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# Recent advances and future perspectives on more sustainable and energy efficient distillation processes

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ABSTRACT

Distillation has held a very strong position in the chemical process industries for well over a century, and has, as a separation method, been around for millennia. The process can be designed directly without the need for experimentation unlike other novel separation processes, and distillation is a standard part of any undergraduate curriculum. So why the ongoing interest in this separation dinosaur? Due to distillation's significant importance in industry, and its associated high energy requirements and thereby contribution to global warming, considerable effort is still needed to make the process more energy efficient, as well as to consider other heating sources beyond traditional fossil fuels. In this work, we will outline the most significant methods currently considered for energy efficiency of distillation, and provide an overview of where we may be heading as a discipline in our quest for a more sustainable chemical engineering future. We will argue that significant improvements have already been made, but more is still required by both industry and legislators. We need to consider a future without the use of fossil fuel-based feedstock or energy sources and switch towards renewable sources, and our future graduates need to be adequately prepared for such a future.



## 1. Introduction

Distillation has been the separation workhorse for the Chemical Process Industries (CPI) for over a century and is by far the most important separation method used, with about 90–95% of all separations in the chemicals and petroleum refining industries (Oak Ridge National Laboratory, 2005). The process can separate mixtures in very large quantities, and into very pure products, based on difference in the boiling points of the components. Given its maturity, design of distillation units is routinely done using commercial software with little, if any, need for experimentation and with only very limited pilot plant testing, mainly only for novel column internals. As distillation relies on boiling point differences, boiling of the fluids is needed to achieve separation and this can require large amounts of energy. A large fraction of the heat required for distillation is typically recovered from within the process itself, for example from reactor effluent (typically operating at elevated temperatures to speed up the reaction) or from the distillation column effluents. The remainder needs to be supplied by external heating. About 30% of the overall energy requirements in industry are for distillation operations, and 90–95% of the separation energy (Oak Ridge National Laboratory, 2005). In 2017, a study found that three quarters of the primary energy in the US still came from fossil fuel resources (National Academies of Sciences, Engineering, and Medicine, 2019). Any reduction in energy usage in distillation will therefore directly contribute to a reduction in the use of fossil fuels, and as such, to a reduction of global warming.

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Process engineers are very energy conscious when designing separation processes, especially when it comes to distillation columns, since creating sufficient reboil action for the required counter-current internal flow is costly, both from an energy, but also from a capital, point of view. The internal re-use of energy is so essential in CPI that it frequently dictates which process design option is economically viable. Processes are continuously being improved, and a design choice will depend on the best-in-class technology that is available at any point in time. For example, with the advent of high efficiency sheet metal packing, all air separation companies deployed structured packing in their low-pressure columns for oxygen separation (Moll, 2014). In doing so, they also realised that high purity argon could be produced simultaneously, thus eliminating the cumbersome step of reacting away the remaining oxygen with hydrogen at ambient temperatures.

Due to the high energy usage, there has been a quest over the past few decades to replace distillation with more energy efficient separation methods, such as membrane separations, or to use alternative sources of energy. When doing so, it is important to keep in mind the entire life cycle of the process, as well as the different forms that energy can take, i.e. heat versus work, and not just focus on the energy consumption in kW as the only indicator of energy efficiency (see Agrawal and Tumbalam Gooty, 2020). It is also important to not consider the chemical process in isolation, but to consider the overall impact based on a cradle-to-grave approach. We will not consider this in detail here, but some work is slowly starting to emerge on this important topic (e.g. Brondani et al., 2020).

In this work, we will discuss current means of reducing energy consumption in distillation, either through more energy efficient designs of a single distillation column, or by intensifying the process in different ways. Distillation is used in many different sectors and in many different forms, for instance short-path distillation for sensitive separations, distillation within food & drink, HiGee separation which is based on centrifugal forces, and micro-distillation as part of lab-on-a-chip (Sorensen et al., 2014). However, we will limit this discussion to chemicals production, within which the majority of large-scale, and energy intensive, applications fall. We will in particular consider the use of renewable energy sources as alternatives to fossil fuels for reboilers. There is a whole separate area of great importance, that of the use of renewal feedstocks for CPI, however, due to space limitations we will not consider these here, only mention that there is great activity both industrially and in academic research to generate products from bio-based feedstocks instead of from petrochemical sources (see Fig. 1). Finally, we will provide our thoughts for the future of this very important separation process, the crown jewel of CPI separations.

## 2. Energy efficiency in distillation

First and foremost, any distillation column needs to be properly designed and operated, meaning the column must have a sufficient number of stages to accomplish the separation at hand with a reasonable energy efficiency. Designers therefore typically target column operations with reflux ratios (RR) that are 20% higher than the minimum reflux ratio ($RR_{min}$); however, future designs will have to become more energy conscious, and where traditional fossil fuels are used, companies will need to receive incentives to lower the target $RR/RR_{min}$. If the incentives are based on balanced energy efficiency legislation such that the correct type of operation is targeted, the use of fossil fuels can be significantly lowered. Note that the optimum may differ where renewable power is available.

