

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/259539105>

# Distillation technology – still young and full of breakthrough opportunities

ARTICLE *in* JOURNAL OF CHEMICAL TECHNOLOGY & BIOTECHNOLOGY · APRIL 2014

Impact Factor: 2.35 · DOI: 10.1002/jctb.4262

---

CITATIONS

20

---

READS

289

## 1 AUTHOR:



[Anton Alexandru Kiss](#)

AkzoNobel

137 PUBLICATIONS 2,000 CITATIONS

SEE PROFILE

# Distillation technology – still young and full of breakthrough opportunities

Anton A. Kiss\*

## Abstract

Throughout history, distillation has been the most widespread separation method. However, despite its simplicity and flexibility, distillation still remains very energy inefficient. Novel distillation concepts based on process intensification, can deliver major benefits, not just in terms of significantly lower energy use, but also in reducing capital investment and improving eco-efficiency. While very likely to remain the separation technology of choice for the next decades, there is no doubt that distillation technology needs to make radical changes in order to meet the demands of the energy-conscious modern society. This article aims to show that in spite of its long age, distillation technology is still young and full of breakthrough opportunities. Moreover, it provides a broad overview of the recent developments in distillation based on process intensification principles, for example heat pump assisted distillation (e.g. vapor compression or compression–resorption), heat-integrated distillation column, membrane distillation, HiGee distillation, cyclic distillation, thermally coupled distillation systems (Petlyuk), dividing-wall column, and reactive distillation. These developments as well as the future perspectives of distillation are discussed in the context of changes towards a more energy efficient and sustainable chemical process industry. Several key examples are also included to illustrate the astonishing potential of these new distillation concepts to significantly reduce the capital and operating cost at industrial scale.

© 2013 Society of Chemical Industry

**Keywords:** heat pumps; HIDIc; dividing-wall column; membrane distillation; HiGee distillation; cyclic distillation; reactive distillation; case studies; industrial examples

## INTRODUCTION

Distillation is a physical process for the separation of liquid mixtures, based on differences in the boiling points or relative volatility of the constituent components. The art of distillation is believed to have originated in China (~800 BC) with early applications in the production of alcoholic beverages and the concentration of essential oils from natural products.<sup>1</sup> Over the centuries, the distillation technique was widely used, and the first books on this topic appeared in Europe – *Liber de arte distillandi simplicia et composite* (Das kleine Distillierbuch) by Hieronymus Brunschwig in 1500, *The Art of Distillation* by John French in 1651, and *La rectification de l'alcool* by Ernest Sorel in 1850.<sup>2</sup>

Originally, distillation was carried out batchwise by heating a liquid mixture in a still/pot and condensing the vapor that boiled off, by air cooling or water-cooled condensers (Fig. 1, left). Actually, distillation comes from the Latin word *destillare* that means 'dripping down' (condense), referring to the dripping of the condensed vapor product from the condenser. In the past century, distillation became the dominant separation process at industrial scale following the development of the petroleum and chemical industries. Presently, distillation is carried out mainly continuously (Fig. 1, right) in vertical hollow columns/towers, with associated piping, heat exchangers, pumps, storage vessels, support structures.<sup>3–6</sup>

Considering the product and feed streams, the separation by distillation requires a decrease of the entropy ( $\Delta S_{\text{dist}} < 0$ ) so it can not happen spontaneously. Consequently, addition of heat is used in practice to make this process thermodynamically possible. Still, the overall efficiency of distillation is rather low due to irreversible

(exergy) losses related to the pressure drop, mass transfer (e.g. re-mixing in separations) and heat transfer (at  $\Delta T > 0$ ):<sup>7–10</sup>

$$\Delta S_{\text{dist}} = (S_D + S_B) - S_F < 0 \quad (1)$$

$$dS = dQ/dT > 0 \quad (2)$$

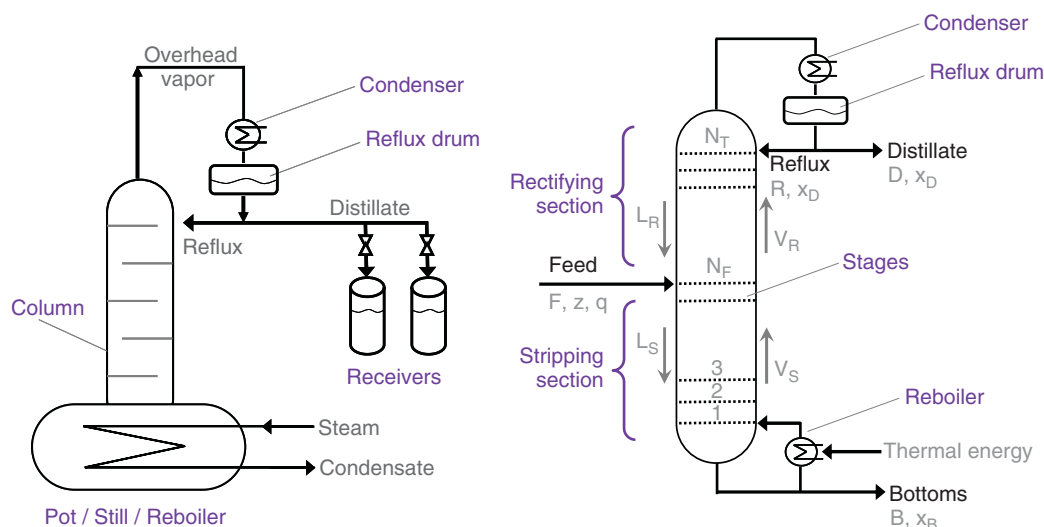
$$\eta = \Delta S_{\text{dist}} / (\Delta S_{\text{dist}} + \Delta S_{\text{irrev}}) \quad (3)$$

Currently, distillation is the most widely used separation method at industrial scale with over 40 000 columns in operation worldwide. Remarkable, almost every product on the market contains chemicals that went through a distillation column. Along with the conventional distillation of binary and multi-component mixtures, several additional methods were developed for breaking azeotropes or close boiling mixtures: pressure swing distillation (PSD), azeotropic and extractive distillation – topics covered in several books and reviews.<sup>3–6,11–18</sup>

Nowadays, the chemical process industry is undergoing a radical transformation towards higher energy efficiency, creation of value from waste, efficient valorization of water and materials, and eventually a truly sustainable bio-based economy. Process

\* Correspondence to: A. A. Kiss, AkzoNobel Research, Development and Innovation, Process Technology ECG, Zutphenseweg 10, 7418 AJ Deventer, The Netherlands. E-mail: Tony.Kiss@gmail.com

AkzoNobel Research, Development and Innovation, Process Technology ECG, Zutphenseweg 10, 7418 AJ Deventer, The Netherlands



**Figure 1.** Schematics of batch distillation (left) and continuous distillation column (right).

intensification (PI) technologies can drastically reduce the overall costs and improve the sustainability of many industrial processes, including distillation based separations. Process intensification is a process design philosophy that improves the process flexibility, product quality, speed to market and inherent safety, with the added benefit of reduced environmental footprint.<sup>19</sup> The main principles of process intensification were well described in the recent research paper of van Gerven and Stankiewicz,<sup>20</sup> as follows: 1 Maximize the effectiveness of intra- and inter-molecular events. 2 Give each molecule the same processing experience. 3 Optimize the driving forces at every scale and maximize the specific surface area to which these forces apply. 4 Maximize the synergistic effects from partial processes. These principles are not entirely new to chemical engineering, but in process intensification, they are seen as explicit goals aimed to be reached by intensified processes. Moreover, the PI interpretation of these principles often goes beyond the boundaries of the classical chemical engineering approach. A completely intensified process is successful in realizing all these process intensification principles, by making use of one or more fundamental approaches in four domains: spatial (structure), thermodynamic (energy), functional (synergy), and temporal (time).<sup>20</sup> In addition, it is worth noting that the PI technologies also adhere to the guiding principles for conceptual design of safe chemical processes, thus providing inherent safety or safety-by-design.

Freund and Sundmacher<sup>21</sup> claimed that knowledge of the existing apparatuses that perform unit operations immediately narrows our creativity in search for new solutions, and they proposed to shift from unit apparatuses to functions. A function (or a fundamental task) describes what should happen, and not how it should happen. Some examples of functions include: mass movement, chemical reaction, mixing, separation, heat transfer, phase change, temperature change, pressure change, form change, etc. An essential function is a function that is needed and unavoidable – e.g. if the feedstock is component A and the product is B, then chemical reaction is an essential function that is required. Notably, the functional based design of chemical processes consists of fewer steps, allows the efficient integration of more functions into one piece of equipment, and provides more freedom of equipment design – thus paving the way to engineering for sustainability.<sup>22</sup>

In the quest for a bio-based economy that poses new separation challenges (e.g. diluted aqueous solutions with azeotropes), hybrid PI technologies can lead the way to more efficient integrated distillation processes.<sup>6,23,24</sup> Therefore, we believe that in spite of its long age, distillation technology is still young and full of breakthrough opportunities, with many exciting developments going on. Note that this overview primarily cites key review papers and reference books – mainly for brevity reasons, but also to give the reader a good starting point for further reading on the topics presented here.

## PROBLEM STATEMENT

In spite of its wide use, distillation has also key drawbacks in terms of high capital costs, due to the large equipment used, and significant operating costs due to the low energy efficiency. In fact, distillation accounts for over 40% of the energy used in the chemical process industry and over 95% of the energy used in separation processes.<sup>10,25</sup> The main problem is the use of costly high quality energy (typically steam) that is rejected at a low temperature in the condenser. Practically, the thermodynamic efficiency of distillation is quite low: from 18% in air separation units, to 12% in crude units and only 5% for ethylene and propylene production.<sup>26</sup> Therefore, higher energy efficiency and lower costs are a must win battle for the players in the chemical process industry. Note that when discussing efficiency there are no unique answers, as the required minimum energy and the possible energy saving depends on operating pressures and temperature span. Moreover, the available heat and cooling sources within a particular chemical plant may also have an impact on the selection of the most suitable distillation technology.

Several developments of distillation aim to solve the problems related to the high investment and operating costs, by tackling various aspects: use of other energy sources (e.g. solar energy),<sup>27</sup> upgrade the discharged energy to use it for driving the reboiler (by heat pumps), use of high gravity forces to reduce the equipment size, combine distillation with reaction or other separations (membrane separation or distillation), use a different operating mode based on separate phase movement to increase the separation efficiency, or integrate more functions into a single operating unit.<sup>6</sup> This paper gives an overview of the recent

developments and the future perspectives of distillation, in the context of changes towards a more energy efficient and sustainable chemical process industry.

## ADVANCED DISTILLATION TECHNOLOGIES

The efficiency of distillation processes can be improved by using 'green' and 'smart' column designs. In addition to applying the principles of green design (e.g. efficient use of materials, energy and water conservation, safe and healthy surroundings), the smart designs consider approaches that use minimal resources (materials, feedstocks, energy, effort) over the process lifetime and that are also safe and environmentally sound.<sup>28</sup> The design of a distillation column and its internals typically involves a trade-off between capacity and efficiency. The smart design of distillation columns involves an approach on three levels:

- **Construction materials and resources.** Great care is taken to minimize the quantity of construction materials used, considering the cradle-to-grave resources consumed by the system, from the column construction through its lifespan. The columns are now constructed with the smallest diameter and lowest practical height. Moreover, the internals (trays and packing) are made as thin as possible, while meeting mechanical needs. Considering the long life of distillation columns (typically over 20 years), nowadays the equipment manufacturers and engineering companies strive to use as little material as possible over a lifespan that is as long as possible.<sup>28</sup>
- **Process design and configuration.** The focus of distillation is to obtain the highest yield with the least amount of energy. This can be achieved by sequencing of multiple columns, modifying the process configuration (e.g. heat integration, heat pumps, new heat-transfer media, other internals, optimized design and advanced control strategies). A review of stages vs energy (Fig. 2) – or column height vs diameter – is an integral part of the column design and configuration process.<sup>6</sup> The classic designs are located to maximize flexibility in design and operation, while reducing sensitivity to process changes. Smarter column designs

imply using more theoretical stages – practically possible within the same space by using more efficient internals – in order to reduce the energy usage by about 10–15%.<sup>28</sup>

- **Internal design optimization.** The physical and transport properties of column internals (e.g. packing and trays) have a strong effect on the column efficiency. The essence of a smart design is to take effective steps in order to maximize the efficiency of column internals and to get the most out of what is available.<sup>28</sup> Packing designs have fewer degrees of freedom than tray designs. After choosing the appropriate liquid distributor and packing type that is best for a particular process, one must determine the packing size that optimizes the bed height vs. column diameter. In the case of trays, the large number of variables that can be changed allows more flexibility in design. Often each set of operating conditions has a different optimal tray design.

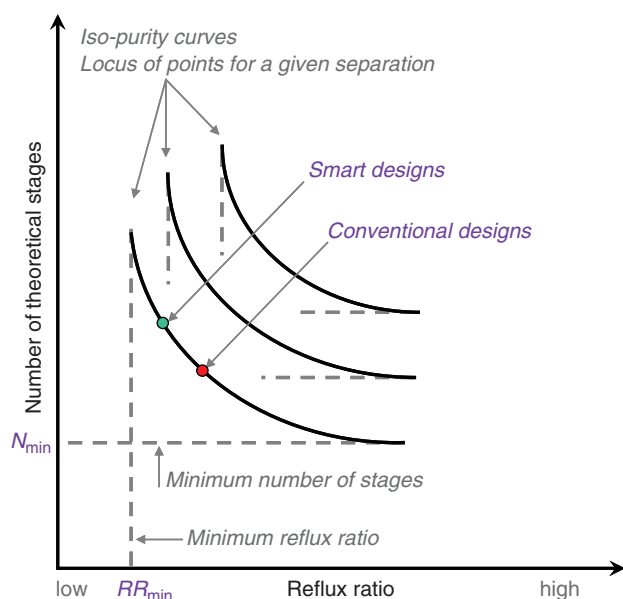
The following sections describe the advanced distillation technologies that were able to, or have the potential to make a strong industrial impact. Moreover, all these distillation technologies still undergo further developments in terms of process design, control and applications.

