process designer: hierarchical reinforcement learning for optimisation-based process design**. *Chem Eng Process* 2022, **180**:108885, https://doi.org/10.1016/j.cep.2022.108885

70. Lee A, Ghouse JH, Eslick JC, Laird CD, Siirola JD, Zamarripa MA, *et al*.: **The IDAES process modeling framework and model library—flexibility for process simulation and optimization**. *J Adv Manuf Process* (3) 2021, **3**, https://doi.org/10.1002/amp2.10095.
•Elaborate presentation of the IDEAS approach for process simulation and optimization, which leverages the open-source, extensible algebraic modeling environment, PYOMO.

71. Donahue MD, Roach BJ, Downs JJ, Blevins T, Baldea M, Eldridge RB: **Deviding wall column control: common practices and key findings**. *Chem Eng Process* 2016, **107**:106-115, https://doi.org/10.1016/j.cep.2016.05.013

72. Waibel Y, Trescher L, Ränger L-M, Grützner T: **First multiple dividing wall column: design and operation**. *Chem Eng Res Des* 2023, **193**:132-144, https://doi.org/10.1016/j.cherd.2023.03.017