### 2.1. *Feed flashing and heat exchange*

Optimal design of distillation units requires optimal choices for the position and state of the feeds, which may include use of a feed-splitting vessel where two-phase feeds are split into vapour and liquid phases that are each directed to their respective optimal feed locations in the main column. Though more costly in terms of capital costs, such a design can provide more than a little gain in extra energy efficiency. This may sound trivial, but once the column is constructed these parameters are fixed, and can no longer be easily changed, at least not without involving an expensive revamp. Feed flashing also provides flexibility and larger margins to handle variations or, for the design of new processes, larger margins for small errors in the thermodynamic modelling. It may also make the column more robust towards feed changes over time (e.g. from an upstream reactor due to catalyst deactivation over time, or to long term catalyst improvements that increase yield and thereby change reactor effluents composition). Feed flashing is common in distillation of LNG that knocks-out the C2+ fraction in demethanisers. These cold columns also use pumparounds to cool the feed before it enters the column, thereby providing internal reboiling action and putting the operating line closer to the equilibrium by minimising exergy losses. Similarly, crude-oil pre-flash and pre-fractionation columns have also been shown to increase the energy efficiency of refineries (Ledezma-Martínez et al., 2018).

Energy requirements for distillation can be reduced by heat integration in various ways, e.g. by direct heat exchange between feeds and run-down, or by using pumparounds. The simplest example is the distillation of crude oil where the heat exchange is mainly between the feed and the pumparounds, i.e. the various run-down product streams. Of course, the higher the feed temperature, the more integrated these networks of inter-exchangers become to fully explore the heat recovery.

### 2.2. *Multi-effect distillation*

Further energy reductions can be obtained by means of integrating condensers and reboilers of two columns that operate at different pressures. The earliest example of this is the Linde two-column configuration for air separation where nitrogen in the high pressure column is condensed against oxygen in the low pressure column in an integrated condenser/reboiler (Kooijman, 2006). This concept is also used in *double-effect* or *multiple-effect distillation*, e.g. for the separation of water and ethylene glycol (EG). In a typical process plant, the ethylene oxide (EO) is diluted 20-fold in water to suppress side reactions in the reactor that would otherwise form higher glycols. The resulting reactor effluent therefore needs to be re-concentrated and this is done step-wise in terms of pressure (Kooijman and Taylor, 2014). Each concentrator's reboiler runs on the heat from the condenser of the preceding column, which operates at a higher pressure. A four or five-fold reduction of the separation heat can be

