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Intensified distillation-based separation processes: Recent developments and perspective

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Abstract

Endeavoring towards greater sustainability has driven process industries to search for opportunities to decrease the production costs, energy consumption, equipment size, and environment impact as well to improve the raw material yields, remote control and process flexibility. Process intensification (PI), which is defined as a set of innovative principles applied to the design of process and equipment to satisfy all those concerns, has become the main trend for improving the process performance. PI is utilized widely in heat transfer, reaction, separation, and mixing, which results in plant compactness, cleanliness and energy efficiency. This paper reviews briefly some of the main intensified separation processes and improvement mechanisms. This study focused mainly on the PI of distillation processes, which are the most important separation methods. In addition to these technologies, the potential and reliability of reactive separation processes are addressed briefly, which would enable industry to achieve higher efficiencies and high capacities. The authors propose and evaluate the membrane-assisted reactive dividing wall column (MRDWC), which is an innovative configuration combining reactive distillation used to overcome chemical equilibrium, and a dividing wall column used to save energy, with a membrane used to overcome the azeotrope in azeotropic distillation systems. Recent developments in current research are summarized to highlight the importance as well as the effects, challenges and future prospects of PI.

Keywords: Process intensification; Separation processes; Reactive separation processes; Innovative systems; Energy efficiency.

1. Introduction

The development of the industrial system in the year 2050 has been well defined in the recent Research Agenda with many strategic sectors, such as water, energy, food, health, etc. expected to take place consistently based on process intensification (PI) principles [1]. They lie in innovative methods for the design of equipment and processes that are expected to achieve significant improvements, such as higher energy efficiency, capital reduction, safety, environment impact, and improved raw material yields [2-3]. On the other hand, there are several hurdles that prevent the rapid implementation of PI technologies in the process industry, such as higher failure risk to the process industry, higher scale-up knowledge uncertainty, higher equipment unreliability, and increased safety, health, and environment risks [4].

Separations, which currently account for 60 to 80% of the process cost in most mature chemical processes, can be improved by PI technologies [5]. Among these separation processes, distillation comprising the largest share of industrial energy use for separations has been received much attention to improve efficiency. Meanwhile, a membrane that consumes less energy has the potential to replace conventional energy-intensive technologies. On the other hand, many challenges need to be overcome before membranes can be scaled up using PI technologies.

Considerable effort has been made in the past to make new developments that go beyond ‘traditional’ separation processes [6]. Materials and process development strategies for improving the separation energy efficiency include replacing high-energy technologies, such as distillation, drying and evaporation, with low energy technologies, such as extraction, absorption, adsorption, membrane separations, crystallization, and physical-property based operations or adopting PI strategies [7]. In particular, to intensify the separation process, there are two areas [6] – process-intensifying equipment, such as Hige referring rotating packed bed (RPB) [8], and process-intensifying methods, such as hybrid process [9], dividing wall column (DWC) [10], integration of reaction and separation [11], and techniques using alternative energy sources, including microwave, centrifugal field and electric fields [3] (Figure 1).

Reactive separations, which are formed through the combination of a selected separation process

with a chemical reaction within a single unit, have attracted considerable attention in industry and academia. This technology can improve the reaction conversion and selectivity by removing the products from the reactive section and circumventing/overcoming the separation boundaries, such as azeotropes in the distillation process [12]. On the other hand, reactive separation processes still have some limitations, such as complex modeling needs, increased operational complexity, limited applications, significant development costs, and extensive equipment design efforts [3].

This paper reviews some of the intensified separation processes and improvement mechanisms. This study focused mainly on the PI of distillation, which has attracted significant interest from industry and academia. In addition to these technologies, the potential and reliability of reactive separation processes are addressed briefly, which would enable the intensification of production processes. This paper proposes and evaluates new efforts for the membrane-assisted reactive dividing wall column (MRDWC), which is an innovative configuration combining reactive distillation used to overcome the chemical equilibrium and the dividing wall column employed to save energy requirement, with a membrane to overcome the azeotrope in azeotropic distillation systems. The most important and interesting recent developments in current main research areas are summarized to highlight the importance as well as the effects, challenges and future prospects of PI.

2. Intensification of separation processes

2.1. Distillation

Distillation is a highly energy demanding unit operation, and numerous modes of energy, or process, intensification alternatives have been proposed and implemented over the years, which are based either on the application of additional and alternative energy forms or on manipulation of the structural parameters [13-14]. Several reports considered intensified distillation, such as DWC [15], internal heat-integrated distillation columns (HIDiC) [16], HiGee distillation [17] and even cyclic distillation [18], as well as innovative reactive distillation [19] and reactive DWC [20], which will be discussed in section 3. High performance trays/packings are not reported in this paper.

2.1.1. DWC

The thermal coupling technique supplies a good mechanism to improve the conventional

distillation sequence [21]. Among the configurations that employ the thermal coupling technique, a DWC has been one of the best PI technologies and the most widely applied in the industry, as shown in [Figure 2](#). This industrially proven technology results in a reduction in the quantity of heat exchangers, enhanced separation efficiency, and energy and capital cost savings. Recently, the application of DWCs was extended to azeotropic [22], extractive [23] and reactive distillations [24].

The design, control and application of DWCs for three component mixtures are well established [25]. Recently, the extension of DWCs to the separation of more than three components including the Kaibel, Sargent and Agrawal arrangements have attracted attention (shown in [Figure 3](#)) [26]. The Agrawal arrangement, which shows better results in this paper, was applied to improve the natural gas recovery process [27]. The Kaibel arrangement is an interesting alternative considering its simplicity by withdrawing a second side stream of a DWC. The design of this column has been almost solved, but operation and control still remain open issues [28]. The Kaibel arrangement is difficult to handle when minimizing the vapor flow rate at given product purities, whereas it appears to be easier to operate when the product purities are free. This arrangement can be used in refinery plants where the product purities does not play a vital role or when a bottleneck problem occurs in the process [28]. Recently, the Kaibel arrangement was studied further via an investigation of the effects of vapor split manipulation [29].

Because DWCs can enhance the energy efficiency in the distillation sequences, considerable effort has been spent to retrofit existing distillation columns for reducing the energy requirements and/or increasing the capacity while the main product purity and recovery are maintained ([Figure 4](#)) [30-32]. In any case, a successful retrofit project normally bases on maximum employment of existing equipment to reduce the investment cost [33]. Thus, a dividing wall can be added into the existing distillation to form DWC for improving energy efficiency. In addition, one of key ideas in debottlenecking is to have the DWC manage the increased load [34].