### Heat pump assisted distillation

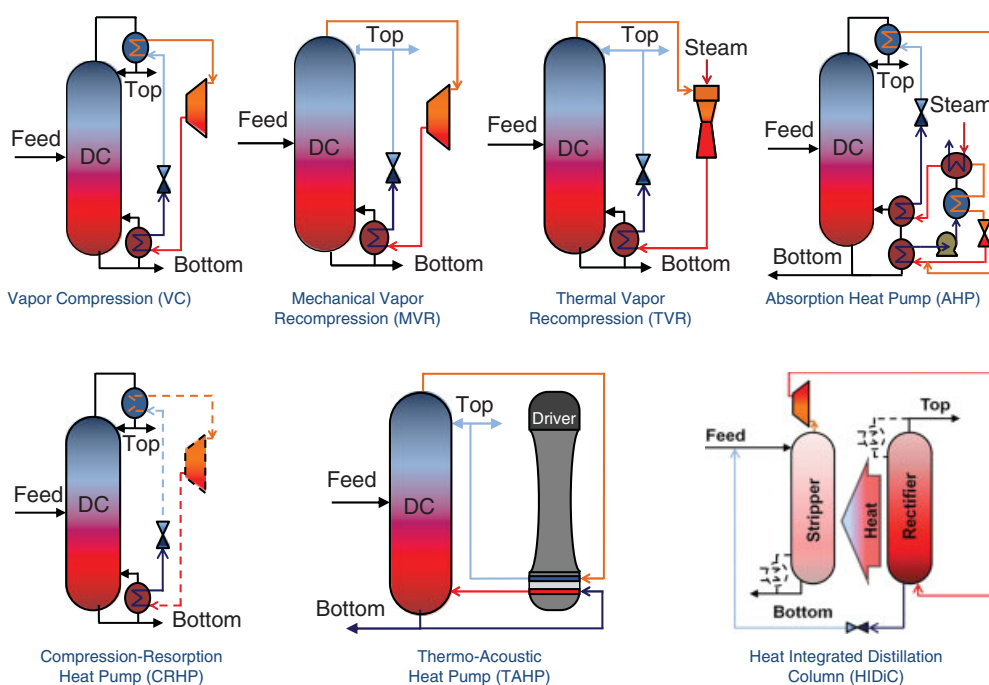
In order to perform the separation task, distillation requires the input of high quality energy in the reboiler while also rejecting a similar amount of heat at lower temperature, in the condenser. Several heat pump concepts have been proposed to upgrade the level of the energy discharged and re-use it in order to reduce the consumption of valuable utilities.<sup>29,30</sup> The temperature lift can be related to the temperature difference between the heat source (condenser) and heat sink (reboiler), which in turn is determined by the product cuts that are separated. In practice, the decision to use heat pumps for distillation should follow a careful investigation of heat integration opportunities based on Pinch analysis. Figure 3 illustrates the main configurations of heat-pump assisted distillation technologies, described hereafter.<sup>6</sup>

Vapor compression (VC) is a classical heat pump design proven already at industrial scale. It uses a specific fluid as heat transfer medium that runs between the heat source and sink through a pipeline.<sup>31</sup> A compressor is installed in between to provide the required work input, while a flash valve closes the cycle. Since all these elements are external to the separation process, the distillation column does not require major modifications, except for the adjustments in heat exchangers for the change in utilities. VC is particularly beneficial when dealing with corrosive or fouling compounds. However, the design is dependent on the ability of the heat transfer fluid to meet the operational, environmental and safety requirements. For most applications, there is no adequate alternative – and even when an acceptable working fluid is found, the energy savings are not always translated into overall economic savings.<sup>32</sup> Moreover, the compressors are quite expensive and hard-to-maintain equipment, and the inefficiencies in obtaining mechanical energy (work) impact heavily the total energy costs.<sup>29</sup>

Mechanical vapor recompression (MVR) is a state-of-the-art industrial system for binary distillation, being widely applied in separation of close boiling components.<sup>33</sup> In such a system, the top vapor is used as heat transfer medium, being fed directly to the compressor. Accordingly, the heat pump also performs the function of the condenser, thus saving one heat exchanger compared with the classic alternative. Moreover, it avoids the need to cool the heat transfer fluid below the boiling point of the



**Figure 2.** Trade-off between capital (stages) and operating (reflux ratio, energy) costs.



**Figure 3.** Heat pump assisted distillation (HPAD) – main configurations.

top product – an issue of importance in the VC scheme for heat transfer purposes. Notably, MVR features slightly higher efficiency and lower investment costs than VC. But MVR does not tackle directly the main drawback of VC: the economic penalty of using a compressor. Similarly, the distillate still has to meet at least the operational requirements for the heat transfer medium, not to mention the criteria for safe and economic compressor operations. Consequently, all these constraints severely limit the application window of MVR technology.

Thermal vapor recompression (TVR) is a variant of the MVR, in which the compressor is replaced by a steam ejector as work input mechanism. The steam ejector uses the Venturi effect to obtain mechanical energy from steam injection into a special variable diameter pipeline.<sup>34</sup> This makes TVR a robust design with reduced capital and maintenance expenditures, as there are no rotating pieces involved – hence it comes as no surprise that TVR has been widely implemented in industry. However, the steam ejector has a relatively low efficiency in converting mechanical energy. Moreover, the design of the steam ejector is crucial in achieving economical operation. There are large changes in steam consumption even at small deviations from the optimal operating point. Notably, the steam input is mixed with the distillate to generate the required pressure. As steam is being added to the vapor distillate, it is clear that the applications of TVR are mostly used for systems producing water as top product. In theory, the motive fluid for the ejector can be (part of) the distillate flow, which could be boiled and used to pressurize the vapor to the pressure level required in the reboiler. Nevertheless, such applications are rarely encountered due to the potential heat transfer losses. An alternative to MVR and TVR is the self-heat recuperation technology, but adding two compressors leads to very long payback times.<sup>29</sup>

Absorption heat pump (AHP) considers thermo-chemical conversion to enhance operational efficiency. In this case, absorption pairs are used as heat transfer fluids (e.g ammonia and water, or lithium bromide and water). AHP is a known cycle, widely applied in refrigeration – but there are also standalone (pilot plant)

implementations of AHP suitable for distillation or multi-stage evaporation processes.<sup>29</sup> The key unit of AHP is the steam driven desorber that separates the absorption pair. One of the components condenses in the reboiler of the distillation column, and then it is flashed to cool down the condenser. Afterward, it is mixed with the other component from the regenerator, to deliver heat in the reboiler through exothermic absorption. The resulting liquid is then pressurized and heated to displace the equilibrium and the whole cycle is repeated. AHP is preferred as it avoids the drawbacks of using a compressor as driver for the heat pump. However, the use of five heat exchangers gives AHP a very pricy installation cost and therefore long payback times.<sup>35</sup>

Compression–resorption heat pump (CRHP) – also called hybrid heat pump – is a recent approach used to take advantage of thermo-chemical sorption processes. CRHP can achieve high temperature levels and lifts, with relatively high coefficient of performance (COP). Note that the COP is defined as the ratio between the amount of heat upgraded ( $Q_b$ ) and the HP energy requirements ( $W$ ):  $COP = (Q_b / W) \leq (T_{reb} / \Delta T_b)$ . CRHP uses the VC scheme in which the working fluid is replaced by an absorption pair.<sup>29</sup> When the vapor zeotropic mixture approaches the reboiler, the condensation and absorption process run at the same time, thus enhancing the heat transfer. This gives CRHP enhanced overall efficiency and reduced energy requirements – a critical issue for economic operations over wider temperature ranges. After the reboiler, the rich mixture is then flashed to take heat from the condenser, evaporating both components from the working pair. The evaporation in the desorber is incomplete so that solution recirculation between the desorber and the resorber and/or wet compression is possible. The hybrid wet compression (HWC) term is used for the cycles where all the solution is sent to the compressor avoiding the use of a solution pump. Nonetheless, solving the issue of wet compression is of crucial importance for the wider implementation of CRHP. At the moment, the issue is still under research at TU Delft (NL), with already successful pilot scale implementations of standalone CRHP in place.<sup>29,30</sup>



The advantages of CHRP are related to the use of environmentally-friendly refrigerants – such as water, ammonia and CO<sub>2</sub> – that can significantly contribute to the improvement of the performance of heating processes. Specifically for industrial heating processes CHRP allows energy performance gains of more than 20% as compared with VC. The use of a mixture allows lower pressure levels, and condensation and evaporation at gliding temperatures – which can result in higher efficiency. Wet compression has the effect of suppressing vapor superheating, and it can also improve the heat pump efficiency. Ammonia–water mixtures can be used as efficient working fluids in CHRP, showing a number of advantages: higher COP because of the use of non-isothermal phase transition of the mixture in the heat exchangers at constant pressure; the mixture allows the achievement of high temperature operation at relatively low operating pressures; the cycle can be designed to show a temperature glide in the resorber that corresponds to the temperature glide of the industrial flow that has to be heated; and for specific operating conditions the performance is significantly better than for the vapor compression cycle.<sup>29,30</sup>

Thermo-acoustic heat pump (TAHP) is the frontrunner in using a different mechanism for the work input. Although it is a relatively new technology, the proof-of-principle stage has been successfully completed – with scaling up currently undergoing intense efforts at ECN.<sup>29,36,37</sup> TAHP features a wide applicability range, much larger than other heat pumps. Basically, TAHP is a

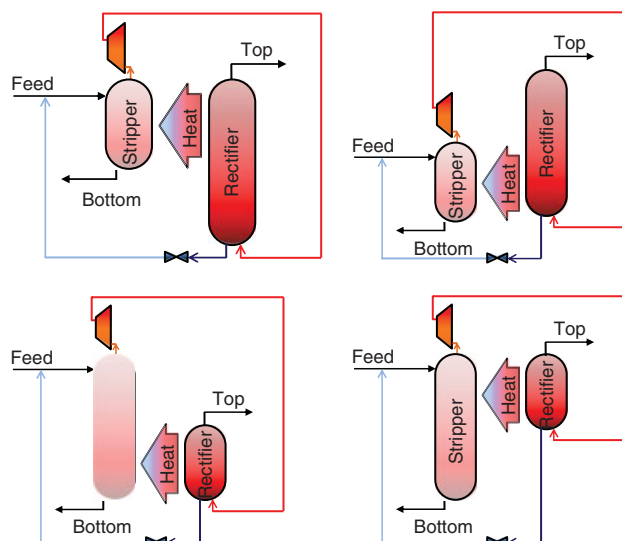
thermo-acoustic device that uses high-amplitude sound waves to pump heat from one place to another.<sup>38,39</sup> The TA device consists of heat exchangers, a resonator, and a regenerator (on traveling wave devices) or stack (on standing wave devices). Depending on the type of engine, a driver or loudspeaker might be used as well to generate sound waves. To limit the space used, an electric driver (linear motor) generates the acoustic power cased inside a resonator, the temperature lifts being determined by the size of resonator, as well as the properties and pressure of the acoustic medium. The resonator – housing the TA engine and the TA heat pump – determines the operating frequency, acts as a pressure vessel and it transports the acoustic power between the components.<sup>37</sup> The noise levels are similar to the current industrial standards (e.g. below 85 db), and since the medium used is a gas (air, noble gas – e.g. helium), the system complies with the safety and environmental regulations, while having no limitations in its applications – it can be applied down to cryogenic temperatures, with temperature lifts of up to 100 °C or even more.<sup>36,40,41</sup>

The most important applications of heat pumps at pilot and industrial scale are listed in Table 1,<sup>6</sup> while many others are reported in the literature. Major benefits are possible in terms of primary energy savings, and total annual costs – in the range of 20–80%.<sup>29</sup> Recently, a comparison of heat pumps and a technology selection scheme were reported, taking into account not only heat pump assisted technologies but also other energy efficient distillation technologies.<sup>29,30</sup>

**Table 1.** Efficiency indicators of heat pump assisted technologies<sup>29</sup>

Technology	Separation task	$\Delta T_b$ [K]	$\Delta T_{lift}$ [K]	COP	PES [%]	$\Delta TAC$ [%]	Remarks
AHP	Butane-Isobutane	15	25	1.9	47	–42	PBT = 0.9
AHP	Water-Acetic acid	55	65	1.7	40	–12	PBT = 7.1
CHRP	Steam production	10	30	9.1	78	–	–
CRHP	Benzene-Toluene	30	<30	8.3	76	–	–
HIDIC	n-pentane-cyclo-pentane	9	20	10.3	71	–	–
HIDIC	Cyclohexane-n-heptane	17	33	9.6	75	–62	PBT = 1.8
HIDIC	Propane-Propylene	7.7	10.9	10.0	80	–72	PBT = 1.2
HIDIC	Methanol–water	35	55	12.9	41	–	–
HIDIC	Benzene-Toluene	30		4.0	46	–46	PBT = 0.9
HIDIC	Acetic acid dehydration	35	55	3.2	27	–	–
MVR	1butene-nbutane	10		5.5	63	–60	PBT = 0.6
MVR	Propane-Propylene	7.6	11.8	–			–60% CO <sub>2</sub>
MVR	Benzene-Toluene	30	35	6.7	70	–	–
MVR	Butane-Isobutane	15	20	6.4	69	–63	PBT = 1.1
MVR	Butane-Isobutane	12.9	35.8	7.2	72	–64	PBT = 0.3
MVR	Propane-Propylene	7.7	24.9	7.5	73	–65	PBT = 1.4
MVR	Acetic acid dehydration	35	55	8.4	50	–	–
MVR	Methanol–water	35	40	6.6	69	–67	PBT = 0.7
TAHP	Methanol–water	35	45	2.0	0	–	–
TAHP	Methanol–water	35	55	2.3	14	–	–
TVR	Methanol–water	35	40	1.1	23	–19	PBT = 1.5
VC	Methanol–water	35	45	3.0	33	–29	PBT = 2.5
VC	1butene-nbutane	10	20	6.2	67	–57	PBT = 1.6
VC	Methanol–water	35	45	4.1	50	–	–
VC	Methanol–water	35	55	3.1	34	–	–
VC	Methanol–water	35	43	5.0	60	–57	PBT = 0.9

Primary energy savings (PES) are the yearly savings of primary energy compared with the primary energy requirements of a conventional column; PBT is the simple payback time (assuming a plant lifetime of 10 years; primary energy cost = €30 MWh<sup>–1</sup>; electrical energy cost = €65 MWh<sup>–1</sup>; boiler efficiency = 0.85; efficiency of electricity conversion = 0.42; investments as proposed in papers). Negative  $\Delta TAC$  means savings;  $\Delta T_b$  is given at the pressure reported in the reference.