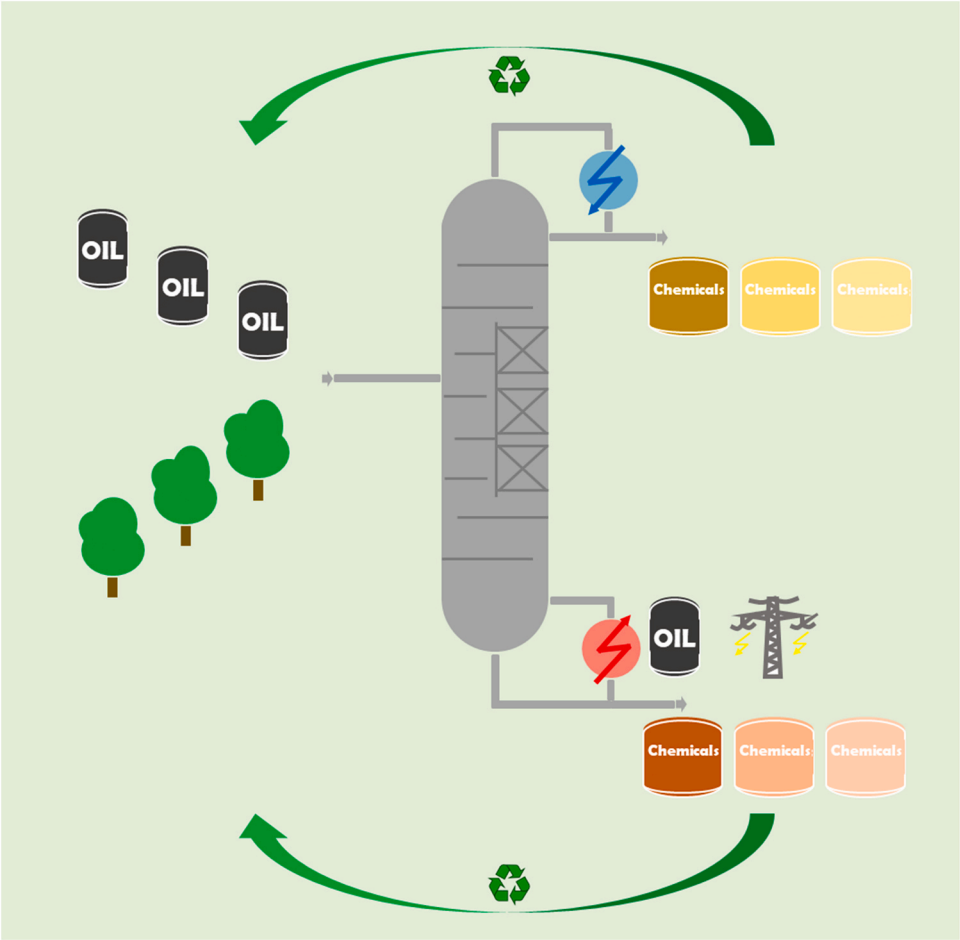


**Fig. 1 – Distillation process with feedstock from either fossil or renewable sources being converted into desired products using fossil fuel or electricity as energy sources, with the products being recycled as part of a cradle-to-grave approach.**

accomplished in this manner, although at the cost of increased capital cost.

Chiang and Luyben (1988) showed that we can apply the *Linde double columns* with combined condenser/reboiler concept to wide-boiling mixtures, by splitting the feed and distilling half of it in a low pressure column and the other half in a high pressure column. The pressure levels are then set such that the heat released in the high pressure condenser drives the low pressure reboiler. Energy savings of up to 40% are possible this way. Until now, this process was designed with two column shells but when this is done in a single column shell by applying a dividing wall over the complete height of the column, then additional capital savings can be realised.

### 2.3. *Vapour recompression*

The same principle can be used in low relative volatility separations where top and bottom products are close boiling, such as for propane-propene (PP) separation, where the overhead vapour is compressed and condensed at the bottom of these columns. We call this heat-pump assisted distillation or Vapour Re-Compression (VRC), and the ratio of heat generated in the reboiler over the amount of power that is input to the compressor, the recovery-factor. For PP splitters, this recovery-factor is roughly 8 and this is why nowadays the majority of PP splitters constructed are heat-pumped. Another classic application is the separation of ethylbenzene and styrene with a recovery-factor of about 3. Frequently, these splitters also deploy inter-reboilers to reduce the column diameter of the stripping section below the feed. In designing VRCs, the reflux is sub-cooled to ensure that the amount of flashing of the liquid reflux is minimised, as this would otherwise unnecessarily increase the vapour load to the compressor. Normally, VRCs are applied for close boiling separations to minimise the compressor ratio required. However, this does not have to be the case. In fact, high recovery-factors can be realized when the heat of vaporization of the overhead is larger than that of the fluid in the reboiler. For example, in the dehydrator of an Ethylene Glycol (EG) process plant, water is recovered overhead and a mixture of EG and heavier glycols in the bottom. When the overhead of such a vacuum column is compressed using dry vapour compressors then the resulting steam is so hot that it can heat-pump the reboiler, and a recovery-factor of 12 can be achieved. Dry compression is revolutionizing the industry and can be very large, see e.g. Impeller.net (2009). Though it is not always the best solution, these compressors are gaining more and more foothold in the CPI. Though they may require installation of a complete spare, they have many advantages over other types of vacuum equipment, such as liquid or steam jets and liquid ring pumps. As the compressor is also electrically operated, we foresee that cheap renewable power is also going to grow the application of these compressors further.

With the advent of cheaper renewable electricity, or stronger incentives given to switching to electric power, the number of VRC applications can be expected to rise, despite

the fact that compressors are expensive, less reliable, and they somewhat limit the turn-down capability of the column. Improvements in compressor technology can of course accelerate this.

### 2.4. Heat integrated distillation column (HIDiC)

The concepts of double-effect distillation and of vapour recompression can be integrated into a heat integrated distillation column (HIDiC) to further reduce energy consumption (Jobson, 2014). The unit has a high-pressure rectifying (top) section and a separate low-pressure stripping (bottom) section. As the temperatures in the rectifying section are thereby higher than those in the stripping section due to the use of different pressures, heat transfer between the two column sections is possible. The overhead vapour of the stripping section will need to be compressed to raise its pressure to that of the rectifying section, and this will require some energy; however, the reboiler and condenser duties can thus be significantly reduced, or even eliminated, especially if a feed preheater is used. Toyo Engineering in Japan were the first to prove this concept on an industrial scale, claiming above 50% reduction in energy consumption compared to conventional distillation with their discrete HIDiC, or D-HIDiC, also denoted SUPERHIDIC, arrangement (Wakabayashi et al., 2019, Toyo Engineering, 2022). The D-HIDiC has been applied to a commercially operated chemical plant at Maruzen Petrochemical Co., Japan, and has been in operation since 2016. The difficult hardware design and higher costs are currently preventing further industrial HIDiC implementations, although this may change if the design can be modularized.