Most reports on the column internal of DWC use the packing type. Recent efforts on the design of DWCs with trays, which is important for systems operated at high vapor loads, using Computational Fluid Dynamics was reported [35]. This study pioneers the studies on the design of

trays or packing type, hydraulic and operating conditions analysis for a range of DWC systems, particularly for applications to floating, production, storage, and off-loading facilities (FPSO) and offshore liquefied natural gas (FLNG), which have significant motion.

DWC applications are expected to increase and become as a standard distillation piece of equipment over the next 50 years [36].

2.1.2. Internally heat-integrated distillation column (HIDiC)

The HIDiC is the most revolutionary approach to a heat pump design [37]. Remarkably, up to 70% energy savings can be achieved using a HIDiC system by utilizing the heat from the rectifying section to boil the stripping part of the column as compared to conventional distillation columns. However, many challenges such as high investment costs, complex design and control problems need to be overcome to conduct the commercial scale [14]. Recently, a development in this area was reported with a trade name, SuperHIDiC (Figure 5), developed by Toyo Engineering Corp. [38]. The separation of multi-component mixtures using this technology is an extremely challenging research issue [37].

2.1.3. HiGee distillation

“Higee”, a synonym for high-gravity technology, utilizing centrifugal fields to form a rotating packed bed (RPB) provides another mechanism to improve separation efficiency [8,39-40]. The fundamentals of mass transfer in RPBs have yet to be explored and understood fully, while the flow patterns inside a rotating packed bed are difficult to observe inside a rotating packing [13]. Recently, a novel high gravity device, the rotating zigzag bed (RZB) (shown in Figure 6), which has a unique rotor combining a rotational part with a stationary one, was developed to overcome the disadvantages of the rotating bed [41].

The application of HiGee distillation is rather new [42], and has not yet been established in industry. Nevertheless, in China, approximately 200 units of a RZB have been commercialized [40]. The offshore applications of distillation may also become feasible because the HiGee unit is easier to operate when there is movement [13,43].

2.1.4. Cyclic distillation

Cyclic distillation is another intensified unit, which has attracted increasing attention. This enhances the separation efficiency based on separate phase movement, which can save energy requirements substantially [44-45]. The cyclic operating mode consisting of a vapor flow period and a liquid flow period can achieve higher separation efficiency, higher quality of products, as well as reduce the energy requirement and number of trays as compared to conventional distillation [18,45].

Kiss listed several limitations of cyclic distillation. The application to vacuum distillation appears to be difficult. The performance improvement is difficult to achieve when the column has more than ten simple trays [46]. Furthermore, the modelling and design of cyclic distillation columns is rather limited. Recently, a cyclic distillation column on the industrial scale was modeled with significantly improved separation efficiency compared to the conventional bubble cap trays column, exceeding 200–300% [45]. Sluice-chamber trays were proposed to prevent the limitation associated to the number of trays (Figure 7) [45,47]. The performance of a pilot-scale cyclic distillation column was first reported for ethanol-water separation [47].

2.2. Other separation processes

Considerable attention has been paid to the development and application of PI on separation, which requires substantial energy in various chemical industries. Table 1 lists the other selected separation processes intensification technologies. In recent years, among the various separation processes available, the membrane has attracted substantial interest from industrial and academic perspectives. Membrane engineering has the potential to contribute towards process intensification by replacing conventional energy-intensive separation techniques, such as distillation and evaporation, to achieve the selective and efficient transport of specific components, to improve the performance of the reactive processes, and finally to provide reliable choices for environmentally-friendly industrial growth [65]. Over the last fifteen years, some membrane-based processes have been commercialized, such as membrane absorbers, membrane extractors, membrane strippers, and membrane bioreactors, while some processes, such as, membrane distillation are in the process of being commercialized [64].

3. Intensification using reactive separations

Over the years, the development and application of reactive separation processes integrating

reaction and separation in a single set of equipment, which resulted in equipment size reduction, improved separation, cheaper process, and reaction efficiency, have attracted significant attention [9]. The integration of a reaction with separation has been investigated extensively for reactive distillation but it has received less attention for reactive absorption, reactive adsorption, reactive extraction, and reactive membrane or membrane reactor.

Reactive distillation (RD) has been the most extensively researched PI method over the last two decades [66]. Compared to conventional reaction-distillation sequences, such so-called RD processes, enable higher reactant conversion, product selectivity, as well as lower energy, water and solvent consumption, leading to reduced investment and operating costs [67]. Normally, the RD is applied to etherification, esterification and alkylation on an industrial scale [68]. On the other hand, compared to design of a conventional distillation column it is much more sensitive to pressure due to the need for a match between the temperature favorable for the reaction and the temperature favorable for separation [69].

The thermal coupling concept, which improves the thermodynamic efficiency, can be used to improve the RD. In particular, thermally coupled distillation sequence (TCDS) and DWC, which are the best examples of proven PI technology, are proposed to form a thermally-coupled reactive distillation sequence (TCRDS) (Figure 8) [70] and reactive dividing wall column (RDWC) (Figure 9), respectively, as an attempt to improve energy efficiency and/or increase the capacity. Up to now, only a few industrial applications of RDWC have been reported [71].

In addition, because membrane separations, such as pervaporation and vapor permeation, are not limited by vapor-liquid equilibrium, they can be considered to separate several non-ideal aqueous-organic mixtures, which form azeotropes [9]. Therefore, a hybrid configuration comprising of membrane assisted RD is attractive for sustainably improving various chemical processes. The separation process is intensified further using a novel configuration of membrane-assisted reactive dividing wall column (MRDWC) (Figure 10), which integrates the RD used to overcome the chemical equilibrium and the DWC employed to save energy, with a membrane to overcome the azeotrope. Note that the unreacted reactant separated by the membrane can be withdrawn or recycled in the

MRDWC. This intensified configuration can also be considered in retrofit design. More detailed research will be needed to understand this process deeply as well as to quantify the synergistic effects between the three unit operations. Insight analysis should be studied, which can be used to define the operating range of this novel process.

Microwave irradiation might lead to enhanced separation efficiency and reaction rates, and thus to higher conversion, which might enhance the reactive distillation performance. Therefore, a systematic investigation of the impact of microwave irradiation on the separation of mixtures and on the reaction was evaluated to prove the potential and feasibility of the concept of microwave-assisted RD [72]. On the other hand, based on the outcome of this study on the separation efficiency of binary mixtures and the reaction itself, the current results indicate that the integration of a microwave field into a RD column would neither enhance the separation efficiency on the macroscopic scale, as present in a RD column, nor enhance the reaction rate. Hence, the conversion or selectivity for the investigated reaction system would be relatively unaffected.