**Figure 4.** Heat integrated distillation column (HIDiC) – alternative configurations.

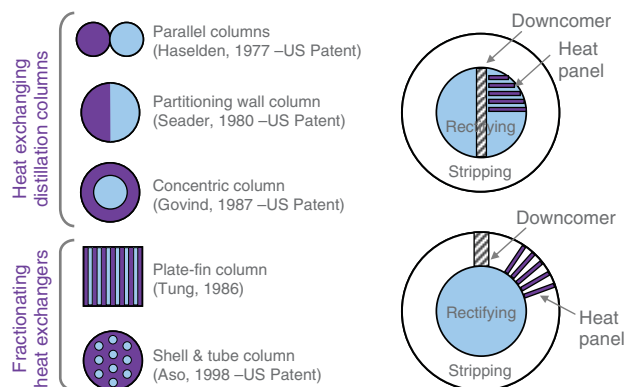
### Heat integrated distillation column

The heat integrated distillation column (HIDiC) is the most radical approach to heat pump design, making use of internal heat integration.<sup>42–47</sup> Instead of using a single point heat source and sink, the whole rectifying section of a distillation column becomes the heat source, while the stripping part of the distillation column acts as a heat sink – thus providing greater potential for energy savings.<sup>29</sup> Moreover, the problem of different sizes for rectifying and stripping sections can be conveniently tackled by using one of the alternative HIDiC configurations – as illustrated in Fig. 4.<sup>6</sup>

The internal heat integration enhances the reachable coefficient of performance, because the required temperature difference for heat transfer is kept low with gliding temperatures across both parts. The work input is provided by a compressor installed at the top outlet of the stripper section, while the heat pump cycle is closed by the valve flashing the liquid bottom outlet of the rectifier section. The practical success of HIDiC technology relies on good hardware performance for both heat and mass transfer tasks, at the same time.<sup>8,48</sup>

Although HIDiC claims among the highest energy savings possible in distillation, the capital investment costs are higher than for conventional distillation – mainly due to the use of an additional compressor and a more complex configuration required for the enhanced heat transfer.<sup>45</sup> Both thermodynamics and bench-scale experimental evaluations proved that HIDiC has much higher energy efficiency than conventional distillation columns for close-boiling components separations. Several simulation studies and experimental evaluations have further confirmed that the process can be operated very smoothly, with no control difficulties.<sup>48,49</sup>

A number of important issues must be considered during the HIDiC design, for example, flexibility to changes in the operating conditions, influence of an impurity or a third component, and process dynamics and operation. These impose strict constraints on the energy efficiency that can be potentially achieved by a HIDiC system. Therefore, trade-off between process design economics and process operation appears to be very important and it has to be carried out with great caution. It is worth noting that among the design and the operating variables, the compression ratio and the heat transfer coefficient and area ( $U$  and  $A$ ) are the ones that most



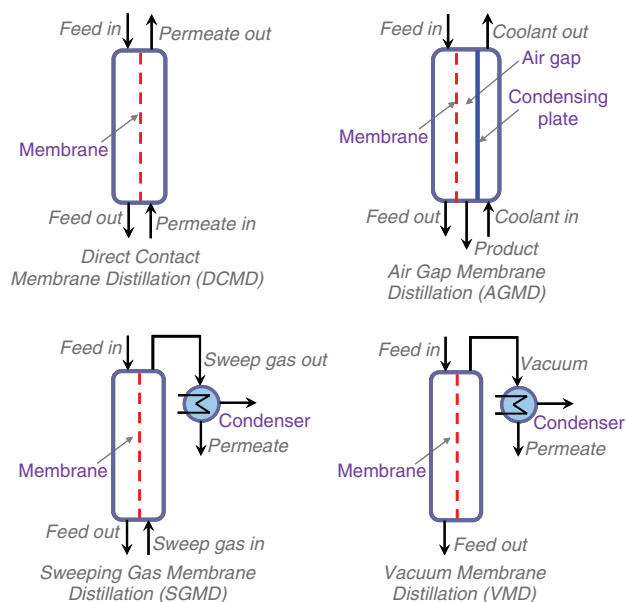
**Figure 5.** Proposed configurations for HIDiC (left). Placement of heat transfer panels in the rectifying or stripping section of a HIDiC (right).

affect the performance of a HIDiC. Consequently, an important research task during recent years was the development of more appropriate configurations, such as: multi-tube and multi-shell, plate-type or even structured-packing HIDiC.<sup>45,47,48</sup> The current directions of development are illustrated in Fig. 5:<sup>6</sup> fractionating heat exchangers (shell-and-tube, plate-fin), or heat exchanging distillation columns (e.g. concentric columns, parallel columns, partitioning-wall columns). Moreover, research and development on HIDiC configurations has so far primarily been confined to the separation of binary mixtures. Considering that multi-component mixture separations represent a major application of distillation columns, the development of a corresponding HIDiC technology is an important and extremely challenging topic for future work – especially if HIDiC becomes associated with other technologies – such as dividing-wall column or reactive distillation.<sup>6</sup>

### Membrane distillation

Membrane distillation (MD) is an emerging technology for separations typically performed by conventional processes such as distillation or reverse osmosis (RO). Compared with other membrane technologies, in the case of MD the driving force is the difference in vapor pressure across the hydrophobic membrane, rather than the total pressure.<sup>50</sup> Even though other membrane separations are applied in the petrochemical industry,<sup>51</sup> membrane distillation is especially useful for applications involving bulk water removal, such as seawater and brackish water desalination, process water treatment and water purification.<sup>52–55</sup> Similar hybrid separation methods based on membrane technology are pervaporation (also known as pervaporative separation) which is used for the separation of mixtures of liquids by partial vaporization through a (non-)porous membrane, and vapor permeation (also called imbibing) which is the penetration of a vapor permeate through a solid.<sup>56</sup>

Membrane distillation is a thermally-driven separation process possible due to phase change. The liquid feed is in direct contact with one of the membrane sides and does not penetrate inside the dry pores. Basically, the hydrophobic nature of the membrane prevents the hydrophilic liquid from entering the pores due to the presence of surface tension forces. Consequently, liquid–vapor interfaces are formed at the entrance of the membrane pores. The driving force of membrane distillation is the trans-membrane vapor pressure difference (which relates to a temperature difference) between the porous hydrophobic surfaces of the membrane. Membrane distillation is actually claimed to be a rather cost effective separation process when alternative sources



**Figure 6.** Membrane distillation configurations.

of energy (geothermal and solar) or waste water are used.<sup>57,58</sup> The most common technologies are shown in Fig. 6 and described hereafter.<sup>55,59,60</sup> Note that the components that pass through the membrane are known as permeate, while the components that do not pass through are known as retentate.

#### Direct contact membrane distillation (DCMD)

The hot solution (feed) is in direct contact with the hot membrane side surface, so evaporation takes place at the feed membrane surface. The vapor is transported to the permeate side due to the vapor pressure difference across the membrane, and condenses inside the membrane module. Since the membrane is hydrophobic, the feed cannot penetrate the membrane (only gas phase exists inside the membrane pores). DCMD is the simplest and most studied configuration. However, the heat lost by conduction through the membrane is higher than in other configurations. Practically, DCMD is best suited for applications in which water is the major permeate component, and where the aqueous solution does not contain non-volatile components.<sup>61</sup> Among all the membrane distillation configurations, characterized by the mode of vapor recovery in the permeate side, DCMD is the simplest to operate and the distillation process can be carried out in any desired membrane configuration, e.g. flat sheet, spiral wound, capillaries or even hollow fibers.<sup>55,60</sup>

#### Air gap membrane distillation (AGMD)

The evaporator channel is similar to that in DCMD, whereas the permeate gap lies between the membrane and a cooled walling and is filled with air. The feed solution is in direct contact with the hot side of the membrane surface only. Stagnant air is introduced between the membrane and the condensation surface. The vapor crosses the air gap to condense over the cold surface inside the membrane cell. Since the permeate fluids are not in direct contact with the membrane surface, AGMD can be applied to remove volatile components from aqueous solutions. Also, by placing an air gap between permeate side and condensing surface, the conductive heat transfer resistance is increased, so less heat is lost. The trade-off is the increase of mass transfer resistance, thus AGMD fluxes are

typically lower than for other membrane distillation configurations. In addition, AGMD is more versatile than DCMD because permeate is condensed on a chilled surface, and not directly by the 'cold' permeate. While in the DCMD configuration the permeate must be diluted to prevent membrane wetting, in the case of AGMD the concentration of the condensed permeate is not a concern since it does not come into contact with the membrane.<sup>50,62</sup>

#### Permeate-gap membrane distillation (PGMD)

This membrane distillation configuration is an enhancement of DCMD, in which a third channel is introduced by an additional non-permeable foil.<sup>62</sup> A key benefit of PGMD is separation of the distillate (permeate) from coolant, as the permeate channel is separated from the condenser channel by a condensation surface. As a consequence, the coolant can be any other liquid, such as cold feed water. Practically, this offers the opportunity to integrate PGMD with an efficient heat recovery system. Compared with DCMD, the PGMD configuration uses the feed water directly as cooling liquid inside the module, thus it requires only one heat exchanger to heat the feed before entering the evaporator.<sup>62</sup> Still, a drawback of PGMD is the low flow velocity of the distillate in the permeate gap, as it leads to poor heat conduction from the membrane surface to the condenser wall. Compared with AGMD, a higher surface related permeate output is achieved as the mass flow is not additionally inhibited by the diffusion resistance of an air layer.<sup>63</sup>

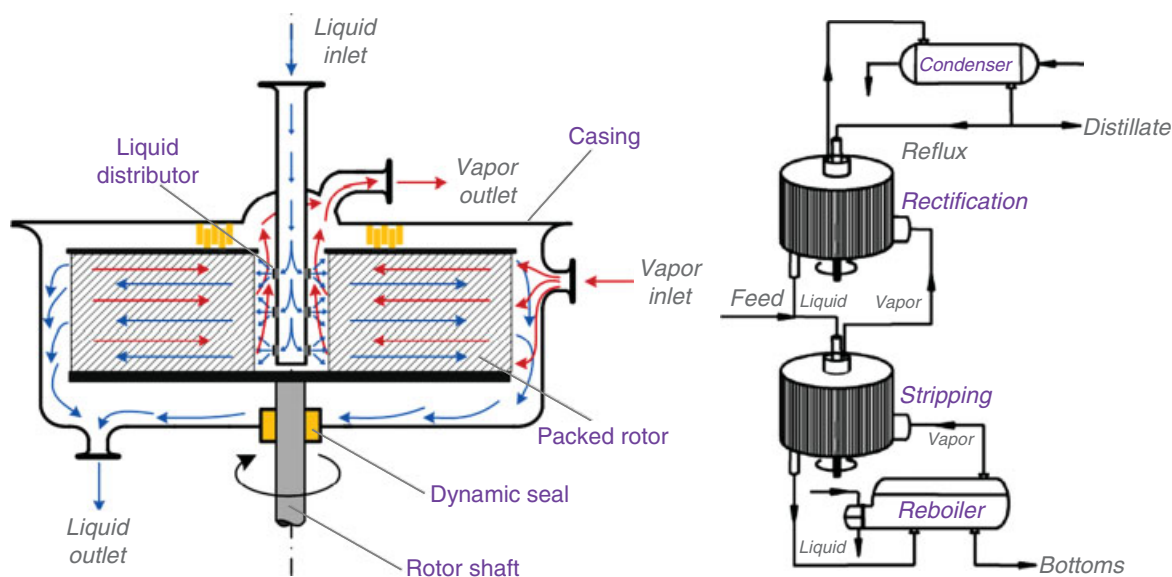
#### Sweeping gas membrane distillation (SGMD)

Also known as air stripping, SGMD uses a channel configuration with an empty gap on the permeate side (same as in AGMD). An inert gas is used to sweep the vapor at the permeate membrane side to condense outside the membrane module. Just as for AGMD, there is a gas barrier to reduce the heat loss, but this is not stationary – this enhances the mass transfer coefficient. The SGMD configuration is very useful for removing volatile compounds from aqueous solutions, but the main drawback is that a small volume of permeate diffuses in a large sweep gas volume, thus requiring a large condenser.<sup>55,60</sup> The SGMD process combines the low conductive heat loss of AGMD with the reduced mass transfer resistance of DCMD. In addition, AGMD and SGMD can be combined in a process called thermostatic sweeping gas membrane distillation (TSGMD). The increase of the gas temperature can be minimized by using a cold wall in the permeate side. The inert gas circulates at almost constant temperature in the cold chamber and collects the vapor that permeates through the membrane.<sup>62</sup> Vapor is partly condensed over the condensation surface (AGMD), the rest being condensed outside the cell by an external condenser (SGMD).

#### Vacuum membrane distillation (VMD)

VMD is based on an air gap channel configuration. The vapor passes through the membrane, and then it is sucked out of the permeate channel (using a vacuum pump) and condenses outside the module, just as in the SGMD. The heat lost by conduction is negligible, and this is considered a great advantage.<sup>50,55,64</sup> Note that the VMD process is similar to and often confused with pervaporation.<sup>65</sup> The key difference between these technologies is the role played by the membrane in the separation. For VMD membrane wetting is avoided, whereas for pervaporation the transport is based on a solution-diffusion mechanism and the membrane is thus preferentially wetted by one of the components. VMD can be applied to remove organic components from aqueous solutions.<sup>50,55</sup>





**Figure 7.** Rotating packed-bed (left) and HiGee distillation using RPB (right).

#### Vacuum multi-effect membrane distillation (V-MEMD)

This is a more integrated membrane distillation configuration that can provide similar energy savings as multi-effect distillation (MED) at lower investment costs, while being applicable also at smaller scales.<sup>64</sup> A typical module (e.g. the *memsys* brand V-MEMD) consists of a steam raiser, evaporation–condensation stages, and a condenser. Each stage recovers the heat of condensation, providing a multiple-effect design. Distillate is produced in each evaporation–condensation stage and in the condenser.<sup>64</sup>

The selection of a certain type of membrane distillation configuration depends upon the flux, volatility and the permeate composition. SGMD and VMD configurations are usually used to remove volatile organics or dissolved gases from aqueous solutions, while AGMD (most versatile MD configuration) and DCMD (least equipment and simplest to operate) are best suited for applications where water is the permeating flux.<sup>55,60</sup> In all membrane distillation configurations, water and the volatile solute evaporate from the liquid–vapor interface on the feed side of the membrane, then diffuse and/or convect across the membrane, being afterwards condensed or removed from the membrane module as vapor on the permeate side. Note that in all membrane distillation configurations, there are several membrane parameters affecting the processes: membrane material (e.g. polypropylene, polyvinylidene fluoride and polytetrafluoroethylene), liquid entry pressure (wetting pressure), membrane thickness, membrane porosity, pore size and pore tortuosity, as well as thermal conductivity – see also the recent reviews.<sup>54,55,59,60,62</sup> Moreover, membrane distillation may also result in a dramatic increase of the contact area between the two phases, usually exceeding an order of magnitude compared with conventional distillation contactors.

#### HiGee distillation

The essence of HiGee technology is replacing the gravitational field by a high centrifugal field achieved by rotating a specially shaped rigid bed, typically a disk with an eye in the center. The higher mass-transfer coefficients and higher flooding limits allow the use of high surface-area packing. In this way, the momentum, heat and mass transfer can be tremendously intensified.<sup>66</sup> Practically,

HiGee distillation uses the rotating packed bed (RPB) concept in a high-gravity field (100–1000 *g*) technology – claiming HETP values as low as 1–2 cm, about 3–6 times higher throughput and an equipment volume reduction of 2–3 orders of magnitude lower compared with that of conventional packed columns.<sup>19,67–70</sup>

Figure 7 shows a schematic diagram of a typical rotating packed bed with a vertical axis,<sup>71</sup> usable in a distillation setup.<sup>70</sup> The rotor is an annular, cylindrical packed bed housed in a casing and driven by a motor. The rotor is made up of diverse porous media, such as wound wire mesh, foam metal, and corrugated sheet metal. The liquid is fed onto the packing at the inner periphery, through a stationary distributor located at the eye of the rotor, and it flows over the packing radially outward by virtue of the centrifugal force as thin films, rivulets and droplets, or films covering the pores of the packing – depending on the type of packing, the gas/liquid flow rates, and the angular velocity. The liquid leaves the packing as a shower of droplets, which is collected by the casing wall and runs downwards along the walls by the action of gravity, leaving the casing. The gas/vapor is tangentially introduced into the casing, entering the packing at the outer periphery, and is forced to flow radially inward countercurrent to the liquid by pressure driving force. The gas leaves the packing at the eye of the rotor through the outlet pipe.<sup>70</sup>

The main component of HiGee devices is the rotor, the structure of which determines the characteristics of different devices. A brief description of the types of rotating beds is given hereafter:<sup>19,67,68</sup>

- Waveform disks – The rotor contains a series of concentric waveform disks that were developed to reduce the gas flow resistance. Besides the surface area of the disk, this type of rotating bed can utilize the extended interfacial area generated by atomization.
- Helical rotating bed – A helical rotating bed features four spiral blades installed on a rotating disk. Due to its small contact area, the mass transfer efficiency is still lower as than a RPB, in spite of longer flow channel and residence time of gas and liquid.
- Multistage spraying rotating bed – A multistage spraying rotating bed is similar to the cross-flow RPB, with the rotor comprising multiple concentric packing rings. In the spraying

zone, the liquid is sprayed into fine droplets with a large interfacial area. Despite lower gas frictional resistance, its drawback is potential liquid entrained by gas flow.