## 3. Process intensification

Process intensification (PI) is a term used when referring to improvements or changes made to a process through the integration of two or more unit operations or through the combination of several physical or chemical phenomena within a unit in an attempt to make the process more profitable, more sustainable or inherently safer. The term became popular in the 1970's, although process intensification examples were found earlier than this. Brief overviews and history of process intensification can be found in the seminal textbook by Reay et al. (2013), as well as by Stankiewicz and Moulijn (2002). In relation to distillation, the main intensified processes, by far, are reactive distillation, dividing wall columns and to some extent hybrid separation processes, and more recently combinations thereof. In the following, we will consider some of the most recent trends for these important processes.

### 3.1. Reactive distillation

*Reactive distillation* (also called *catalytic distillation*) is perhaps the most successful example of process intensification. The interest in reactive distillation kicked-off around the 1990′s, with the most famous example being that of the Eastman-Kodak high-purity methyl acetate process which replaced a process consisting of a reactor followed by a number of separation columns with a single reactive distillation unit (Siirola, 1996). The main benefit of the reactive column is the integration of the reaction within the column shell, thus eliminating the need for a separate reactor, and often also the need for multiple downstream separation units. The integration saves both capital and energy costs, obtained through improvements in both reaction selectivity and reaction yield due to the simultaneous reaction and separation within a single vessel. The key challenge for the design and operation of reactive distillation is ensuring that the best windows of operation for the reaction and for the separation coincide, and that these overlap within a sensible temperature and pressure range.

Not all reactions lend themselves to reactive distillation, as the reaction must be fast enough to proceed towards equilibrium as the reactants move through the column. The boiling points of the reactants and products must also be such that these can easily be separated, typically but not necessarily, with one product over the top of the column and the other product through the bottom. The reactive distillation process can be homogeneous, either without a catalyst or with a liquid catalyst added as a feed or together with one of the reactants, or heterogeneous where the catalyst is integrated into the column internals in a specified section of the column, or both.

The interest in reactive distillation has been significant, and increasing, since the 1990′s. A recent Scopus search (August 2022) reported 2721 documents since 1990 with '*reactive distillation*' in either the title, mentioned in the abstract or as a keyword, with the majority, 2493 documents, of these since 2000. Of these, 1731 were journal articles, 479 were conference papers and 146 were book chapters. A separate google patent search found over 22,000 patents involving some form of 'reactive distillation' since 2000, but a great many of these never saw industrial application.

A number of the literature studies were related to quite specific processes or applications, whilst others focused on the more fundamental aspects of reactive distillation, considering the general impact of reaction or separation parameters on the overall process performance. Most studies have been motivated by a desire to reduce capital costs, operating costs (mainly in the form of energy demand), or both. Many of the studies are optimisation studies based on either minimising energy consumption or total annualised cost (TAC), with the latter providing a more comprehensive basis for comparison between different process alternatives.

Design of distillation processes is almost exclusively done based on computational tools, however, including a reaction within a distillation column poses challenges from a computational point of view due to fairly complex dynamics and the potential for multiple steady states as highlighted early on by Taylor and Krishna (2000). At the time the Eastman-Kodak methyl acetate process was developed, there were no commercially available simulation programmes capable of modelling reactive distillation, however, most process simulators today will have this option, e.g. AspenPlus or gPROMS Process. The use of these tools must nevertheless be approached with some caution, as use of standard equilibrium-based models may not capture the dynamics of fast diffusion effects associated with reactions, nor may reaction conversion and selectivity be adequately described without a non-equilibrium based model. In addition, initialisation, simulation, and above all optimisation, using these simulators remains a challenge from a numerical point of view due to the close interaction between the various phenomena, particularly if also considering a cost based objective function.

Most of the focus in the recent literature has been on the design aspects of the reactive distillation unit and the

associate operating parameters, i.e. in determining the required number of stages, the feed locations of the reactants (and potentially also the liquid catalyst if homogeneously catalysed), the reactive zone within the column (if heterogeneously catalysed), and the reflux ratio. Tsatse et al. (2021) recently presented a novel methodology for the simultaneous optimisation of design and operation of a complex reactive distillation process, considering a number of complex process alternatives including pre-/side-reactor, side-stripper, additional columns etc., based on a superstructure approach and considering a detailed cost-based objective function. Some authors have also considered catalyst selection and catalyst amount, which clearly also are key design decisions. Kroeze et al. (2021) presented a method to determine the minimum amount of catalyst needed to operate a heterogeneous reactive distillation, without requiring rigorous simulations or optimisations, and recommended that the actual amount of catalyst considered at the design stage should be six times this minimum.