A novel PI approach integrating a cyclic operation and RD in a single unit that outperforms classic RD was recently proposed [73]. This study developed a rigorous mathematical model and tested it with the synthesis of dimethyl ether to reveal the key benefits of a RD with cyclic operation mode.

Table 1 summarizes the brief mechanisms, main applications and recent status of other selected reactive separation processes. Up to now, RD and RA have been commercialized, whereas some processes, such as reactive adsorption, reactive extraction and membrane reactors (**Figure 11**) still require significant fundamental research and development before becoming viable on a commercial scale.

4. Industrial separation process applications

Because PI can reduce the investment cost, inventory and improve heat management/energy utilization, it is expected to have wide ranging applicability, ranging from petrochemicals and bulk chemicals [4], fine chemical and pharmaceuticals industries [3] to biofuels [74], carbon capture [75] and offshore processing [76]. Owing to the large volume production of petrochemicals and bulk

chemicals, reducing energy consumption and environmental impact are significant motivations of technology innovation. On the other hand, achieving improvements in selectivity, yield and processing time are more important for fine chemicals and pharmaceuticals because the energy cost comprises a smaller fraction of the production cost [7].

4.1. Intensified separation systems in petrochemicals and bulk chemicals

Numerous applications PI technologies have been applied in petrochemicals and bulk chemicals. Among them, reactive distillation [77] and DWCs are the most popular technologies with a range of applications. In particular, reactive distillation and DWCs have been implemented on the commercial scale in the petrol–chemical industry more than 150 times [78] and more than 100 times [4,79], respectively. Future applications in these industries can consider many types of innovative multifunctional processes, such as RDWC, extractive DWC and hybrid configurations.

4.2. Intensified separation systems in fine chemicals and pharmaceuticals industries

As discussed above, obtaining enhancements in selectivity, yield and processing time in the pharmaceutical and fine chemicals industries area are more important to their cost competitiveness than reducing energy costs due to the small fraction of production costs. Most efforts in this area have focused on reaction intensification. Electrostatic fields have been employed to improve the penicillin extraction process [3]. Drying, which is a commonly used technique for pharmaceutical applications, has been intensified using ultrasound, microwave, electromagnetic techniques, etc. [80-81].

4.3. Intensified separation systems in renewable energies (biofuel)

The production of biofuels already takes advantages of using advanced PI technologies, such as reactive separation processes [82]. Most studies on reactive separation processes for biodiesel production were based solely on conventional reactive distillation [83-84], or alternatives, such as entrainer-based [85] or dual reactive distillation [86] or reactive absorption [87-88]. In particular, a novel reactive-absorption-based biodiesel process was proposed, which is a simple and robust process, achieving high conversion and selectivity, with no thermal degradation of products, and no waste streams, as well as reducing the capital investment and operating costs [87]. Pervaporation, which is also described as a PI technology, can be applied to biodiesel production [82].

The application of advanced or intensified distillation systems is expected to be promising when continuing to develop the concept of biorefineries away from single product systems to multiple product systems [89-90]. In addition, the integration of bio-based raw materials into existing conventional plants will further push those intensified systems or hybrid processing [89]. On the other hand, challenges to implement distillation systems into biotechnological processes remain with respect to the operating conditions, such as handling solid systems (e.g. enzymes, cells) and highly viscous systems, which will require the development of new distillation systems, such as Hige distillation, which could fill this gap in specific cases [12].

4.4. Intensified separation systems in carbon capture

An area of chemical engineering technology that has possibly grown most rapidly within the past few years is carbon capture, whose main aim is to reduce CO₂ emissions from all plants that burn fossil fuels, such as steelworks, offshore facilities, chemical plants, and perhaps the largest challenge, power generation plants on shore, in particular, but not limited to, coal-fired power stations [3]. Normally, a packed column is designed to removing CO₂ by chemical absorption [91-92]. To improve the mass transfer rate in a conventional packed bed, a rotating doughnut-shaped packing device, which refers to Hige or RPB, was suggested [93]. Furthermore, membrane technology can be considered a promising separation method that releases the disadvantages of a gas absorption tower [94]. Considerable efforts have been made to increase the membrane performance with two main approaches: gas permeation and membrane contactor. On the other hand, there is still a significant gap between the laboratory and commercial scales in the industry [95]. This is particularly important for intensifying the desorption process in the stripper. In particular, agitation, ultrasound and microwave can be used to improve the release of CO₂ [3,96].

4.5. Intensified separation systems in offshore processing

Normally, trays are preferred in the distillation of hydrocarbons. On the other hand, trays should not be applied to the distillation and separation columns of an offshore plant, such as FPSO and FLNG, which must have the ability to withstand waves [97]. Therefore, packed type column designs are suitable because the columns can withstand motion [76]. The walls formed by the corrugated

sheets reduce the impact of motion and make structured packing a better choice than random packing [98]. Furthermore, the use of a DWC for offshore FLNG plants, forming an energy-efficient and compact NGL recovery process has been suggested [76].

In seawater deaeration or deoxygenation, contact plays an important role in the process with the most popular techniques for contacting being packed, tray or bubble columns, or agitated vessels [3]. Significant intensification can be obtained using either HiGee technology or the tangential injection of liquid into a static vessels [99]. Kvarner recently investigated a membrane absorption technology for removing CO₂ from turbine exhaust gases in offshore applications [61]. Substantial reduction on investment and operating costs are expected as compared to the conventional amine separation process [100].

5. Conclusions

Economic and environmental considerations have encouraged many separation processes in chemical industries to focus on PI-based innovative engineering solutions. In addition, using alternative energy sources, such as microwaves, centrifugal field, electric fields, combining a column into one unit forming DWC or the integration of reaction and separation into a single unit forming reactive separation is one of the most radical approaches of PI applications in separation processes. In particular, advances in reactive separation technology have many benefits in green processing technology, such as reducing the energy requirements, improving the reaction rate, enhancing the productivity and selectivity, and ultimately leading to high-efficiency separation processes. These technologies are promising and need to overcome several challenges to unleash its full potential. Further improvement, i.e., the development of an innovative configuration of MRDWC for azeotropic mixtures is an interestingly challenging research issue. Hybrid separation configurations combining RD or TCRDS or RDWC with other separation technology are also a challenge for future considerations of supplementing the capability of each unit. Furthermore, different PI methods and different driving forces, such as microwaves, magnetism, gravity, and others need to be considered for integration in a unique system to achieve synergy effects in PI research and development. To have the smooth development of separation processes, other issues, such as new catalysts, membrane material,

new solvent, better rotary machine, cheaper equipment fabrication, reliable control systems, etc. have also been considered.