- Rotating packed bed with blade packing – A reported packing consists of 12 blades arranged within the RPB, spaced  $30^\circ$  apart where the gas and liquid were contacted counter currently.<sup>72</sup> The mass transfer coefficients obtained ( $K_L a$ ) were in the range  $0.02\text{--}0.11\text{ s}^{-1}$ .<sup>72</sup>
- Rotating zig-zag bed (RZB) – The RZB design is characterized by a unique rotor that combines coaxially a rotating disc with a stationary disc. Compared with RPB, the RZB can function without liquid distributors, eliminate one dynamic seal, and easily accommodate an intermediate feed in continuous distillation processes. RZB also effectively increases the contact time for gas and liquid phases thereby significantly increasing the mass transfer coefficients.<sup>70</sup>
- Rotating split packing bed – In a HiGee contactor, the gas phase velocity is not much improved compared with the liquid velocity. In fact, the tangential gas velocity in the rotor is nearly the same as that in the packing. Consequently, there is not much enhancement in the gas side mass transfer coefficient.<sup>67</sup> To overcome this, a radically different rotor design can be used. The rotor is composed of two sets of alternate annular rings: one set fixed to the top plate, and the other set to the bottom plate. The two sets of rings are rotated in the counter direction or co-direction driven by two motors to promote the tangential slip velocity between the gas and the packing.<sup>73</sup> This dramatically increases the inter-phase velocities and hence the gas phase mass transfer coefficient ( $\sim 300\text{ L s}^{-1}$ ) with metal foam packing – specific surface area of  $2500\text{ m}^2\text{ m}^{-3}$ .<sup>74</sup>

The vapor–liquid counter-current flow is horizontal in case of HiGee distillation and not vertical, as is typical for conventional operation. Basically, this means that the capacity depends on the height of the rotor, while the separation efficiency is determined by the diameter of the rotor – in contrast to classic distillation where the diameter gives the rate, while the height of the column gives the separation efficiency (Fig. 8). Moreover, in the case of HiGee the separation efficiency varies with the rotational speed, having a maximum at the optimal rpm value. Replacing the vertical gravitational force by the centrifugal force has many important benefits for HiGee distillation:<sup>19,69</sup>

- Very high volumetric mass transfer coefficients, leading to reduced equipment size. Compact equipment is also convenient for installation, troubleshooting, and maintenance.
- Gas flow velocity can be dramatically increased and the tendency to flood is reduced, thus higher hydraulic capacity is possible.
- The rotor is practically self-cleaning and it does not suffer from plugging, which is especially beneficial to treatments of fouling and solid-containing systems.
- Larger driving force of liquid flow due to high rotational speed allows the use of non-Newtonian or very viscous Newtonian fluids (e.g. stripping monomers, polymer solvents).
- Micro-mixing at molecular scale is extremely intensified, and this is particularly beneficial to the preparation of nano-particles.
- The gas-liquid contact in a RPB is characterized by low liquid holdup, thus the time required to reach steady state operation is drastically reduced. Moreover, the short liquid residence time – due to small equipment size and high flow rates – contributes to avoiding the decomposition of heat-sensitive materials (e.g. thermally unstable).

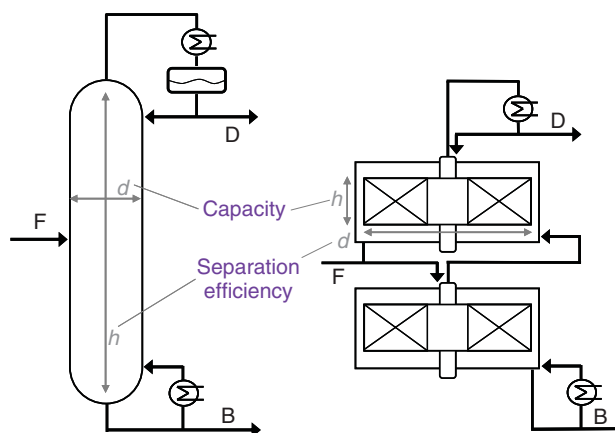


Figure 8. Design analogy between conventional and HiGee distillation.

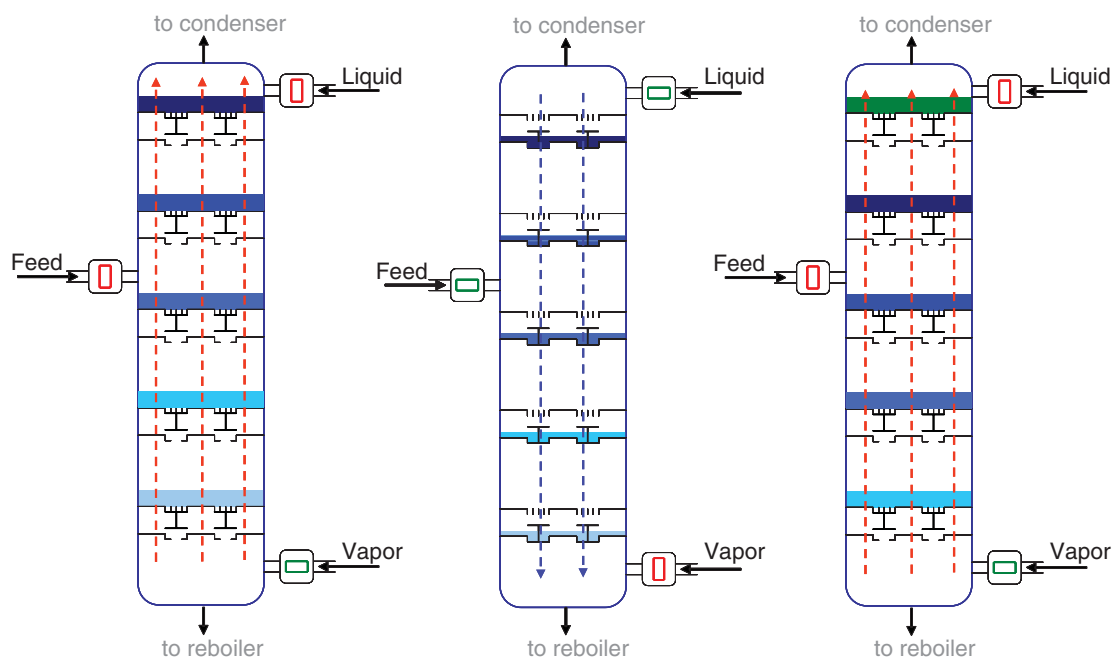
- The thinner liquid film and small inventories favor processing of valuable materials.
- The RPB unit is unaffected by moderate disturbance in orientation, which practically relaxes a major limitation of using conventional columns in ship-mounted or portable units where only very small deviations from the vertical are normally acceptable.

Nonetheless, HiGee distillation has also some disadvantages, such as additional energy requirements (electricity), problems related to the reliability and longevity due to the moving parts, mechanical stability issues, as well as complicated hydrodynamics, sealing and bearings.<sup>67,70</sup>

### Cyclic distillation

Cyclic distillation (CyDist) emerged as another important trend for improving distillation performance, enhancing the separation efficiency through pseudo-steady-state operation based on separate phase movement (SPM) and providing up to 50% energy savings.<sup>75–77</sup> Basically, cyclic operation can be achieved by controlled cycling, stepwise periodic operation, a combination of these two, or by stage switching. Controlled cycling appears to be the simplest scheme and it is therefore the preferred option. The cyclic operation was demonstrated on columns equipped with various types of internals: plates (brass, mesh-screen, bubble cap, sieve, packed-plate) and trays with sluice chambers. Essentially, a cyclic distillation column has an operating cycle consisting of two key operations: 1 a vapor flow period, when vapor flows upwards through the column and liquid remains stationary on each plate, and 2 a liquid flow period, when vapor flow is stopped, reflux and feed liquid are supplied, and liquid is dropped from each tray to the one below – as shown in Fig. 9.<sup>6</sup> As a result, the throughput of such a column using the controlled cycle mode of operation is typically over two times higher than the conventional throughput. A precise analogy exists between the cyclic and conventional distillation with liquid-phase concentration gradients across the plates of the column. This analogy reduces to the substitution of time as independent variable (cyclic distillation), for distance in the case of conventional distillation.

Nonetheless, the practical limitations of cyclic operation must also be taken into account. The application of cyclic operation to vacuum distillation seems rather difficult, and the performance enhancement critically depends on complete separation between the liquid and vapor flow periods. However, the more recently



**Figure 9.** Working principle of cyclic distillation: vapor period (left and right) alternating with liquid period (centre).

proposed sluice-chamber trays seem to avoid the limitations of simple trays.<sup>77</sup> Cyclic distillation was carried out at pilot scale, for the separation of methanol–water or methyl-cyclohexane and n-heptane (5 plates, 100 mm diameter). At production scale, cyclic distillation is already used in the food industry (in Ukraine) for concentrating alcohol, from about 8 %wt to 27–45 %wt ethanol. MaletaCD ([maletacd.com](http://maletacd.com)) implemented several cyclic distillation columns of 15 stages, 0.5 m diameter and 20 m<sup>3</sup> day<sup>-1</sup> capacity.<sup>77</sup> Other potential applications include biofuels (bioethanol, biodiesel, biobutanol), organic synthesis, specialty chemicals, gas processing, and petrochemicals.

The literature review indicates several benefits of cyclic operation over the conventional operating mode:

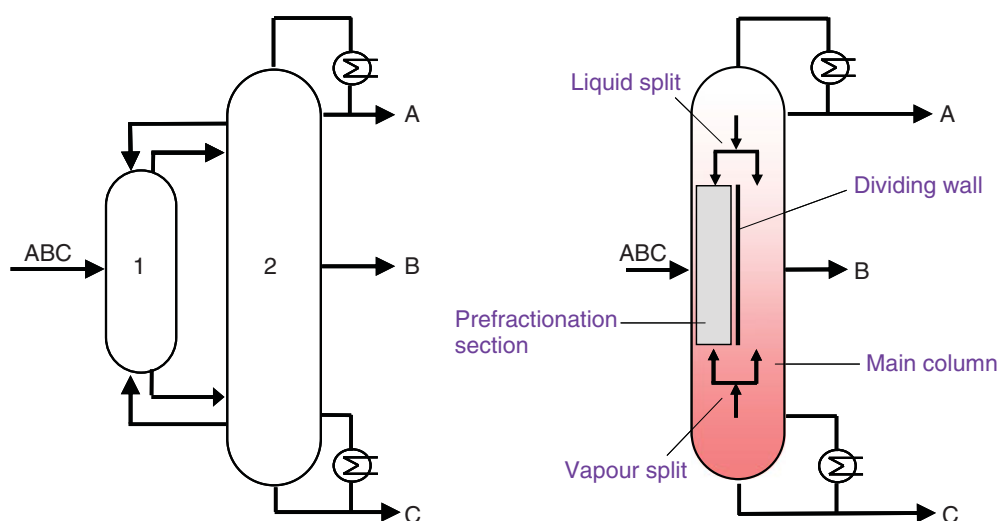
- High tray efficiencies (140–300% Murphree efficiency), meaning that at the same vapor flow rate a required purity can be obtained using fewer trays – hence lower CapEx.
- Reduced energy requirements, meaning that a required purity can be achieved with lower vapor flow rates, at the same number of trays – thus high savings in OpEx (30–50%).
- Higher throughput and equipment productivity compared with conventional distillation.
- The columns can be operated for either maximum capacity (liquid period longer than the vapor period) or for maximum efficiency (vapor period longer than the liquid period).
- For a fixed vapor flow period, the flood rate is different for every liquid flow period selected – increasing with the liquid period, until it reaches a constant maximum.
- Increased quality of the products, due to the higher separation efficiency.
- Smaller pressure drops on trays compared with conventional steady-state operation.
- The cyclic distillation configuration and operation allows larger liquid holdups that can be beneficial for reactive distillation concepts, such as catalytic cyclic distillation (CCD) – a novel setup that combines the benefits of RD with those of cyclic operation mode.

### Dividing-wall column

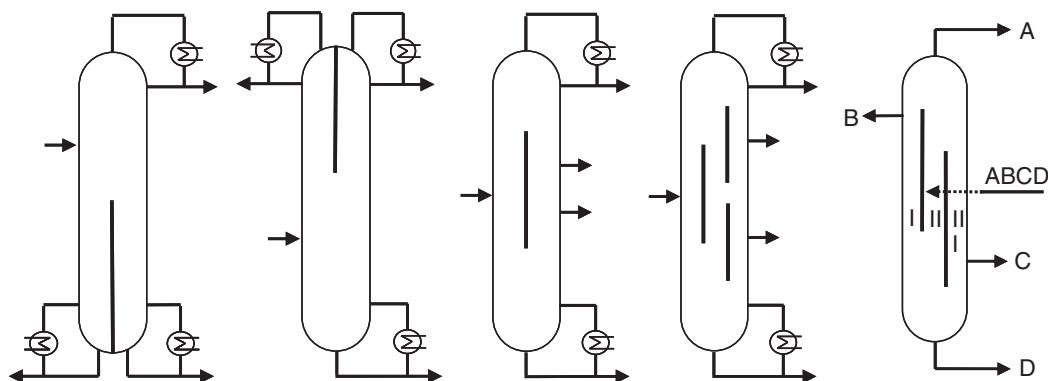
The separation of multi-component mixtures requires typically a direct or indirect sequence of at least two distillation columns. A more energetically favorable alternative configuration that avoids the remixing of internal streams is the so-called Petlyuk distillation.<sup>10</sup> Basically, one condenser and reboiler are effectively replaced by thermal (heat) coupling of the pre-fractionator with the main column, while the required condenser and reboiler are attached to the main column. Dividing-wall column (DWC) is a practical implementation that allows further equipment integration and cost savings by integrating the two distillation columns of a Petlyuk configuration into a single shell – as shown in Fig. 10.<sup>78–82</sup>

In a typical DWC, the feed is introduced into the prefractionator side facing the partition wall. Deflected by the wall, the lightest component flows upward and exits the column as top distillate, while the heaviest component drops down and is withdrawn as bottom product. The mid-boiling component is initially entrained up and down with both streams. However, the fluid that goes upward subsequently separates in the upper part and then it falls down on the opposite side of the wall. Similarly, the amount of mid-boiling component that goes toward the bottom separates in the lower part, and then flows up to the back side of the wall, where the entire mid-boiling product is recovered by a side draw stream. At the top of the dividing-wall section, the liquid coming down from the rectifying section is split between the two sides, a part of the total liquid being sent to the prefractionator side and the rest to the side stream section of the column. Assuming similar hydrodynamic conditions on both sides of DWC, the vapor flow is split proportionally to the cross-sectional area of each side. Unlike classic columns with a side draw, a DWC is capable of delivering high purity side product, thus being able to produce several pure components in one unit.<sup>81</sup>

DWC technology found great appeal in the chemical industry – with Montz and BASF as the leading companies – because it offers some major benefits compared with classic distillation



**Figure 10.** Petlyuk configuration (left) and dividing-wall column (right).



**Figure 11.** Alternative configurations: bottom and top split column, Kaibel column and multi-partitioned DWC (Sargent and Agrawal arrangements).