Whilst many of the studies found in the open literature consider steady state design of reactive distillation, some also consider the rather more challenging aspects of operability and control. Reactive distillation is inherently difficult to control due to the high degree of interaction between the controlled variables, and due to the reduced number of degrees of freedom. A process which appears both feasible and attractive at steady state may prove to be a nightmare to operate, or may even be inoperable. Tsatse et al. (2022a,b) considered the impact of reaction and separation, as well as design parameters, on the controllability of reactive distillation processes. They systematically investigated the impact of uncertainty, whilst also considering the relevant control system and potential redesign of the column including additional ancillary equipment, with the aim to make the process more robust and to mitigate risk. Iftakher et al. (2021) considered a driving force approach to integrated design and control, and Iftakher et al. (2022) used this and another similar approach in their development of a computer-aided toolbox, which can be used to consider integrated design and control of general reactive processes.

Reactive distillation has found widespread use in industry over the past decades, as homo- and heterogeneously catalysed columns, packed and trayed, and with large diameters (i.e. > 4 m). Most of these were first tested at a pilot-scale plant. Scale-up challenges remain related to our fundamental understanding of the process, in particular, the interactions between reaction kinetics, residence time in the column internals, as well as catalyst behaviour and the interaction between reaction kinetics and the thermodynamic phenomena of the vapour-liquid equilibrium of the separation. Further experimental studies, which consider these phenomena and how they affect the design and subsequently the control of reactive distillation, are still needed. The design, including its associated control system must be flexible and robust enough to mitigate not only disturbances similar to that of a regular distillation column, but also modelling uncertainties at the design stage related to the reaction kinetics, which can be somewhat uncertain for new reactions, as well as uncertainties in fluctuating market demands. To achieve this, good experimental kinetic data is needed, as are simulation models of sufficient level of detail, and optimisation methods that can handle the numerical complexities in solution.

### 3.2. *Dividing wall columns*

The second most important process intensification method related to distillation is the use of a wall within the distillation column, separating the feed side of the column from a side-product removal side within the so-called *dividing wall column* (DWC), first described as a column in 1946 (Wright, 1946), but with a sequence involving a prefractionator suggested in a patent already in 1942 (Brugma, 1936) and also considered even earlier by Monroe (1935). Dividing wall columns have not attracted quite the same widespread academic interest as has reactive distillation, but is nevertheless widely used in industry with units existing today with diameters of over 6 m and heights of over 100 m (Olujic et al., 2009). Kaibel (2014) provided a very clear overview of these intensified systems, including a brief overview of its history since the first reported industrial unit at BASF in 1985. Kiss (2013) considered advanced distillation technologies, including extensive discussion of dividing wall columns, and Olujic et al. (2009) provided a nice overview of equipment improvement trends.

Dividing wall columns allow a ternary separation into three pure components to take place in a single column, which traditionally would have required two columns in series, either as a direct or as an indirect sequence. The middle-boiling component is removed as a side-stream from the product side of the wall, and the dividing wall ensures that this stream is not contaminated by the feed that enters at the opposite, or feed, side. The wall may be fixed or not within the column and is generally placed in the middle of the column, extending above and below the locations of the feed and the middle-boiling product side-draw. The liquid reflux is split between the two sides of the wall, with this split thereby becoming a degree of freedom. The vapour stream coming up from the bottom of the column is generally not controlled and will be split and rise up at either side of the wall depending on the pressure drop on that side. The pressure drop is a function of the location of the wall relative to the centre, and of the pressure drop caused by the liquid flow rates and the column internals on either side. Some authors have, however, nevertheless considered using the vapour flow as an independent degree of freedom (e.g. Hu et al., 2018). Chen and Agrawal (2020) presented a convenient classification method to classify dividing wall arrangements into five types based on three parameters: (1) the location of the ends of the dividing wall with respect to the top and bottom ends of the column shell; (2) the number of condensers and reboilers associated with the dividing wall; and (3) the number and type of transfer streams across the dividing wall.

The main benefit of a dividing wall arrangement is saving in terms of capital costs as only a single shell is needed, as well as an often significant saving in energy costs. Energy savings of up to 45% have been reported in some studies, depending on the feed concentration, the relative volatilities and the product purities. There are drawbacks with dividing wall columns, as with all good things, as the column must be operated at a single pressure due to the vapour transfer, whilst for a traditional direct or indirect sequence different pressures can be used in the two columns. The dividing wall column is also generally taller than either of the two columns in a traditional sequence.

A lot of academic work related to dividing wall columns has focused on the fundamental aspects of the heat integration and in considering the fundamental thermodynamic principles of the thermal coupling. The analysis is often made with reference to the behaviour of a *Petlyuk* arrangement (Petlyuk, 2004), which consists of a pre-fractionator without a reboiler or a condenser that is thermally coupled with a main column. This arrangement is thermodynamically equivalent to a dividing wall column. To make simulation and optimisation easier, most authors therefore consider the thermodynamically equivalent Petlyuk-based column sequences in their work as the heat duties will be the same.