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References

- [1] A. Gorak, A. Stankiewicz, *Research Agenda for Process Intensification: Towards a Sustainable World of 2050*, Amersfoort, **2011**.
http://3me.tudelft.nl/fileadmin/Faculteit/3mE/Actueel/Nieuws/2011/docs/DSD_Research_Agenda.pdf
- [2] E. Drioli, A. Brunetti, G. D. Profio, G. Barbieri, *Green Chemistry*. **2012**, *14*, 1561-1572. DOI: 10.1039/C2GC16668B
- [3] D. Reay, C. Ramshaw, A. Harvey, *Process Intensification, Engineering for Efficiency, Sustainability and Flexibility*, 2nd Edition, Butterworth-Heinemann **2013**.
- [4] J. Harmsen, *Chem. Eng. Process.* **2010**, *49(1)*, 70–73. DOI: 10.1016/j.cep.2009.11.009
- [5] A.J. Ragauskas, C.K. Williams, B.H. Davison, G. Britovsek, J. Cairney, C.A. Eckert, W.J. Frederick Jr., J.P. Hallett, D.J. Leak, C.L. Liotta, J.R. Mielenz, R. Murphy, R. Templer, T. Tschaplinski, *Science* **2006**, *311*, 484–489. DOI: 10.1126/science.1114736
- [6] A.I. Stankiewicz, J. A. Moulijn, *Chem. Eng. Prog.* January **2000**, 22-34.
- [7] U.S. Department of Energy. *Process Intensification – Chemical Sector Focus 2 Technology Assessment*.
<http://energy.gov/sites/prod/files/2015/02/f19/QTR%20Ch8%20-%20Process%20Intensification%20TA%20Feb-13-2015.pdf>
- [8] C. Ramshaw, R.H. Mallinson, *US Patent 4 283 255*, **1981**.
- [9] C. Buchaly, P. Kreis, A. Górak, *Chem. Eng. Process.* **2007**, *46(9)*, 790–799. DOI: 10.1016/j.cep.2007.05.023

- [10] R.O. Wright, US Patent 2 471 134, 1949.
- [11] H. Schmidt-Traub, A. Górak, *Integrated Reaction and Separation Operations: Modelling and experimental validation*, Springer, Verlag Berlin Heidelberg, 2006.
- [12] P. Lutze, A. Gorak, *Chem. Eng. Res. Des.* 2013, 91(10), 1978–1997. DOI: 10.1016/j.cherd.2013.07.011
- [13] E. Sørensen, K. F. Lam, D. Sudhoff, in *Distillation: Operation and Applications, Edition* (Eds: A. Górak, H. Schoenmakers), 1st Edition, Elsevier, New York 2014.
- [14] A. Gorak, A. Stankiewicz, *Ann. Rev. Chem. Biomol. Eng.* 2011, 2, 431–451. DOI: 10.1146/annurev-chembioeng-061010-114159
- [15] F. O. Barroso-Muñoz, S. Hernández, J. G. Segovia-Hernández, H. Hernández-Escoto, V. Rico-Ramírez, R.-H. Chávez, *Chem. Eng. Technol.* 2011, 34(5), 746–750. DOI: 10.1002/ceat.201000388
- [16] M. Gadalla, L.J. Jimenez, Ž. Olujic, P.J. Jansens, *Comput. Chem. Eng.* 2007, 31(10), 1346–1354. DOI: 10.1016/j.compchemeng.2006.11.006
- [17] D. Sudhoff, M. Leimbrink, M. Schleinitz, A. Górak, P. Lutze, *Chem. Eng. Res. Des.* 2015, 94, 72-89. DOI: 10.1016/j.cherd.2014.11.015
- [18] C. Pătruț, C. S. Bîldea, I. Liță, A. A. Kiss, *Sep. Purif. Technol.* 2014, 125, 326–336. DOI: 10.1016/j.seppur.2014.02.006
- [19] J. Stichlmair, T. Frey, *Chem. Eng. Technol.* 1999, 22(2), 95–103. DOI: 10.1002/(SICI)1521-4125(199902)22:2
- [20] S. Hernández, R. Sandoval-Vergara, F. O. Barroso-Muñoz, R. Murrieta-Dueñas, H. Hernández-Escoto, J. G. Segovia-Hernández, V. Rico-Ramírez, *Chem. Eng. Process.* 2009, 48(1), 250-258. DOI: 10.1016/j.cep.2008.03.015
- [21] M. Errico, B. G. Rong, G. Tola, I. Turunen, in *Proc. of the European Congress of Chemical Engineering*, Copenhagen, 2007.
- [22] A. A. Kiss, R. M. Ignat, *Sep. Purif. Technol.* 2012, 98, 290–297. DOI: 10.1016/j.seppur.2012.06.029

- [23] S. Tututi-Avila, A. Jimenez-Gutierrez, J. Hahn, *Chem. Eng. Process.* **2014**, *82*, 88-100. DOI: 10.1016/j.cep.2014.05.005
- [24] A. A. Kiss, D. J. P. C. Suszwalak, *Comput. Chem. Eng.* **2012**, *38*, 74-81. DOI: 10.1016/j.compchemeng.2011.11.012
- [25] I. Dejanović, Lj. Matijašević, Ž. Olujić, *Chem. Eng. Process.* **2010**, *49(6)*, 559-580. DOI: 10.1016/j.cep.2010.04.001
- [26] A. C. Christiansen, S. Skogestad, K. Lien, *Comput. Chem. Eng.* **1997**, *21*, 237-242. DOI: 10.1016/S0098-1354(97)87508-4
- [27] N. V. D. Long, M. Y. Lee, *Asia-Pacific J. Chem. Eng.* **2012**, *7(S1)*, S71-S77. DOI: 10.1002/apj.643
- [28] M. Ghadrđan, I. J. Halvorsen, S. Skogestad, *Chem. Eng. Res. Des.* **2011**, *89(8)*, 1382–1391. DOI: 10.1016/j.cherd.2011.02.007
- [29] M. Ghadrđan, I. J. Halvorsen, S. Skogestad, *Chem. Eng. Process.* **2013**, *72*, 10– 23. DOI: 10.1016/j.cep.2013.06.014
- [30] B. Slade, B. Stober, D. Simpson, *ICHEME. Symp. Ser. No. 152*, **2006**.
- [31] A. A. Kiss, R. M. Ignat, *Chem. Eng. Technol.* **2013**, *36(7)*, 1261–1267. DOI: 10.1002/ceat.201300133
- [32] N. V. D. Long, M. Y. Lee, *J. Chem. Eng. Japan* **2014**, *47*, 87-108. DOI: <http://doi.org/10.1252/jcej.13we067>
- [33] K.A. Amminudin, R. Smith, *Chem. Eng. Res. Des.* **2001**, *79(7)*, 716–724. DOI: 10.1205/026387601753192037
- [34] N. V. D. Long, S. H. Lee, M. Y. Lee, *Chem. Eng. Process.* **2010**, *49(8)*, 825-835. DOI: 10.1016/j.cep.2010.06.008
- [35] M. A. Rodríguez-Ángeles, F. I. Gómez-Castro, J. G. Segovia-Hernández, A. R. Uribe-Ramírez, *Chem. Eng. Process.* **2015**, *97*, 55-65. DOI:10.1016/j.cep.2015.09.002
- [36] M.A. Schultz, D.G. Stewart, J.M. Harris, S.P. Rosenblum, M. S. Shakur, D.E. O'Brien, *Chem. Eng. Prog.* May **2002**, 64–71.