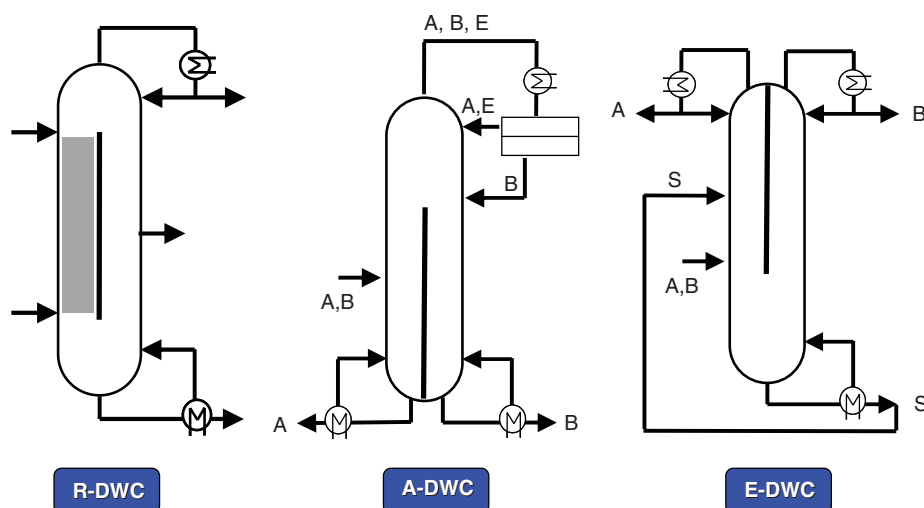
design: high thermodynamic efficiency due to reduced remixing effects, 25–40% lower energy requirements, high purity for all product streams, reduced maintenance costs, small footprint and up to 30% lower investment costs due to the reduced number of equipment units.<sup>83–86</sup> Nonetheless, despite its many benefits, one should keep in mind that DWC has some limitations as well: operation at a single pressure, larger size (diameter and height) compared with any single column of a conventional separation sequence, and larger temperature span across the column which requires more expensive utilities and limits the potential application of heat pumps.<sup>6</sup>

The design and control of dividing-wall columns are nowadays quite well established,<sup>81,87,88</sup> and the original DWC concept was further extended to other useful configurations – such as split-column, Kaibel column or even multi-partitioned dividing-wall column, as illustrated in Fig. 11.<sup>82,89</sup> Several short-cut and detailed methods are described in the literature for the design of dividing-wall columns, and rigorous DWC simulations can be performed with commercial process simulators such as Aspen Plus, ChemCAD, HYSYS, ProSim, etc. Additional dynamic simulations can provide insight into the behavior of the DWC system, and valuable guidance for choosing the appropriate control strategy. Although more complex to control, recent studies and industrial experience indicate that the control of DWC units is in fact satisfactory, provided that an appropriate control structure is implemented.<sup>88</sup> Moreover, the dividing-wall

column technology is not limited to ternary separations alone, but it could be used also in azeotropic separations, extractive distillation and reactive distillation – DWC configurations shown in Fig. 12.<sup>6,82,90–95</sup>

Although the DWC concept has been already patented in the early 1940s, the first theoretical work by Petlyuk was published only in 1965, and it took another 20 years until a company (BASF) implemented it at industrial scale.<sup>78,81</sup> Since its first industrial application in 1985, DWC has moved from a conceptual to a proven technology, steadily growing in number and size of applications.<sup>82</sup> In principle, DWC units are built as both tray and packed columns although the majority of them have been constructed by Montz (and used by BASF) as packed columns. Most of the industrial DWC units are exploited by BASF SE (over 70 units) although other companies – such as Bayer AG, Dow Chemical Co, Lonza, LG Chem Ltd – have also started employing DWC technology, with over 125 applications in total by 2010.<sup>6,82</sup> Table 2 conveniently summarizes the current DWC applications available at applied research and industrial scale.<sup>6,82</sup>

Initially, the DWC technology found application mainly for systems with low fractions of light and heavy boiling components, but currently DWC technology is exploited for the separation of a broad spectrum of chemicals, such as hydrocarbons, alcohols, aldehydes, ketones, acetals, amines and others. DWC can also be used to conduct azeotropic, extractive and reactive distillation without major changes to the types of internals used, while showing a remarkable



**Figure 12.** Dividing-wall column used for reactive distillation (R-DWC), azeotropic distillation (A-DWC) and extractive distillation (E-DWC).

**Table 2.** Industrial applications of dividing-wall columns<sup>6,82</sup>

Applied research and industrial applications	Additional information/remarks
<b>Ternary separations</b> Benzene-toluene-xylene fractionation Separation of hydrocarbons from Fischer-Tropsch synthesis unit  Separation of benzene from pyrolysis gasoline Separation of C7+ aromatics from C7+ olefin/paraffin Mostly undisclosed systems  Undisclosed systems	ExxonMobil Linde AG, Tray column, H = 107 m, D = 5 m Uhde, 170 000 mt yr <sup>-1</sup> feed capacity UOP, five DWC, Tray tray BASF / Montz, over 70 columns, D = 0.6–4 m, P = 2 mbar to 10 bar Sumitomo Heavy Ind., Kyowa Yuka, Sulzer Chemtech Ltd. (20 DWC), Koch Glitsch (10 DWC)
<b>Multi-component separations</b> Recovery of four component mixtures of fine chemical intermediates  Integration of a product separator and an HPNA stripper	BASF/Montz, Single wall column, H = 34 m, D = 3.6 m, deep vacuum UOP, 5 product streams
<b>Retrofit of conventional columns to DWC</b> Recovers mixed xylenes from reformat motor gasoline Separation of (iso)paraffins. Production of isohexane Separation and purification of 2-ethylhexanol (2-EH) Undisclosed systems	Koch-Glitsch, D = 3.8–4.3 m, tray column, over 50% energy savings Koch-Glitsch Dual operation possible MW Kellogg
<b>Reactive DWC</b> $\text{MeOH} + \text{BuOH} + \text{AcOH} \leftrightarrow \text{AcOMe} + \text{AcOBu} + \text{H}_2\text{O}$ $\text{DMC} + \text{EtOH} \leftrightarrow \text{DEC} + \text{MeOH}$ Methyl Acetate + Water $\leftrightarrow$ Methanol + Acetic Acid Isoamylenes + Ethanol $\leftrightarrow$ Tertiary Amyl Ethyl Ether Ethanol + Acetic Acid $\leftrightarrow$ Ethyl Acetate + Water Reactive distillation with 10 chemical species Isobutane + Ethanol $\leftrightarrow$ Ethyl Tertiary Butyl Ether Ethanol + Acetic Acid $\leftrightarrow$ Ethyl Acetate + Water Methanol + Isobutylene $\leftrightarrow$ Methyl Tertiary Butyl Ether Ethanol + Ethylene $\leftrightarrow$ Ethoxyethanol Methanol $\leftrightarrow$ Dimethyl Ether + Water	Rate-based model/AspenTech ACM Aspen Plus <sup>®</sup> or PRO/II  Aspen DISTIL and HYSYS, CSTR Aspen Plus <sup>®</sup> and Aspen Dynamics Aspen Plus (RADFRAC) Aspen HYSYS Aspen Plus <sup>®</sup> Aspen Plus <sup>®</sup>
<b>Azeotropic DWC</b> Ethanol dehydration	Aspen Plus (RADFRAC)  Entrainer: cyclohexane, n-pentane
<b>Extractive DWC</b> Separation of toluene and non-aromatics with N-formyl-morpholine Crude butadiene from a crude C4 using N-methyl-pyrrolidone (NMP) as solvent Bioethanol dehydration	Uhde, 28000 mt yr <sup>-1</sup> feed capacity BASF, Both trays and packing  Ethylene glycol used as solvent



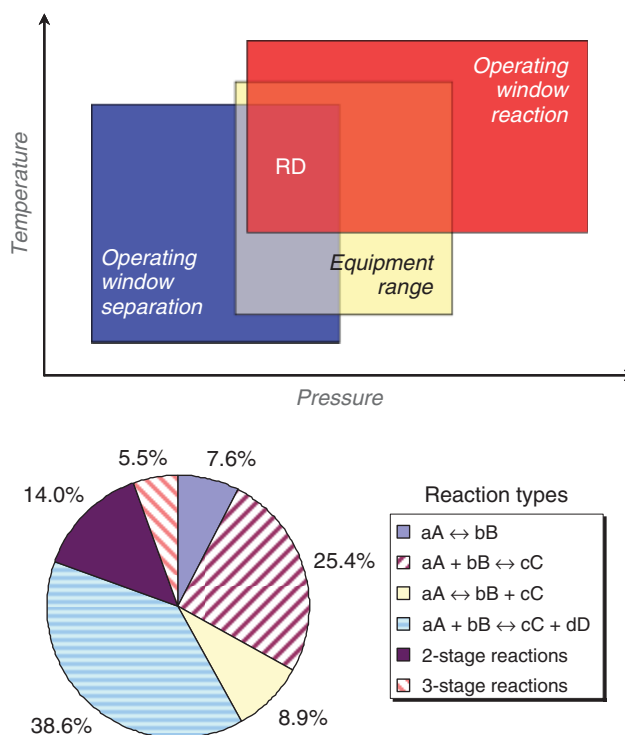
reduction in investment and operating costs. The current research on dividing-wall column technology is aimed at acquiring theoretical and experimental knowledge that supports further development and implementation of these highly integrated applications. For example, the reactive dividing-wall column (R-DWC) can be considered an ultimate efficiency approach due to the integration of reactive distillation with dividing-wall column technology. Relevant research is still required to provide the required evidence to further develop and validate the proposed models.<sup>6,81,82</sup>

### Reactive distillation

In traditional chemical processes, reaction and separation are usually carried out in different sections of the plant, using separate equipment often being operated under different conditions. Recycle streams are frequently needed to improve conversion and selectivity, minimize the production of undesired by-products, reduce the energy requirements, and improve process controllability. The recent economic and environmental considerations have encouraged industry to focus on technologies that are more efficient and require less energy, at further reduced investment costs. In reactive distillation (RD), benefits can be realized by using the reaction to improve separation (e.g. overcoming azeotropes, reacting away contaminants, avoiding difficult separations) or by using separation to improve reactions (e.g. enhancing overall rates, overcoming reaction equilibrium limitations, improving selectivity) – the maximum effect being achieved when both aspects apply.<sup>6,96–99</sup>

In a RD process, reaction and distillation take place in the same piece of equipment, the reactants being converted with the simultaneous separation of the products and recycling of unused reactants. This implies that the boiling points of the products must be different from those of the reactants. Since both operations occur simultaneously in the same unit, there must be a proper match between the conditions required for reaction and separation – as shown in Fig. 13.<sup>100</sup> RD setups may consist of multiple catalyst systems, gas and liquid traffic over the catalyst, separation, mass flow, and enthalpy exchange – all of them being optimally integrated in a single processing unit, a key feature of process intensification.<sup>101–103</sup> By continuously removing the products, reactive distillation makes it possible to use only the stoichiometric reactants ratio (neat operation) and to pull the equilibrium to high conversions.<sup>99</sup> This is in contrast to the typical practice of using an excess of one of the reactants to push the equilibrium toward the desired products, at the penalty of having to recover and recycle the unreacted raw materials.<sup>6</sup>

Remarkably, over 1100 articles and 800 US patents on RD were published during the past 40 years, covering in total over 235 reaction systems.<sup>99</sup> Figure 13 provides a convenient overview of these systems classified into various chemical reaction types, while Table 3 lists the most important applications so far: (trans-)esterification, hydrolysis, polyesterification, etherification, hydration and dehydration, (trans-)alkylation, isomerization, (de-)hydrogenation, amination, condensation, chlorination, nitration – all these reactions being limited by the chemical equilibrium.<sup>6,98,100,104,105,106</sup> Figure 14 illustrates some reactive distillation configuration alternatives, ranging from a conventional reactive distillation column to reactive DWC, and RD columns combined with a pre-reactor, side reactors or even membrane separation units.<sup>6</sup>



**Figure 13.** Overlapping windows of operating conditions and reaction types for RD.

Note that a small number of industrial applications of RD have been around for several decades, but even today the RD crown is still carried by the Eastman process that reportedly replaced a methyl acetate production plant with a single RD column using 80% less energy at only 20% of the investment costs.<sup>99</sup> Nowadays, the application with the largest number of installations remains the methyl tertiary butyl ether (MTBE) that is used in gasoline blending. CDTECH, the major commercial RD technology provider, has licensed until now more than 200 commercial scale processes operated worldwide at capacities of 100–3000 kt yr<sup>-1</sup> for the production of ethers (MTBE, TAME, ETBE), hydrogenation of aromatics and light sulfur hydro-desulfurization, ethyl benzene and isobutylene production.<sup>106</sup> Sulzer ChemTech also reports several industrial scale applications such as synthesis of ethyl, butyl and methyl acetates, hydrolysis of methyl acetate, synthesis of methylal, methanol removal from formaldehyde and fatty acid esters production.<sup>24,106</sup>

Reactive distillation can be further integrated with membrane separation thus combining the benefits of reactive and hybrid separation processes in a highly intensified process unit.<sup>56,107</sup> Although reactive distillation and membrane separations are established technologies, the combination of them is relatively new with only a few publications reported so far.<sup>107–110</sup> More recently, the use of microwaves to enhance a reactive distillation process was also reported as a remarkable process intensification improvement.<sup>111,112</sup>

### CASE STUDIES

This section presents a number of selected case studies that illustrate some of the most promising advanced distillation concepts (e.g. dividing-wall column and reactive distillation) and their applications in various important industrial processes.