As for reactive distillation, rigorous simulation of dividing wall columns can be challenging since no commercial software currently offers a dividing wall structure as part of their model library. A simulation must therefore be constructed, cleverly, based on individual column sections and reboilers/condensers. The thermal interactions within the dividing wall column make this a challenging numerical problem, which is exacerbated when also considering optimisation. Simulations of such column networks often fail even to initialise unless the initial values are quite close to a realistic design. For the same reason, deterministic optimisation methods often fail when the algorithm proposes a next optimisation step with unrealistic column dimensions or operation. This all became much easier with the advent of the free ChemSep LITE tool which includes the parallel column model of Zhou et al. (2018, 2019a,b). It runs as a CAPE-OPEN unit operation inside any compliant commercial software. This tool allows multiple dividing walls, as well as multiple condensers and reboilers. In the commercial version, the thermal interactions within the dividing wall column can also be included. The tool also allows the study of maldistribution and effect of pinches (Kooijman et al., 2022).

Design methods based on shortcut calculations have been considered to help with numerical challenges by providing initial estimates for key design variables when using rigorous computational software. A relatively simple visualisation method for finding the minimum total vapour flow was first presented by Halvorsen (2001). More recently, Duanmu et al. (2022) proposed a shortcut design method for complex distillation structures based on a simple optimisation procedure, which can be used even with Excel, to determine good starting points for rigorous design including for dividing wall columns.

Variations on the dividing wall column arrangement exist whereby the wall is placed either at the very top or at the very bottom of the column shell, and units such as these have been operated in industry since 2004 (Kaibel, 2014). These columns can be regarded as a single-shell alternative to a main column with an attached side column. The change in the wall position changes the thermal coupling from the classical two-way transfer in the regular dividing wall column to a one-way liquid-only transfer, sometimes referred to as *reduced-vapour dividing wall columns* (RV-DWC) (Agrawal, 2000). If the wall extends to the bottom, then two separate reboilers are needed, whilst if it extends to the top then two condensers are needed. It has also been proposed to have the wall extending all the way from the top to the bottom, thus requiring both two reboilers and two condensers, as well as a means of transporting material from the feed side of the unit to the product side. It is also possible to combine the reboilers and condensers, respectively, into a single heat exchanger unit serving both sides of the column (Agrawal, 2000). The reduce-vapour arrangements can be further enhanced by the use of vapour recompression, resulting in even lower total annualised costs (Duanmu and Sorensen, 2022).

The concept of dividing wall columns can be extended to more than three components by either adding more side streams, e.g. in the so-called *Kaibel* column for quaternary systems, or by adding additional walls within the unit in the so-called *Sargent* arrangement. A further extension of the two-wall arrangement, called an *Agrawal* arrangement, is having the feed entering between the two walls and with the two middle boiling components being withdrawn from one side each (Kiss, 2013). More complex arrangements have also been suggested, with these different variations of the dividing wall column combined with a smaller pre- or post-column.

As for reactive distillation, what looks good on paper in terms of the steady state design is not always easy to operate or control, so also for dividing wall arrangements. However, the reduction in degrees of freedom in dividing wall columns is generally not a showstopper in terms of performance, and dividing wall columns have been operating very successfully in industry for over four decades. Yildirim et al. (2011) provided a nice overview of control aspects related to dividing wall columns, and more recently, Villegas-Uribe et al. (2021) proposed control structures also for Kaibel, Sargent and Agrawal arrangements.

Lately, researchers have also considered highly intensified process arrangements of *reactive dividing wall arrangements*, whereby a reaction is taking place within the dividing wall column, mainly on the feed side of the wall. Such an arrangement is promising, as it can lead to very attractive process integration, but it has not yet been implemented on an industrial scale (Kaibel, 2014). Recently, however, Weinfield at al. (2022) presented a test system for a reactive dividing wall column including an experimental investigation of a laboratory scale unit. This, together with other similar studies, will hopefully pave the way for industrial acceptance also of these systems.

As for reactive distillation, dividing wall columns are now considered established process intensification technology in industry, providing excellent improvements in energy performance compared to traditional processes. Industrial penetration is still somewhat limited because few column internal vendors could provide the hardware, and process engineers do not routinely consider the technology during the initial design phase of new processes. This is to some extent because dividing wall columns are not part of most undergraduate teaching. Furthermore, few lab setups have been available for industry to test such concepts. This will change now that ample examples are available (Donahue et al., 2016, Preißinger et al., 2019, Kalita and Gentry, 2018, Kalita et al., 2018a,b), and simulation can be simplified with tools such as ChemSep. Still, the number of implementations will rise much more rapidly if new legislation provides incentives for revamping old units for better energy efficiency, or if it only allows new facilities with best-in-class operations. Challenges still remain in terms of the design of these units; however, wider usage is expected, in particular, of the more complex arrangements of different wall locations, for multi-component systems and for reactive systems, operations that offer even further scope for energy savings.