- [37] A. A. Kiss, Z. Olujic, *Chem. Eng. Process.* **2014**, *86*, 125–144. DOI: 10.1016/j.cep.2014.10.017
- [38] CHEMENTATOR, This distillation column promises substantial energy reductions, *Chemical Engineering*, (www.che.com), January 2012, 10.
- [39] C. Ramshaw, *The Chem. Eng.* **1983**, 389, 13–14.
- [40] G.Q. Wang, Z.C. Xu, J.B. Ji, *Chem. Eng. Res. Des.* **2011**, *89(8)*, 1434–1442. DOI: 10.1016/j.cherd.2011.02.013
- [41] G. Q. Wang, O. G. Xu, Z. C. Xu, J. B. Ji, *Ind. Eng. Chem. Res.* **2008**, *47(22)*, 8840–8846. DOI: 10.1021/ie801020u
- [42] C.C. Lin, T.J. Ho, W.T. Liu, *J. Chem. Eng. Japan* **2002**, *35 (12)*, 1298–1304. DOI: <http://doi.org/10.1252/jcej.35.1298>
- [43] C. Ramshaw, *US 4 715 869*, **1987**.
- [44] R.A. Gaska, M.R. Cannon, *Ind. Eng. Chem.* **1961**, *53(8)*, 630–631. DOI: 10.1021/ie50620a022
- [45] V.N. Maleta, A.A. Kiss, V.M. Taran, B.V. Maleta, *Chem. Eng. Process.* **2011**, *50(7)*, 655–664. DOI: 10.1016/j.cep.2011.04.002
- [46] A. A. Kiss, *Advanced distillation technologies-design, control and applications*, Wiley, UK, **2013**.
- [47] B. V. Maleta, Al. Shevchenko, O. Bedryk, A. A. Kiss, *AIChE J.* **2015** (Accepted). DOI: 10.1002/aic.14827
- [48] L. Agarwal, V. Pavani, D. P. Rao, N. Kaistha, *Ind. Eng. Chem. Res.* **2010**, *49(20)*, 10046–10058. DOI: 10.1021/ie101195k
- [49] O. Yildirim, A. A. Kiss, N. Huser, K. Lessmann, E. Y. Kenig, *Chem. Eng. J.* **2012**, *213*, 371–391. DOI: 10.1016/j.cej.2012.09.121
- [50] L. Joss, M. Gazzani, M. Hefti, D. Marx, M. Mazzotti, *Ind. Eng. Chem. Res.* **2015**, *54*, 3027–3038. DOI: 10.1021/ie5048829
- [51] Y. Y. Loy, X.L. Lee, G.P. Rangaiah, *Sep. Purif. Technol.* **2015**, *149*, 413–427. DOI: 10.1016/j.seppur.2015.06.007

- [52] H. An, B. Feng, S. Su, *Int. J. Greenhouse Gas Control.* **2011**, (1)5, 16–25. DOI: 10.1016/j.ijggc.2010.03.007
- [53] M. A. T. Bisschops, S. H. van Hateren, K. Ch. A. M. Luyben, L. A. M. van der Wielen, *Ind. Eng. Chem. Res.* **2000**, 39(11), 4376–4382. DOI: 10.1021/ie990927b
- [54] K. Y. Rani, C. Sumana, in *Industrial catalysis and separations : innovations for process intensification*, Edition (Eds: B. M. Reddy, K. V. Raghavan) , CRC Press, Taylor & Francis Group, Boca Raton, **2014**.
- [55] Gitesh, Podbielniak Contactor: A Unique Liquid-Liquid Extractor - Part 1, <http://www.pharmaceuticalonline.com/doc/podbielniak-contactor-a-unique-liquid-liquid-0003>, 2000.
- [56] L. J. Austin, L. Banczyk, H. Sawistowski, *Chem. Eng. Sci.* **1971**, 26, 2120–2021.
- [57] M. D. Vetal, V. G. Lade, V. K. Rathod, *Chem. Eng. Process.* **2013**, 69, 24–30. DOI: 10.1016/j.cep.2013.01.011
- [58] A. Keshav, S. Chand, K. L. Wasewar, *J. Chem. Eng. Data* **2008**, 53 (7), 1424–1430. DOI: 10.1021/je7006617
- [59] S. Lim, S. S. Hoong, L. K. Teong, S. Bhatia, *Bioresour. Technol.* **2010**, 101(18), 7169–7172. DOI: 10.1016/j.biortech.2010.03.134.
- [60] A. Alkudhiri, N. Darwish, N. Hilal, *Desalination* **2012**, 287, 2–18. DOI: 10.1016/j.desal.2011.08.027
- [61] H. Herzog, O. Falk-Pedersen, *5th Int. Conf. on Greenhouse Gas Control Technol.* Cairns, Australia, August **2000**.
- [62] E. Drioli, A. I. Stankiewicz, F. Macedonio, *J. Membrane Sci.* **2011**, 380(1–2), 1– 8. DOI: 10.1016/j.memsci.2011.06.043
- [63] C. Charcosset, *J. Chem. Technol. Biotechnol.* **1998**, 71(2), 95–110. DOI: 10.1002/(SICI)1097-4660(199802)71:2<95::AID-JCTB823>3.0.CO;2-J
- [64] K. K. Sirkar, A. G. Fane, R. Wang, S. R. Wickramasinghe, *Chem. Eng. Process.* **2015**, 87, 16–25. DOI: 10.1016/j.cep.2014.10.018