**Table 3.** Main industrial applications of reactive distillation<sup>6</sup>

Reaction type	Catalyst/ internals
<b>Alkylation</b>	
Alkyl benzene from ethylene/propylene and benzene	Zeolite $\beta$ , molecular sieves
<b>Amination</b>	
Amines from ammonia and alcohols	H <sub>2</sub> and hydrogenation catalyst
<b>Carbonylation</b>	
Acetic acid from CO and methanol / dimethyl ether	Homogeneous
<b>Condensation</b>	
Diacetone alcohol from acetone	Heterogeneous
Bisphenol-A from phenol and acetone	N/A
Trioxane from formaldehyde	Strong acid catalyst, zeolite ZSM-5
<b>Esterification</b>	
Methyl acetate from methanol and acetic acid	H <sub>2</sub> SO <sub>4</sub> , Dowex 50, Amberlyst-15
Ethyl acetate from ethanol and acetic acid	N/A
2-methyl propyl acetate from 2-methyl propanol and acid	Katapak-S
Butyl acetate from butanol and acetic acid	Cation exchange resin
Fatty acid methyl esters from fatty acids and methanol	H <sub>2</sub> SO <sub>4</sub> , Amberlyst-15, Metal oxides
Fatty acid alkyl esters from fatty acids and alkyl alcohols	H <sub>2</sub> SO <sub>4</sub> , Amberlyst-15, Metal oxides
Cyclohexyl carboxylate from cyclohexene and acids	Ion exchange resin bags
<b>Etherification</b>	
MTBE from isobutene and methanol	Amberlyst-15
ETBE from isobutene and ethanol	Amberlyst-15/pellets, structured
TAME from isoamylene and methanol	Ion exchange resin
DIPE from isopropanol and propylene	ZSM 12, Amberlyst-36, zeolite
<b>Hydration / Dehydration</b>	
Mono ethylene glycol from ethylene oxide and water	Homogeneous
<b>Hydrogenation / Dehydrogenation</b>	
Cyclohexane from benzene	Alumina supported Ni catalyst
MIBK from benzene	Cation exchange resin with Pd/Ni
<b>Hydrolysis</b>	
Acetic acid and methanol from methyl acetate + water	Ion exchange resin bags
Acrylamide from acrylonitrile	Cation exchanger, copper oxide
<b>Isomerization</b>	
Iso-parafins from n-parafins	Chlorinated alumina and H <sub>2</sub>
<b>Nitration</b>	
4-Nitrochlorobenzene from chlorobenzene + nitric acid	Azeotropic removal of water
<b>Transesterification</b>	
Ethyl acetate from ethanol and butyl acetate	Homogeneous
Diethyl carbonate from ethanol and dimethyl carbonate	Heterogeneous
Vinyl acetate from vinyl stearate and acetic acid	N/A
<b>Unclassified reactions</b>	
Monosilane from trichlorosilane	Heterogeneous
Methanol from syngas	Cu/Zn/Al <sub>2</sub> O <sub>3</sub> and inert solvent
DEA from monoethanolamine and ethylene oxide	N/A
Polyesterification	Autocatalytic

## Polyesters synthesis

Polyester (unsaturated) resins are important chemicals, used in key applications such as sheet or bulk moulding compound, printer toners, and fiberglass reinforced plastics (FRP). These unsaturated polyesters are formed by the reaction of polyols (e.g. ethylene glycol) with saturated or unsaturated dibasic acids (e.g. maleic or phthalic acid). The reaction scheme is rather complex and includes several types of reactions: ring opening, poly-esterification, isomerisation and saturation. At industrial scale, the unsaturated polyesters are still produced using batch reactors and distillation columns, with a total production time of about 12 h, in a process plagued by batch-to-batch inconsistencies and high capital and operating costs.

In a series of papers by Shah *et al.*,<sup>113–116</sup> a novel reactive distillation process was proposed as an enhanced process alternative able to reduce the production time and to achieve a better quality of the product at lower costs. With reactive distillation, complete conversion can be achieved in a short time, as the water by-product is continuously removed from the system. Reliable kinetic and thermodynamic models were developed, and subsequently used in rigorous simulations testing various process alternatives – as shown in Fig. 15.<sup>115,116</sup> Moreover, various internals configurations (packing and trays) were evaluated and the experimental validation of the process was successfully carried out at pilot scale using two configurations: a reactive distillation column alone, and a RD column coupled with a pre-reactor.<sup>115</sup> The product specification of the polyester produced in the continuous reactive distillation column was compared with the polyester product manufactured at industrial scale. Remarkably, it was found that the product specifications of the polyester produced in the reactive distillation column was comparable with that of the polyester produced in industry, in a classic batch process.

The reported results show that the total production time in a reactive distillation system is only 1.8–2 h, which is actually 6–8 times lower than the batch process of 12 h.<sup>115,116</sup> Remarkably, for the reactive distillation column coupled with a pre-reactor the improvements were very promising: 90% lower reaction volume, 93% shorter production time, and 66% energy savings compared with the traditional batch process. Overall, using reactive distillation clearly improves the polyester process in all domains of structure, energy and time compared with the traditional batch process used at industrial scale.

## Bioethanol dehydration

Bioethanol is a very promising alternative fuel, produced in large amounts as it can be easily used in existing fuel systems and engines. Bioethanol production relies on several processes: corn-to-ethanol, sugarcane-to-ethanol, basic and integrated lignocellulosic biomass-to-ethanol. The raw materials undergo several pre-treatment steps and then enter the fermentation stage where bioethanol is produced. A common feature is the production of diluted bioethanol (typically in the range of 5–12%wt ethanol) that needs to be further concentrated beyond the azeotropic composition, to purities exceeding 99–99.8%wt ethanol.<sup>93,94</sup>

Several energy demanding separation steps are required to reach the purity target, mainly due to the presence of the well known binary azeotrope ethanol–water (95.63%wt ethanol). The first step is carried out in a pre-concentration distillation column (PDC) that concentrates bioethanol from 5–12% up

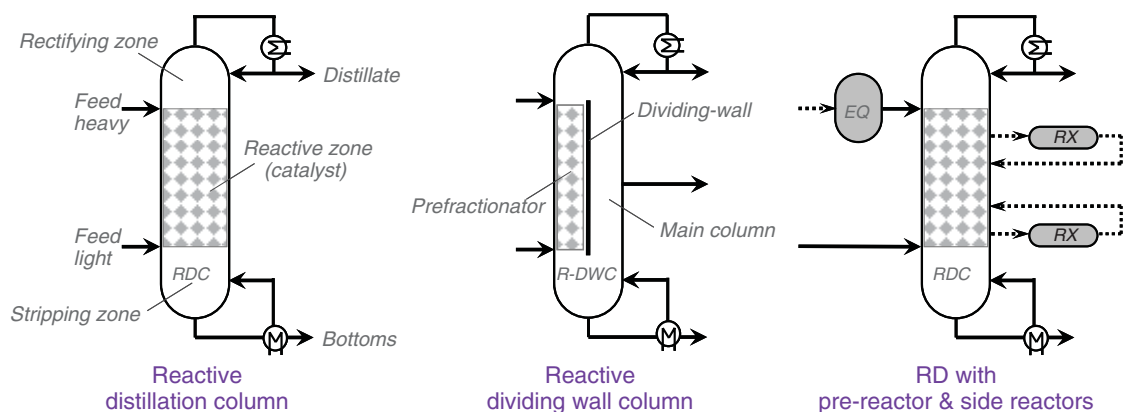


Figure 14. Reactive distillation configurations.

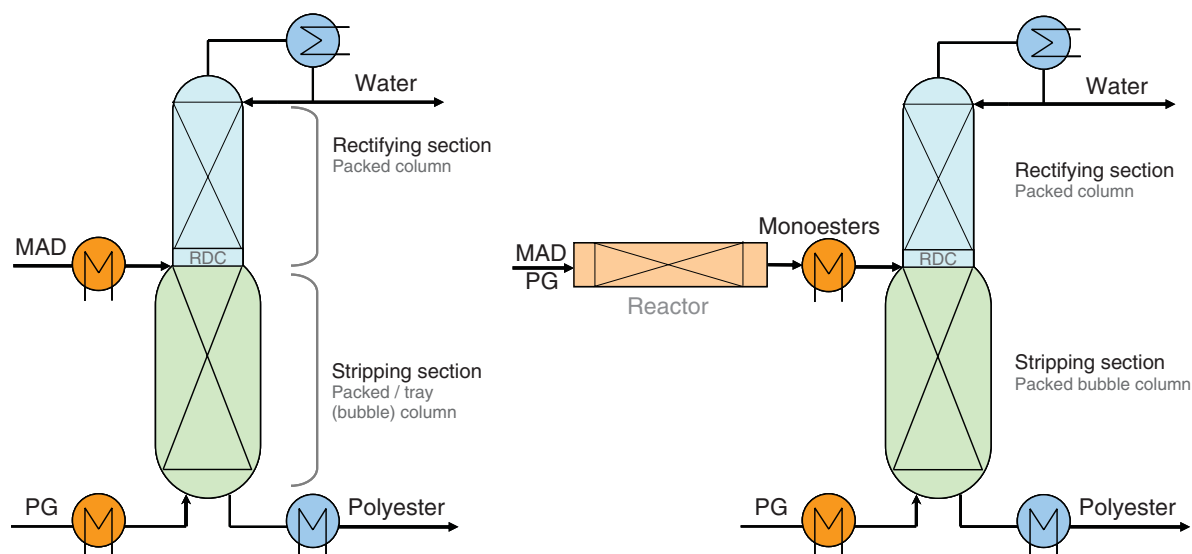


Figure 15. Reactive distillation configurations for synthesis of unsaturated polyesters – e.g. from maleic anhydride (MAD) and propylene glycol (PG).

to 92.4–94%wt. The second step is ethanol dehydration up to concentrations above the azeotropic composition. This is typically carried out in an extractive distillation column (EDC) followed by a solvent recovery column (SRC). Although extractive distillation presents relatively high energy costs, it is still the option of choice in the case of large-scale production of bioethanol fuel – being preferred over pervaporation, adsorption, pressure-swing distillation, azeotropic distillation, or hybrid methods combining these options.<sup>95,117–120</sup>

In a series of studies by Kiss *et al.*,<sup>93,94</sup> E-DWC systems were proposed for extractive distillation, including or not the pre-concentration distillation column (PDC). The feed considered was the diluted stream (10%wt) obtained by fermentation. This is distilled to near-azeotropic composition of 93.5%wt ethanol, and then dehydrated to a purity of over 99.8%wt ethanol in order to comply with all standards.

Figure 16 shows the conventional extractive distillation (ED) process used for bioethanol dehydration, as well as the novel E-DWC that combines three towers into just one column.<sup>94</sup> In this column, the feed side (prefractionator) acts as the PDC unit. Water is removed as liquid side stream, but an additional side reboiler is required in order to return the required amount of water vapors to the column. The liquid feed stream is fed on top

of the prefractionator side, thus serving as a reflux to the PDC section. The vapor leaving the feed side of the E-DWC has a near azeotropic composition. Solvent is added at the top of the E-DWC, this section acting in fact as the EDC unit of the conventional sequence. Ethanol is separated here as high purity top distillate, and removed as main product. The liquid flowing down the top section (EDC) is collected and distributed only to the (SRC) side opposite to the feed side (pre-fractionator) and further down the bottom of the E-DWC. This complete redistribution of the liquid flow is required to avoid the presence and loss of solvent on the feed side (PDC section). In the SRC section of the column, the solvent is separated as bottom product and then recycled in the separation process.

High purity and recovery is obtained for all three products of the extractive dividing-wall column: ethanol as top distillate, water as side product and EG solvent as recovered bottom product. In contrast to the well-known DWC configuration, the side stream is collected here from the same (feed) side of the column, not the opposite. The single-step E-DWC alternative is the most efficient in terms of energy requirements allowing energy savings of 17% (specific energy use of 2070 kWh ton<sup>-1</sup> ethanol) while being the least expensive in terms of capital investment and operating costs (about 17% lower total annual costs).<sup>94</sup>

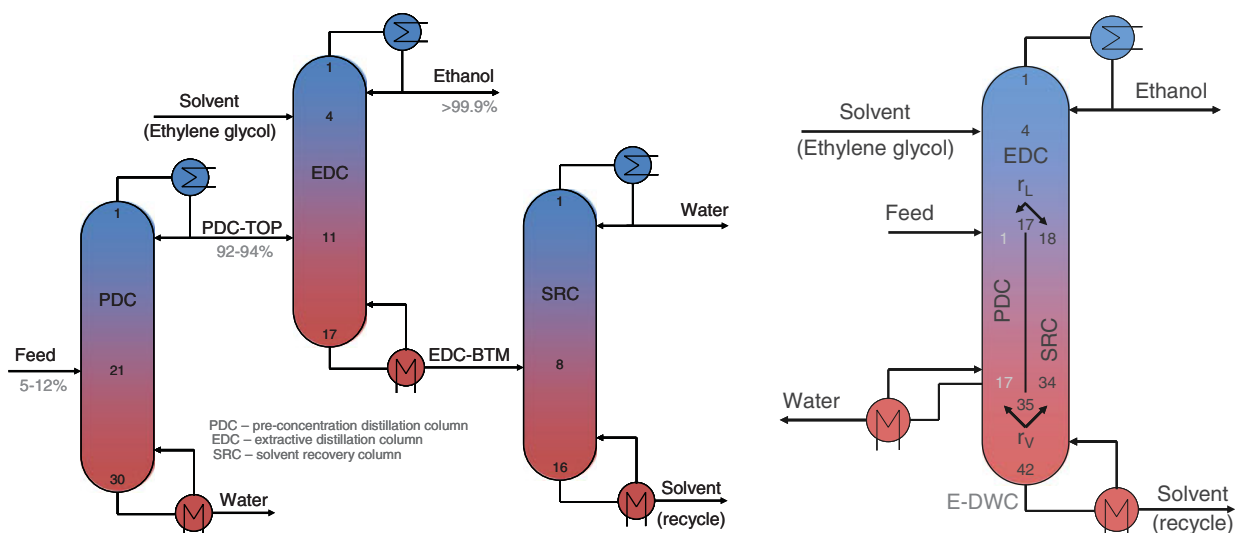
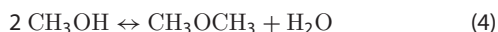


Figure 16. Bioethanol dehydration by extractive distillation: conventional process vs DWC.

### Dimethyl ether production

Dimethyl ether (DME) is of great interest due to its use as clean fuel for diesel engines or in combustion cells, as a precursor to organic compounds, as well as a green aerosol propellant. Currently, DME is produced by conversion of various feedstock such as natural gas, coal, oil residues and bio-mass into syngas (CO and H<sub>2</sub>), followed by a two-step process: methanol synthesis and then methanol dehydration. Methanol is produced first from syngas over a copper-based catalyst (Cu/Zn, Cu/Zn/Al, Cu/Zn/Co), and then it is dehydrated over a solid catalyst in order to produce dimethyl ether. The methanol dehydration step takes place at temperatures of 250–400°C and pressures up to 20 bars. Different types of solid acid catalysts can be used, but  $\gamma$ -alumina is the preferred one due to its thermal stability, mechanical resistance, high surface area and catalytic properties.<sup>121</sup> The current industrial process involves a gas-phase reactor (70–80% conversion of methanol), followed by a direct sequence of two distillation columns that deliver high-purity DME (over 99.99%wt).