### 3.3. *Hybrid separation processes*

The final main process intensification method involving distillation that we will consider is that of hybrid separations processes. In a hybrid process, two different separation units are integrated together into a single process. What constitutes a hybrid is not always clear in the literature, however, we will use the definition recommended by Skiborowski and Gorak (2016): "*Hybrid separation processes are defined as the combination of at least two different, externally integrated unit operations, which contribute to one and the same separation task by means of different physical phenomena*". Hybrid separation processes are characterized by a mutual interdependency between the different unit operations within the design, where one unit operation overcomes the main limitations of the other(s). Hybrid distillation consisting of a distillation column and a membrane network is perhaps the most studied example of this form of process intensification, however, hybrids of distillation combined with crystallization, adsorption, liquid-liquid extraction or adsorption have also been suggested (Skiborowski and Gorak, 2016).

When considering azeotropic or close-boiling systems, separation using a single conventional distillation column is not possible and other methods such as azeotropic, extractive or pressure-swing distillation are required. These processes are fairly energy intensive as they generally require multiple columns. Hybrids of distillation and membranes have been suggested as process alternatives, with pervaporation or vapour permeation being the preferred membrane process. It should be noted that the hybrids of distillation with a membrane as discussed here is very different to the concept of *hybrid membrane distillation*. Membrane distillation is a thermally-based membrane process typically used to extract freshwater from various water sources (Naidu et al., 2020), i.e. does not involve distillation in the context considered in this paper.

In terms of simulation and optimisation, as for the other process intensification methods, adding a membrane network to the design problem increases the numerical challenges significantly due to the interactions between the two (or more) individual unit operations. Authors have often simplified the problem by ignoring the membrane network in terms of modules or stages, and either only considered a generic membrane area (Singh and Rangaiah, 2019), or have limited the number of membrane stages in series (Koch et al., 2013), with the optimal number of stages often considered manually. Recently, Chia and Sorensen (2022) proposes a superstructure optimization strategy for the optimal design of hybrid distillation/pervaporation processes, and discussed different solution alternatives for how to handle the integer nature of the membrane network. A similar approach was used by Chia et al. (2022) who found the hybrid dividing wall column to be comparable in terms of total annualised costs to standard hybrid distillation, but requiring less space.

The same way that reactive distillation has been considered within a dividing wall column, one may take the intensification even further and propose a *hybrid reactive dividing wall* arrangement. This arrangement has been considered briefly in the literature (Holtbruegge et al., 2015; Li et al., 2020). As for reactive dividing wall columns, the hybrid variation has also not yet been implemented industrially to our knowledge, but may be an attractive alternative in the future for certain separations.

## 4. Using electric power in the process industry

Above we have discussed different means of increasing the energy efficiency of distillation processes, both as standard columns, but also for intensified processes such as reactive distillation and dividing wall columns. We have, however, not considered from where the remaining energy that is required for reboiling in the columns is coming. Traditionally, all large-scale energy usage in industry has been based on fossil fuels, which is clearly a major contributor to greenhouse gasses and therefore should be reduced, and preferably eliminated. When renewable power becomes sufficiently and cheaply available, its lower price level may cause a demise in the use of conventional fossil fuels for reboiling. Though renewable power will not be available all the time, the surplus can be used within the chemical processes in a variety of modes: 1) To electrolyse water into hydrogen and oxygen; 2) To directly replace fossil fuels in steam boilers; 3) In electric heaters, or E-heaters, for hot oil loops or for molten salt loops; 4) In E-reboilers and feed E-heaters that act on the process fluids directly; or 5) replace steam drives for compressors with electrical drives.

Since the storage of chemical intermediates and products is often much more easily accomplished than storage of power, energy intensive production of industrial chemicals itself may even become an efficient means to 'store' surplus solar/wind power, as long as the production process has a large turndown ratio. Here, the turndown of reactors and distillation columns often limits applications, although we foresee a renewed interest in hardware with higher turndown for this reason.

Note that these uses will need to compete with other ways of storing renewable power, e.g. hydraulic storage (pumping water up to higher water reservoirs), charging lithium battery operated electric vehicles, and long distance transportation to areas with low production of renewable power. Furnaces and molten salt pose the most interesting uses for renewable power as they operate at high temperatures. In these high temperature applications, fossil fuels are less efficient when air is used instead of pure oxygen.