- [65] E. Drioli, E. Curcio, *J. Chem. Technol. Biotechnol.* **2007**, *82* (3), 223-227. DOI: 10.1002/jctb.1650
- [66] K. Cheng, S.J. Wang, D.S.H. Wong, *Comput. Chem. Eng.* **2013**, *52*, 262-271. DOI: 10.1016/j.compchemeng.2013.02.001
- [67] T. Keller, in *Distillation: Equipment and Processes*, Edition (Eds: A. Gorak, Z. Olujic), Elsevier, New York **2014**.
- [68] Z. Lei, B. Chen, Z. Ding, *Special Distillation Processes*, Elsevier, Amsterdam **2005**.
- [69] W. L. Luyben, C. C. Yu, *Reactive distillation, design and control*, John Wiley & Sons, New Jersey **2008**.
- [70] N. Nguyen, Y. Demirel, *Energy* **2011**, *36*(8), 4838–4847. DOI: 10.1016/j.energy.2011.05.020
- [71] Ö. Yildirim, A. A. Kiss, E. Y. Kenig, *Sep. Purif. Technol.* **2011**, *80*(3), 403–417. DOI: 10.1016/j.seppur.2011.05.009
- [72] K. Werth, P. Lutze, A. A. Kiss, A. I. Stankiewicz, G. D. Stefanidis, A. Górak, *Chem. Eng. Process.* **2015**, *93*, 87–97. DOI: 10.1016/j.cep.2015.05.002
- [73] C. Patrut, C. S. Bildea, A. A. Kiss, *Chem. Eng. Process.* **2014**, *81*, 1–12. DOI: 10.1016/j.cep.2014.04.006
- [74] L. C. Nhien, N. V. D. Long, M. Y. Lee, *Chem. Eng. Res. Des.* (Accepted), **2015**. DOI:
- [75] A.S. Joel, M. Wang, C. Ramshaw, E. Oko, *Int. J. Greenhouse Gas Control.* **2014**, *21*, 91–100. DOI: 10.1016/j.ijggc.2013.12.005
- [76] S. G. Lee, N. V. D. Long, M. Y. Lee, *Ind. Eng. Chem. Res.* **2012**, *51*(30), 10021-10030. DOI: 10.1021/ie2029283
- [77] V. H. Agreda, L. R. Partin, W. H. Heise, *Chem. Eng. Prog.* **1990**, *86* (2), 40–46.
- [78] G.J. Harmsen, *Chem. Eng. Process.* **2007**, *46* (9), 774– 780. DOI: 10.1016/j.cep.2007.06.005
- [79] G. Parkinson, *Chem. Eng. Process.* May **2007**, 8–11.
- [80] M. Benali, T. Kudra, *Dry. Technol.* **2010**, *28*(10), 1127–1135. DOI: 10.1080/07373937.2010.502604

- [81] R. H. Walters , B. Bhatnagar, S. Tchessalov, K. Izutsu, K. Tsumoto, S. Ohtake, *J. Pharm. Sci.* **2014**, *103 (9)*, 2673-2695. DOI: 10.1002/jps.23998.
- [82] A.A. Kiss, *Process intensification technologies for biodiesel production – Reactive separation processes*, Springer, Heidelberg, **2014**.
- [83] F. Omota, A.C. Dimian, A. Bliet, *Chem. Eng. Sci.* **2003**, *58(14)*, 3159–3174. DOI: 10.1016/S0009-2509(03)00165-9
- [84] A.A. Kiss, A.C. Dimian, G. Rothenberg, *Energy & Fuels* **2008**, *22(1)*, 598–604. DOI: 10.1021/ef700265y
- [85] A.C. Dimian, F. Omota, A. Bliet, *Chem. Eng. Process.* **2004**, *43(3)*, 411–420. DOI: 10.1016/S0255-2701(03)00125-9
- [86] A.C. Dimian, C.S. Bildea, F. Omota, A.A. Kiss, *Comput. Chem. Eng.* **2009**, *33(3)*, 743–750. DOI: 10.1016/j.compchemeng.2008.09.020
- [87] A. A. Kiss, *Sep. Purif. Technol.* **2009**, *69(3)*, 280–287. DOI: 10.1016/j.seppur.2009.08.004
- [88] A. A. Kiss, C. S. Bildea, *Bioresour. Technol.* **2011**, *102(2)*, 490–498. DOI: 10.1016/j.biortech.2010.08.066
- [89] P. Lutze, in *Distillation: Operation and Applications*, Edition (Eds: A. Górak, H. Schoenmakers), 1st Edition, Elsevier, New York **2014**.
- [90] W. Soetaert, E.J. Vandamme, *Industrial Biotechnology-Sustainable Growth and Economic Success*, 1st edition, Wiley-VCH, Verlag GmbH & Co., Weinheim **2010**.
- [91] P. C. Luo, Z. B. Zhang, Z. Jiao, Z. X. Wang, *Ind. Eng. Chem. Res.* **2003**, *42(20)*, 4861–4866. DOI: 10.1021/ie030029m
- [92] J. Wallace, S. Krumdieck, *J. Mech. Eng. Sci.* **2005**, *219*, 1225–1233. DOI: 10.1243/095440605X32011
- [93] H. Cheng, C. Tan, *Sep. Purif. Technol.* **2011**, *82*, 156–166. DOI: 10.1016/j.seppur.2011.09.004
- [94] P. Luis, T. V. Gerven, B. V. der Bruggen, *Prog. Energy Combust. Sci.* **2012**, *38(3)*, 419–448. DOI: 10.1016/j.pecs.2012.01.004

- [95] P. Luis, B. V. der Bruggen, *Greenhouse Gas. Sci. Technol.* **2013**, 3(5), 318–337. DOI: 10.1002/ghg.1365
- [96] R. Cherbański, E. Molga, *Chem. Eng. Process.* **2009**, 48 (1), 48–58. DOI: 10.1016/j.cep.2008.01.004
- [97] Y. M. Lee, T. I. Cho, J. H. Lee, O. Y. Kwon, *Offshore Technology Conf.*, Texas, U.S.A, May **2008**.
- [98] L. Spiegel, M. Duss, in *Distillation: Equipment and Processes*, Edition (Eds: A. Górak, Ž. Olujić) 1st Edition, Elsevier, New York **2014**.
- [99] B. Waldie, in *Proc. of the 1st Int. Conf. on Science, Engineering and Technology of Intensive Processing*, Nottingham University **1995**.
- [100] A. Stankiewicz, in *Process Intensification: History, Philosophy, Principles*, Edition (Eds: A. Stankiewicz, J.A. Moulijn), Marcel Dekker, New York **2004**.