Figure 17 illustrates the simplified conventional flowsheet for methanol dehydration, along with the ternary diagram of the process. The equilibrium limited dehydration reaction of vaporized methanol is carried out in a fixed-bed catalytic reactor:



The outlet of the reactor – consisting of DME, water and unreacted methanol – is cooled and subsequently distilled in the first tower to yield pure dimethyl ether. The unreacted methanol is separated from water in a second distillation column and recycled back to the reactor. A major problem of this process is the high investments costs for several units that require a large overall plant footprint, as well as the associated energy requirements.

One approach to reduce the capital and operating costs is to integrate the two distillation columns used for DME purification and methanol recovery into only one dividing-wall column – as shown in Fig. 18.<sup>122</sup> DME and water are separated as top and bottom end high purity products (>99.99%wt), while methanol accumulates towards the middle of the column, being withdrawn as a side stream (>99%wt) and then recycled in the process. The reported process alternative requires less equipment and 20% lower capital costs (TIC = \$1,412,490), with

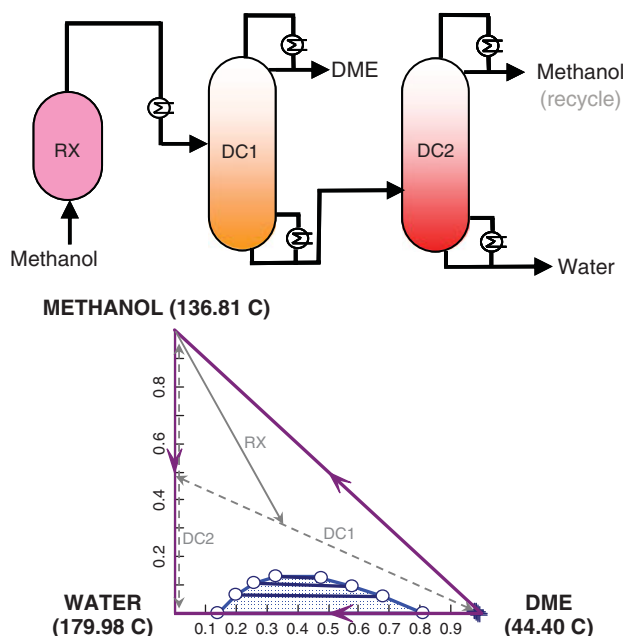
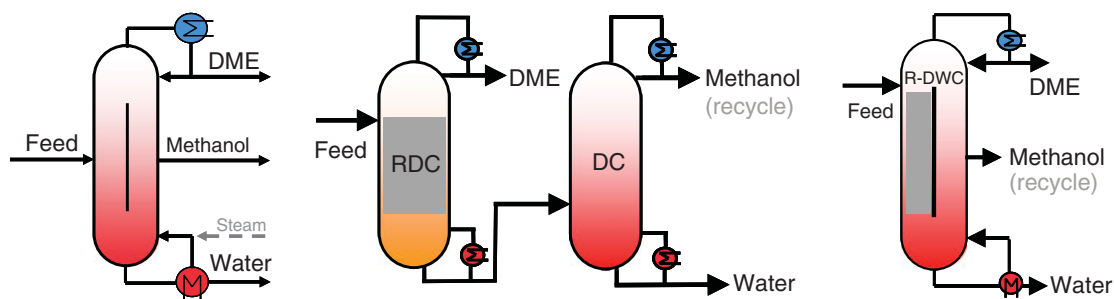


Figure 17. DME production: simplified process flowsheet and ternary diagram.

28% savings in energy and total annual costs (TAC = \$1,138,984 for a 100 kt yr<sup>-1</sup> plant), compared with the conventional distillation sequence.<sup>122</sup>

Reactive distillation (RD) could be also used a process alternative, since it can successfully combine the functions of the reactor and the DME purification column into one unit, as shown in Fig. 18. However, a further improved alternative combining all functions into one unit is based on a reactive DWC (Fig. 18). Methanol is fed on top of the reactive zone where the solid catalyst is located, while DME is produced as top distillate, water as bottom product, and the unreacted methanol as side stream product that is recycled. The reactive DWC unit has 35 stages in total, with the reactive zone located on stages 8–31 on the feed side, and a common stripping section (stages 32–35) as well as a common rectifying zone (stages 1–7). The methanol stream is





**Figure 18.** Process alternatives based on single-step separation in a DWC, reactive distillation process, and all-in-one reactive DWC.

fed into stage 8, at the top of the reactive zone – the feed side of the DWC acting as the RD zone where the solid acid catalyst is present. High purity (99.99%wt) DME is delivered as distillate, while similar high-purity water is obtained as bottom product. The unreacted methanol is collected as side product, and then recycled back to the process. The results reported show that the process using a reactive dividing-wall column has superior performance compared with the conventional or reactive distillation process: high energy savings of up to 60%, as well as around 30% lower capital investment costs. The methanol conversion in the reactive dividing-wall column is 50%, and the specific energy requirements are only  $0.56 \text{ kWh kg}^{-1} \text{ DME}$ .<sup>92,95</sup>

## CONCLUDING REMARKS

Although considered a mature technology, distillation is still young and full of breakthrough opportunities, as significant cost reductions and high energy efficiency can be achieved by employing various approaches based on process intensification principles (e.g. maximized effectiveness, driving forces, and synergy). For example, several heat pump concepts have been proposed to upgrade the level of the energy discharged and re-use it in order to reduce the consumption of valuable utilities. These heat pumps have no intrinsic (temperature) limitations and therefore, their application range is quite large within the chemical process industry. Temperature lifts of up to  $30\text{--}100^\circ\text{C}$  are feasible, leading to significant savings of up to 80% in the primary energy requirements for distillation.<sup>29</sup>

Membrane distillation is a promising technology for separation and purification processes, but it still needs further exploration and optimization to become a mature technology applicable at industrial scale. Compared with other membrane separation processes, the main advantages of using membrane distillation are low operating temperatures (which means that low-grade heat such as solar energy, waste heat and geothermal can be used), high rates of rejection for non-volatile components (salts, colloids), possibility to work with high solute concentrations in the feed or even with near saturated solutions, and lower hydrostatic pressure than used in pressure driven membrane processes. However, the practical application of MD is limited by permeate flux decay (due to concentration and temperature polarization effects, membrane fouling and total or partial pore wetting), uncertain energy and economic costs for each membrane distillation configuration and application, membrane distillation modules not yet commercially available for large-scale applications, and risk of pore wetting – since only vapor and gases must be present inside the pores.<sup>55,60</sup>

Although many commercial applications of HiGee are known in absorption, stripping, and reactive precipitation only very

few commercial applications in distillation have been reported so far.<sup>67,70</sup> A key reason is that several problems such as the dynamic seal, middle feed, liquid distributor and the multi-rotor configuration have not been properly addressed. In order to successfully solve these problems, a novel kind of HiGee device was recently proposed and developed – the so called rotating zigzag bed (RZB) that contains a unique rotor. The RZB fills the gap in HiGee distillation and it has the potential for a bright future in process intensification.<sup>70</sup>

Cyclic distillation uses a cyclic operating mode that can bring new life to old distillation columns, providing several key benefits, such as increased column throughput, low energy requirements and high separation performance. Moreover, the separate phase movement has more degrees of freedom that contribute to a good process control.<sup>77</sup> The main obstacle for the widespread implementation of cyclic distillation is the pseudo-steady-state operation that requires special operator training and additional safety measurements.

Dividing-wall column is one of the best examples of a proven process intensification technology in distillation, as it allows significantly lower investment and operating costs (typically 25–40%) while also reducing the equipment and carbon footprint. Considering the number and variety of industrial applications, dividing-wall column technology can already be considered a success story of process intensification in distillation and it will certainly develop into a standard type of equipment in the near future. Many applications are known today, mainly concerning separations of ternary mixtures. The development and implementation efforts focus nowadays on the separation of more than three components or applications of extractive, azeotropic and reactive distillation in a dividing-wall column.<sup>6,82</sup>

Reactive distillation brings tremendous benefits to equilibrium limited chemical systems, resulting in significantly lower investment and operating costs, as well as reduced plant footprint. The industrial applications of reactive distillation are flourishing as the scientific community and the technology providers remove the barriers for implementation, develop heuristic process synthesis rules and expert software to identify the attractiveness and technical feasibility of reactive distillation.<sup>24,113</sup>

## ACKNOWLEDGEMENT

Financial support from the Stichting Hoogewerff-Fonds is gratefully acknowledged by the author – winner of the Hoogewerff Jongerenprijs 2013. This review paper is based on the award lecture given on 23 April 2013, in The Hague, at the joint conference including the 9th European Congress



of Chemical Engineering (ECCE-9), 2nd European Congress of Applied Biotechnology (ECAB-2), European Process Intensification Conference (EPIC2013) and the 12th Netherlands Process Technology Symposium (NPS-12).

## REFERENCES

- 1 Resetaritis MR and Lockett MJ, Distillation, in *EncPhys Sci Technol*, 3rd edn. 547–559 (2003). DOI: 10.1016/B0-12-227410-5/00182-4
- 2 Forbes RJ, *A Short History of the Art of Distillation*. Brill, Leiden, The Netherlands (1970).
- 3 Kister HZ, *Distillation - Design*. McGraw-Hill, USA (1992).
- 4 Kister HZ, *Distillation - Operation*. McGraw-Hill, USA (1992).
- 5 Kister HZ, *Distillation Troubleshooting*. John Wiley & Sons, Hoboken, New Jersey (2006).
- 6 Kiss AA, *Advanced Distillation Technologies - Design, Control and Applications*. Wiley, Chichester (2013).
- 7 Freshwater DC, Thermal economy in distillation. *Trans Inst Chem Eng* **29**:149–160 (1951).
- 8 Taylor R and Krishna R, *Multi-Component Mass Transfer*. Wiley, New York (1993).
- 9 de Koeijer GM and Kjelstrup S, Application of irreversible thermodynamics to distillation. *Int J Thermodynam* **7**:107–114 (2004).
- 10 Petlyuk FB, *Distillation Theory and its Application to Optimal Design of Separation Units*. Cambridge University Press, New York (2004).
- 11 Holland CD, *Fundamentals of Multi-Component Distillation*. McGraw Hill, New York (1981).
- 12 Stichlmair JG and Fair JR, *Distillation - Principles and Practice*. Wiley-VCH, New York (1998).
- 13 Doherty MF and Malone MF, *Conceptual Design of Distillation Systems*. McGraw-Hill, New York (2001).
- 14 Lee FM and Wytcherley RW, Azeotropic Distillation. In *Encyclopedia of Separation Science* 990–995 (2000). DOI: 10.1016/B0-12-226770-2/00681-5
- 15 Lee FM, Extractive Distillation. In *Encyclopedia of Separation Science* 1013–1022 (2000). DOI: 10.1016/B0-12-226770-2/04801-8
- 16 Mujtaba IM, *Batch Distillation - Design and Operation*. Imperial College Press, London (2004).
- 17 Lei Z, Chen B and Ding Z, *Special Distillation Processes*. Elsevier, Amsterdam (2005).
- 18 Luyben WL, *Distillation Design and Control using Aspen Simulation*. John Wiley & Sons, Hoboken, New Jersey (2006).
- 19 Reay D, Ramshaw C and Harvey A, *Process Intensification - Engineering for Efficiency, Sustainability and Flexibility*, 2<sup>nd</sup> edn. Butterworth-Heinemann, Oxford (2013).
- 20 van Gerven T and Stankiewicz A, Structure, energy, synergy, time - the fundamentals of process intensification. *Ind Eng Chem Res* **48**:2465–2474 (2009).
- 21 Freund H and Sundmacher K, Towards a methodology for the systematic analysis and design of efficient chemical processes - Part 1: from unit operations to elementary process functions. *Chem Eng Process* **47**:2051–2060 (2008).
- 22 Jonker G and Harmsen J, *Engineering for Sustainability: A Practical Guide for Sustainable Design*. Elsevier, Amsterdam (2012).
- 23 Sundmacher K, Kienle A and Seidel-Morgenstern A (eds), *Integrated Chemical Processes: Synthesis, Operation, Analysis, and Control*. Wiley-VCH, Weinheim (2005).
- 24 Harmsen GJ, Process intensification in the petrochemicals industry: drivers and hurdles for commercial implementation. *Chem Eng Process* **49**:70–73 (2010).
- 25 Felder R and Rousseau W, *Elementary Principles of Chemical Processes*. John Wiley & Sons, Hoboken, New Jersey (2005).
- 26 Haselden G, Approach to minimum power consumption in low-temperature gas separation. *Trans Inst Chem Eng* **36**:123–132 (1958).
- 27 Sampathkumar K, Arjunan TV, Pitchandi P and Senthilkumar P, Active solar distillation - a detailed review. *Renew Sustain Energy Rev* **14**:1503–1526 (2010).
- 28 Summers DR and Pilling M, Be smart about column design. *Chem Eng Prog* **Nov**:32–38 (2012).
- 29 Kiss AA, Flores Landaeta SJ and Infante Ferreira CA, Towards energy efficient distillation technologies - making the right choice. *Energy* **47**:531–542 (2012).
- 30 van de Bor DM and Infante Ferreira CA, Quick selection of industrial heat pump types including the impact of thermodynamic losses. *Energy* **53**:312–322 (2013).
- 31 Annakou O and Mizsey P, Rigorous investigation of heat pump assisted distillation. *Heat Recov Syst CHP* **15**:241–247 (1995).
- 32 Omidéyi TO, Parande MG, Supranto S, Kasprzycki J and Devotta S, The economics of heat pump assisted distillation systems. *Heat Recov Syst CHP* **5**:511–518 (1985).
- 33 Fonyo Z and Mizsey P, Economic applications of heat pumps in integrated distillation systems. *Heat Recov Syst CHP* **14**:249–263 (1994).
- 34 Fonyo Z and Benko N, Comparison of various heat pump assisted distillation configurations. *J Chem E Trans* **76A**:348–360 (1998).
- 35 Díez E, Langston P, Ovejero G and Dolores Romero M, Economic feasibility of heat pumps in distillation to reduce energy use. *Appl Therm Eng* **29**:1216–1223 (2009).
- 36 Spoelstra S, Saving energy in distillation with thermoacoustic heat pumps. ECN Brochure B-07-008, Petten, The Netherlands (2008).
- 37 Tijani MEH and Spoelstra S, A high performance thermoacoustic engine. *J Appl Phys* **110**, Article Number: 093519: 1–6 (2011). DOI: 10.1063/1.3658872
- 38 Xiao JH, Thermoacoustic theory for cyclic flow regenerators. 1. Fundamentals. *Cryogenics* **32**:895–901 (1992).
- 39 Herman C and Travnicek Z, Cool sound: the future of refrigeration? Thermodynamic and heat transfer issues in thermoacoustic refrigeration. *Heat Mass Transfer* **42**:492–500 (2006).
- 40 Vanapalli S, Tijani MEH and Spoelstra S, Thermoacoustic-stirling heat pump for domestic applications. *Proc ASME Fluids Eng Div Summer Conf* **2**:111–116 (2010).
- 41 Bassem MM, Ueda Y and Akisawa A, Thermoacoustic stirling heat pump working as a heater. *Appl Phys Express* **4**, Article Number: 107301: 1–3 (2011). DOI: 10.1143/APEX.4.107301
- 42 Nakaiwa M, Huang K, Owa M, Akiya T, Nakane T, Sato M and Takamatsu T, Energy savings in heat-integrated distillation columns. *Energy* **22**:621–625 (1997).
- 43 Olujic Ž, Fakhri F, de Rijke A, de Graauw J and Jansens PJ, Internal heat integration - the key to an energy-conserving distillation column. *J Chem Technol Biotechnol* **78**:241–248 (2003).
- 44 Gadalla M, Olujic Z, de Rijke A and Jansens PJ, Reducing CO<sub>2</sub> emissions of internally heat-integrated distillation columns for separation of close boiling mixtures. *Energy* **31**:2409–2417 (2006).
- 45 de Rijke A, Development of a concentric internally heat integrated distillation column (HIDiC). PhD thesis, TU Delft, The Netherlands (2007).
- 46 Gadalla MA, Internal heat integrated distillation columns (iHIDiCs) - new systematic design methodology. *Chem Eng Res Des* **87**:1658–1666 (2009).
- 47 Bruinsma OSL, Krikken T, Cot J, Sarić M, Tromp SA, Olujic Ž and Stankiewicz AI, The structured heat integrated distillation column. *Chem Eng Res Des* **90**:458–470 (2012).
- 48 Nakaiwa M, Huang K, Endo A, Ohmori T, Akiya T and Takamatsu T, Internally heat-integrated distillation columns: a review. *Chem Eng Res Des* **81**:162–177 (2003).
- 49 Fukushima T, Kano M and Hasebe S, Dynamics and control of heat integrated distillation column (HIDiC). *J Chem Eng Japan* **39**:1096–1103 (2006).
- 50 Khayet M, Membranes and theoretical modeling of membrane distillation - a review. *Adv Colloid Interface Sci* **164**:56–88 (2011).
- 51 Ravanchi MT, Kaghazchi T and Kargari A, Application of membrane separation processes in petrochemical industry - a review. *Desalination* **235**:199–244 (2009).
- 52 Curcio E and Drioli E, Membrane distillation and related operations - a review. *Sep Purif Rev* **34**:35–86 (2005).
- 53 Suk DE and Matsuura T, Membrane based hybrid processes - a review. *Sep Sci Technol* **41**:595–626 (2006).
- 54 Susanto H, Towards practical implementations of membrane distillation. *Chem Eng Process* **50**:139–150 (2011).
- 55 Alkudhiri A, Darwish N and Hilal N, Membrane distillation - a comprehensive review. *Desalination* **287**:2–18 (2012).
- 56 Lipnizki F, Field RF and Ten PK, Pervaporation-based hybrid process: a review of process design, applications and economics. *J Membr Sci* **153**:183–210 (1999).
- 57 Mericq J-P, Laborie S and Cabassud C, Evaluation of systems coupling vacuum membrane distillation and solar energy for seawater desalination. *Chem Eng J* **166**:596–606 (2011).