When water is electrolysed typically only the hydrogen is targeted. This hydrogen can be used as a direct replacement for methane or natural gas, e.g. in cracking furnaces, although many different further pathways are currently under evaluation, e.g. conversion to ammonia (which can be more efficiently stored as liquid than as hydrogen), but also to all kinds of chemical intermediates and hydrocarbons (that can also serve as fuels and/or oxygenates). Initial industrial electrolysers are currently under front end engineering & design (FEED) and expected to start in the near future (2023/24). The subsequent processes are still under development but we can expect a large number of different pathways to evolve. Which of these will become commercial successes is still hard to see, but many will require separations by means of distillation:

- **Electrolysis** could become much more efficient if the produced oxygen also finds a use, e.g. into an oxidative industrial process. In the past, the use of pure oxygen has improved the efficiency of many processes that deploy gas loops, e.g. in the production of ethylene oxide. It should be noted that storage of hydrogen involves an expensive

liquefaction step where a lot of energy is lost. As such, a swing mode operation, where the energy intensive chemical intermediates are only produced at times of power surplus, and drawn from storage at times of power shortage, is probably the better choice

- **Steam boilers** using electric electrodes are now well established. Saturated steam systems operating at 282 °C and 60 MW using 25 kV connection can run at 99% efficiency (e.g. see Parat (2022) or other vendors, and Ehresman, 2020). These electric boilers are much more compact than conventional systems, typically one-quarter to one-half the size of fuel fired boilers with similar output. In addition, they require no fuel storage; do not produce any pollution such as smoke, dust, or ashes; do not contain any moving parts; and are much more silent in operation. They have a larger turndown ratio than conventional boilers and can operate as low as a ten percent of output, avoiding inefficiencies and the need for steam blow-down. The absence of fuel residue simplifies the boiler cleaning, and nothing in the steam boiler is hotter than the steam itself.
- **Regular electric resistance heaters** using copper or nickel resistance wire insulated with magnesium oxide in protective tubing already have been widely applied. The exchanger can operate from as low as 100°C up to 260 °C. When more expensive nickel-chrome (80/20) alloy resistance wiring is used together with stainless steel tubing, temperatures of up to 650 °C can be handled. For low duties (< 1 MW) typically Low Voltage (LV, < 750 V) is used but to obtain high efficiencies, and for larger duties (< 12 MW), Medium Voltage (MV, < 6 kV) is required. Of course, tubing diameter must increase (OD to 15–22 mm) for a sufficient thick insulation layer. At low temperatures, life spans are typically 20 years. By switching individual elements on and off, exchangers can turndown to just a few percent of the normal duty. As such, a surplus in renewable electricity can be expected to drive the market of these exchangers for process plants into rapid growth.

Electricity surplus market conditions are still years away, and vendors should use this time to expand their experience with process fluids beyond water and heating oils. Though fouling is not a direct problem for the heating elements, these elements can create hot spots, and can pose safety risks without proper control. Not all vendors offer this, and life-span estimates may not be as long as projected. Vendor offerings are still limited, e.g. in maximum physical size for bundles such that larger duties can only be realized using parallel exchangers, negating the economies of scale in large plants. The ease of application is also hindered by the lack of electric exchangers in design software packages. As vendors are developing their exchangers, we foresee more industrial implementations. It is very likely that within a few years, the chemical process industry will have gained sufficient confidence to start applying electric heaters and reboilers on a more common basis.

## 5. Conclusions

Distillation has had a unique position in the chemical process industries for over a century, and it is expected that its importance as the separation process of choice for fluids will continue for a long time to come. Recent concerns over climate change have inspired industrial designers and academic researchers alike to look for more energy efficient and environmentally friendly distillation process.

Process intensification with reactive distillation, as well as dividing wall columns, have become common in new designs of petrochemical process plants. With typical fossil fuel savings ranging from 25% to 50% the potential for reduction in gas emissions contributing to global warming is too significant to not be exploited fully. Therefore, it is expected that even more advanced designs with multiple walls and/or reactive sections will soon find industrial applications to maximize the potential for energy savings.

Further down the road, the advent of surplus, cheap, renewable electric power will allow a more wide-spread use of, for instance vapour recompression in distillation, with potentially significant savings. The surplus power will enable direct and indirect electric reboiling, as well as running (more) compressors, thus allowing the chemical process industry to further decarbonise, in line with the current legislative climate change goals. As such, improvements in compressor reliability and electric reboiler design will play a significant role in materialising these savings.

Hand-in-hand with the industrial advances much go education. It is essential that energy efficiency becomes an integral part of any university separation course, and that tomorrow's engineers have a thorough understanding of the potentials for improvement that these more advanced distillation processes can offer. Methods such as the McCabe-Thiele's diagram are still important to explain distillation concepts, however, it is reactive distillation; dividing wall columns; hybrid processes; vapour recompression, and different energy sources that now needs to take centre stage in the undergraduate curriculum. It is unlikely that an undergraduate course will have sufficient space to teach the design of novel processes in detail, however, all future graduates should have a basic understanding of process intensification and energy efficiency and how this can be applied to distillation.

## Declaration of Competing Interest

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

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