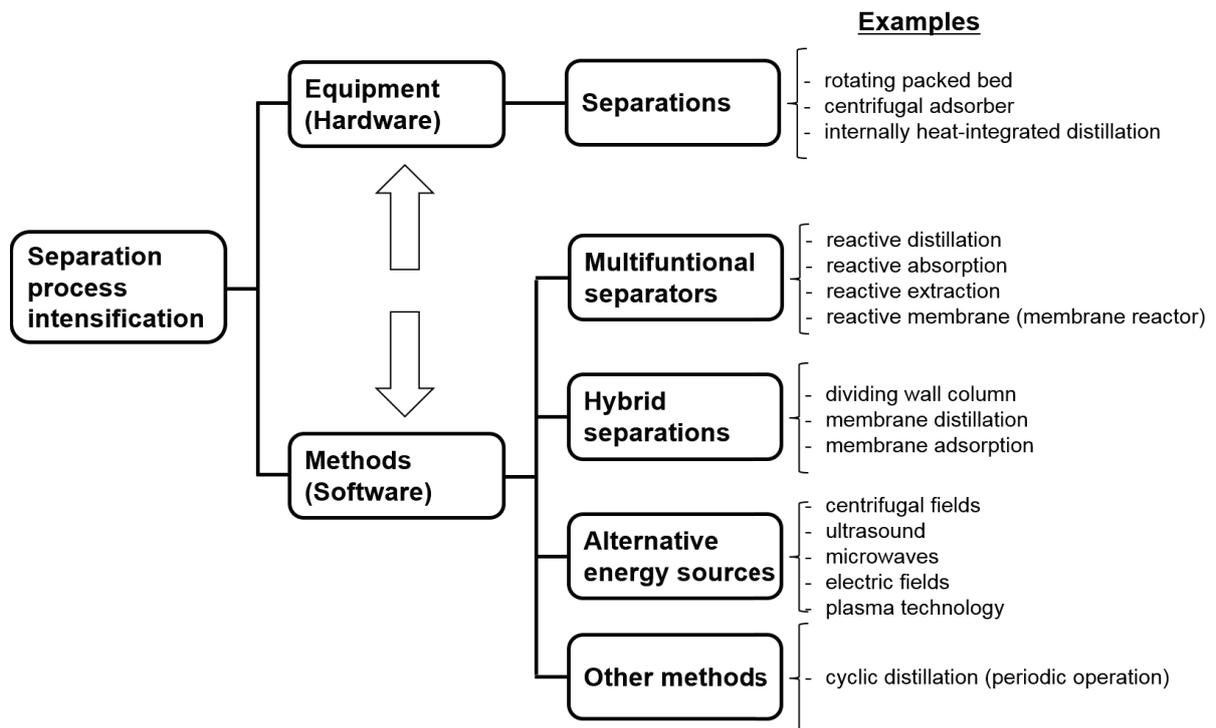


Figure 1. Separation process intensification toolbox.

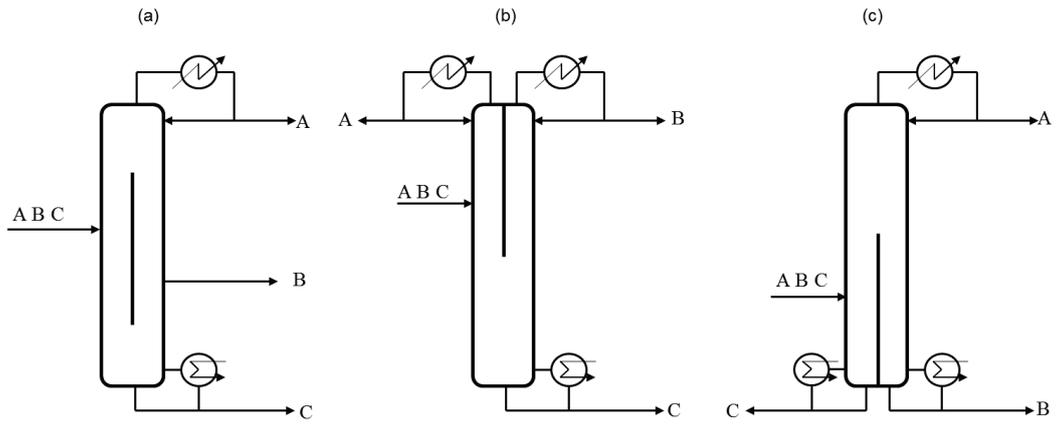


Figure 2. Schematic diagram of the (a) DWC, (b) TDWC and (c) BDWC.