- 58 Hausmann A, Sancio P, Vasiljevic T, Weeks M and Duke M, Integration of membrane distillation into heat paths of industrial processes. *Chem Eng J* **211**:378–387 (2012).
- 59 El-Bourawi MS, Ding Z, Ma R and Khayet M, A framework for better understanding membrane distillation separation process. *J Membr Sci* **285**:4–29 (2006).
- 60 Hassan AS and Fath HES, Review and assessment of the newly developed MD for desalination processes. *Desal Water Treatment* **51**:574–585 (2013).
- 61 Burgoyne A, and Vahdati MM, Direct contact membrane distillation. *Sep Sci Technol* **35**:1257–1284 (2000).
- 62 Camacho LM, Dumee L, Zhang JH, Li JD, Duke M, Gomez J and Gray S, Advances in membrane distillation for water desalination and purification applications. *Water* **5**:94–196 (2013).
- 63 Koschikowski J, Entwicklung von energieautark arbeitenden Wasserentsalzungsanlagen auf Basis der Membrandestillation. Fraunhofer Verlag, Germany (2011).
- 64 Jiao B, Cassano A and Drioli E, Recent advances on membrane processes for the concentration of fruit juices: a review. *J Food Eng* **63**:303–324 (2004).
- 65 Vane LM, A review of pervaporation for product recovery from biomass fermentation processes. *J Chem Technol Biotechnol* **80**:603–629 (2005).
- 66 Ramshaw C, HiGee distillation - an example of process intensification. *Chem Eng* **389**:13–14 (1983).
- 67 Rao DP, Bhowal A and Goswami PS, Process intensification in rotating packed beds (HiGee): an appraisal. *Ind Eng Chem Res* **43**:1150–1162 (2004).
- 68 Trent DL, Chemical processing in high-gravity fields, in *Re-Engineering the Chemical Processing Plant: Process Intensification*, ed by Stankiewicz A and Moulijn JA. Marcel Dekker, New York (2004).
- 69 Zhao H, Shao L and Chen JF, High-gravity process intensification technology and application. *Chem Eng J* **156**:588–593 (2010).
- 70 Wang GQ, Xu ZC and Ji JB, Progress on HiGee distillation - introduction to a new device and its industrial applications. *Chem Eng Res Des* **89**:1434–1442 (2011).
- 71 TU Dortmund website: [www.fvt.bci.tu-dortmund.de/cms/en/research/research\\_topics/Process\\_intensification\\_by\\_unit\\_operation\\_design/index.html](http://www.fvt.bci.tu-dortmund.de/cms/en/research/research_topics/Process_intensification_by_unit_operation_design/index.html) (last accessed on 20 October 2013).
- 72 Lin CC, Ho TJ and Liu WT, Distillation in a rotating packed bed. *J Chem Eng Japan* **35**:1298–1304 (2002).
- 73 Chandra A, Goswami PS and Rao DP, Characteristics of flow in a rotating packed bed (HIGEE) with split packing. *Ind Eng Chem Res* **44**:4051–4060 (2005).
- 74 Reddy KJ, Gupta A and Rao DP, Process intensification in a HIGEE with split packing. *Ind Eng Chem Res* **45**:4270–4277 (2006).
- 75 Gaska RA and Cannon MR, Controlled cycling improves various processes. *Ind Eng Chem* **53**:630–631 (1961).
- 76 McWhirter JR and Cannon MR, Controlled cycling distillation in a packed-plate column. *Inst Eng Chem* **53**:632–634 (1961).
- 77 Maleta VN, Kiss AA, Taran VM and Maleta BV, Understanding process intensification in cyclic distillation systems. *Chem Eng Process* **50**:655–664 (2011).
- 78 Kaibel G, Distillation columns with vertical partitions. *Chem Eng Technol* **10**:92–98 (1987).
- 79 Kolbe B and Wenzel S, Novel distillation concepts using one-shell columns. *Chem Eng Process* **43**:339–346 (2003).
- 80 Aspiron N and Kaibel G, Dividing wall columns: fundamentals and recent advances. *Chem Eng Process* **49**:139–146 (2010).
- 81 Dejanović I, Matijašević L and Olujić Ž, Dividing wall column - a breakthrough towards sustainable distilling. *Chem Eng Process* **49**:559–580 (2010).
- 82 Yildirim O, Kiss AA and Kenig EY, Dividing wall columns in chemical process industry: a review on current activities. *Sep Purif Technol* **80**:403–417 (2011).
- 83 Schultz MA, Stewart DG, Harris JM, Rosenblum SP, Shakur MS and O'Brien DE, Reduce costs with dividing-wall columns. *Chem Eng Prog* **98**:64–71 (2002).
- 84 Parkinson G, Dividing-wall columns find greater appeal. *Chem Eng Prog* **103**:8–11 (2007).
- 85 Pendergast JG, Vickery D, Au-Yeung P and Anderson J, Consider dividing wall columns. *Chem Process*, 19 Dec 2008, Article 245 (2008). URL: <http://www.chemicalprocessing.com/articles/2008/245/>
- 86 Olujić Ž, Jödecke M, Shilkin A, Schuch G and Kaibel B, Equipment improvement trends in distillation. *Chem Eng Process* **48**:1089–1104 (2009).
- 87 Kim YH, Structural design and operation of a fully thermally coupled distillation column. *Chem Eng J* **85**:289–301 (2002).
- 88 Kiss AA and Bildea CS, A control perspective on process intensification in dividing-wall columns. *Chem Eng Process* **50**:281–292 (2011).
- 89 Ghadrani M, Halvorsen IJ and Skogestad S, Optimal operation of Kaibel distillation columns. *Chem Eng Res Des* **89**:1382–1391 (2011).
- 90 Kiss AA, Pragt H and van Strien C, Reactive dividing-wall columns - how to get more with less resources? *Chem Eng Commun* **196**:1366–1374 (2009).
- 91 Kiss AA, Segovia-Hernandez JG, Bildea CS, Miranda-Galindo EY and Hernandez S, Reactive DWC leading the way to FAME and fortune. *Fuel* **95**:352–359 (2012).
- 92 Kiss AA and Suszwalak DJ-PC, Innovative dimethyl ether synthesis in a reactive dividing-wall column. *Comput Chem Eng* **38**:74–81 (2012).
- 93 Kiss AA and Suszwalak DJ-PC, Enhanced bioethanol dehydration by extractive and azeotropic distillation in dividing-wall columns. *Sep Purif Technol* **86**:70–78 (2012).
- 94 Kiss AA and Ignat RM, Innovative single step bioethanol dehydration in an extractive dividing-wall column. *Sep Purif Technol* **98**:290–297 (2012).
- 95 Kiss AA, Novel applications of dividing-wall column technology to biofuel production processes. *J Chem Technol Biotechnol* **88**:1387–1404 (2013).
- 96 Baur R, Higler AP, Taylor R and Krishna R, Comparison of equilibrium stage and nonequilibrium stage models for reactive distillation. *Chem Eng J* **76**:33–47 (2000).
- 97 Taylor R and Krishna R, Modelling reactive distillation. *Chem Eng Sci* **55**:5183–5229 (2000).
- 98 Sundmacher K and Kienle A (eds), *Reactive Distillation: Status and Future Directions*. Wiley-VCH, Weinheim (2003).
- 99 Luyben WL and Yu CC, *Reactive Distillation Design and Control*. John Wiley & Sons, Hoboken, New Jersey (2008).
- 100 Kiss AA and Bildea CS, A review on biodiesel production by integrated reactive separation technologies. *J Chem Technol Biotechnol* **87**:861–879 (2012).
- 101 Stankiewicz A, Reactive separations for process intensification: an industrial perspective. *Chem Eng Process* **42**:137–144 (2003).
- 102 Noeres C, Kenig EY and Gorak A, Modelling of reactive separation processes: reactive absorption and reactive distillation. *Chem Eng Process* **42**:157–178 (2003).
- 103 Gorak A and Stankiewicz A, Intensified reaction and separation systems. *Ann Rev Chem Eng Biomol Eng* **2**:431–451 (2011).
- 104 Dimian AC, Bildea CS, Omota F and Kiss AA, Innovative process for fatty acid esters by dual reactive distillation. *Comput Chem Eng* **33**:743–750 (2009).
- 105 Kiss AA, Heat-integrated reactive distillation process for synthesis of fatty esters. *Fuel Process Technol* **92**:1288–1296 (2011).
- 106 Harmsen GJ, Reactive distillation: the front-runner of industrial process intensification: a full review of commercial applications, research, scale-up, design and operation. *Chem Eng Process* **46**:774–780 (2007).
- 107 Buchaly C, Kreis P and Górak A, Hybrid separation processes - combination of reactive distillation with membrane separation. *Chem Eng Process* **46**:790–799 (2007).
- 108 Aiouache F and Goto S, Reactive distillation-pervaporation hybrid column for tert-amyl alcohol etherification with ethanol. *Chem Eng Sci* **58**:2465–2477 (2003).
- 109 Steinigeweg S and Gmehling J, Transesterification processes by combination of reactive distillation and pervaporation. *Chem Eng Process* **43**:447–456 (2004).
- 110 Rewagad RR and Kiss AA, Modeling and simulation of a pervaporation process for fatty ester synthesis. *Chem Eng Comm* **199**:1357–1374 (2012).
- 111 Nuchter M, Ondruschka B, Bonrath W and Gum A, Microwave assisted synthesis - a critical technology overview. *Green Chem* **6**:128–141 (2004).
- 112 Altman E, Stefanidis GD, van Gerven T and Stankiewicz AI, Process intensification of reactive distillation for the synthesis of n-propyl propionate: the effects of microwave radiation on molecular separation and esterification reaction. *Ind Eng Chem Res* **49**:10287–10296 (2010).

- 113 Shah M, Kiss AA, Zondervan E and de Haan AB, A systematic framework for the feasibility and technical evaluation of reactive distillation processes. *Chem Eng Process* **60**:55–64 (2012).
- 114 Shah M, Kiss AA, Zondervan E and de Haan AB, Influence of liquid back mixing on a kinetically controlled reactive distillation process. *Chem Eng Sci* **68**:184–191 (2012).
- 115 Shah M, Kiss AA, Zondervan E and de Haan AB, Pilot-scale experimental validation of unsaturated polyesters synthesis by reactive distillation. *Chem Eng J* **213**:175–185 (2012).
- 116 Shah M, Kiss AA, Zondervan E and de Haan AB, Evaluation of configuration alternatives for multi-product polyester synthesis by reactive distillation. *Comput Chem Eng* **52**:193–203 (2013).
- 117 Meirelles A, Weiss S and Herfurth H, Ethanol dehydration by extractive distillation. *J Chem Technol Biotechnol* **53**:181–188 (1992).
- 118 Vane LM and Alvarez FR, Membrane-assisted vapor stripping: energy efficient hybrid distillation-vapor permeation process for alcohol-water separation. *J Chem Technol Biotechnol* **83**:1275–1287 (2008).
- 119 Frolkova AK and Raeva VM, Bioethanol dehydration: state of the art. *Theoret Found Chem Eng* **44**:545–556 (2010).
- 120 Kiss AA and Ignat RM, Optimal economic design of a bioethanol dehydration process by extractive distillation. *Energy Technol* **1**:166–170 (2013).
- 121 Muller M and Hubsch U, Dimethyl ether, in *Ullmann's Encyclopedia Industrial Chemistry*, 7<sup>th</sup> edn. Wiley-VCH, Weinheim (2005).
- 122 Kiss AA and Ignat RM, Revamping dimethyl ether separation to a single-step process. *Chem Eng Technol* **36**:1261–1267 (2013).