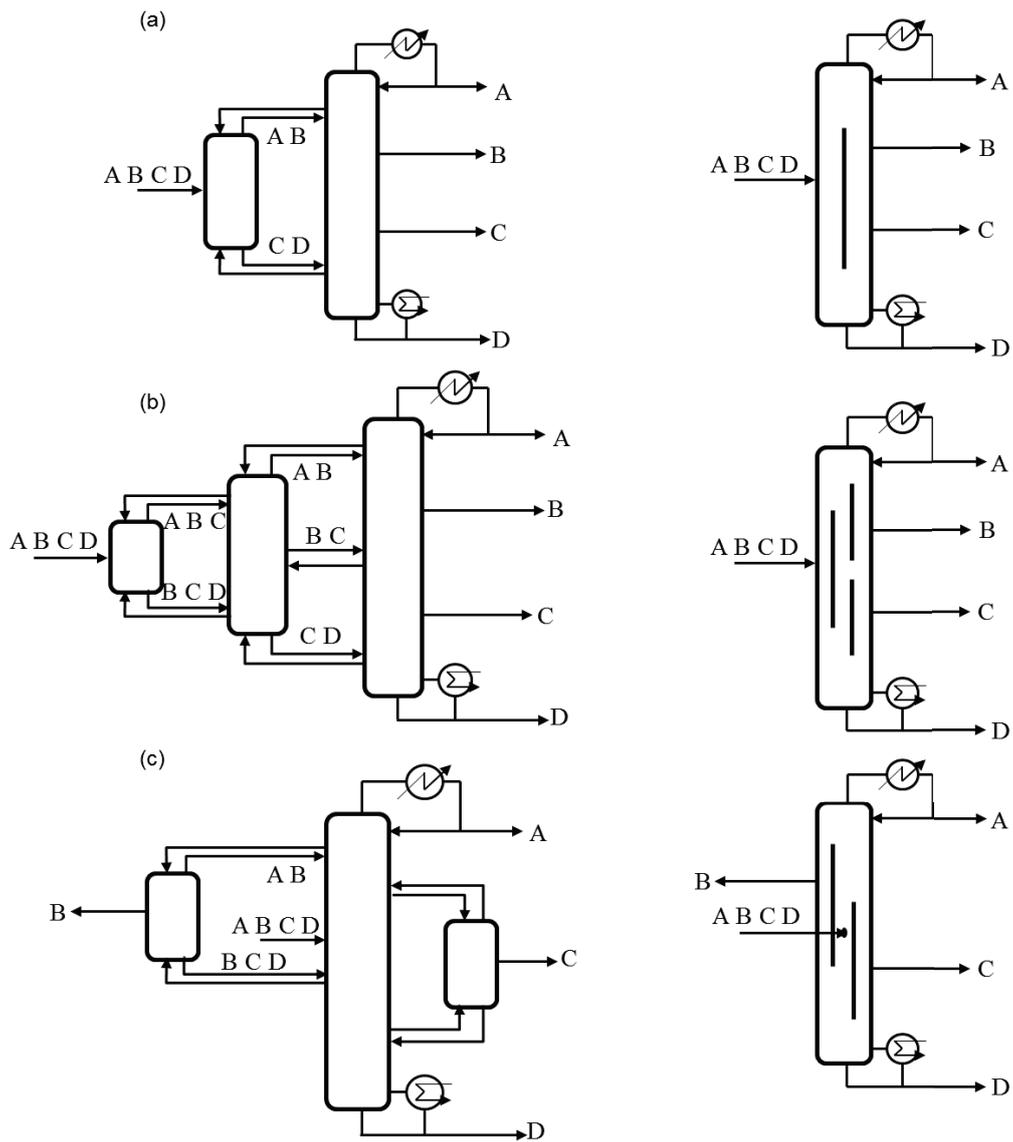


Figure 3. Schematic diagram of the (a) Kaibel, (b) Sargent and (c) Agrawal arrangement.

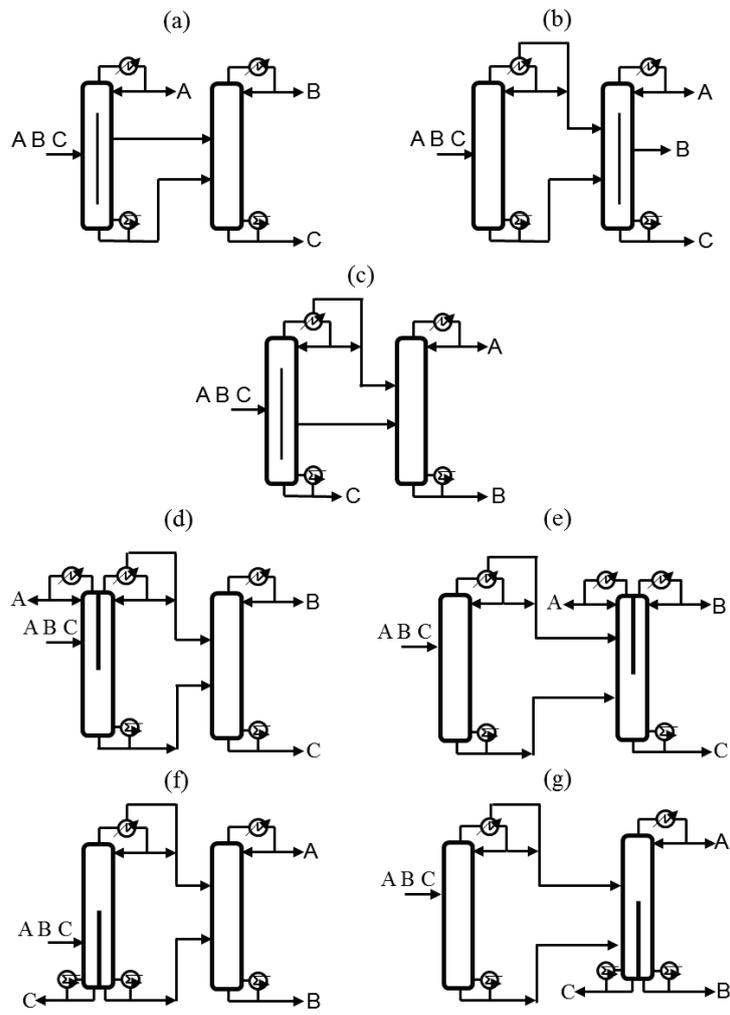


Figure 4. Schematic diagram of promising configurations for retrofit using DWC.

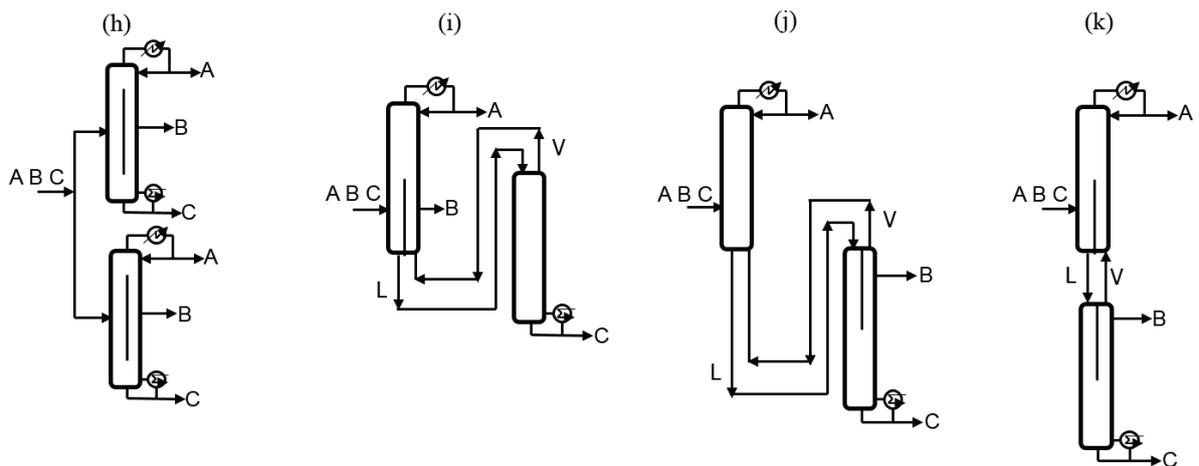


Figure 4. Schematic diagram of promising configurations for retrofit using DWC (continued).

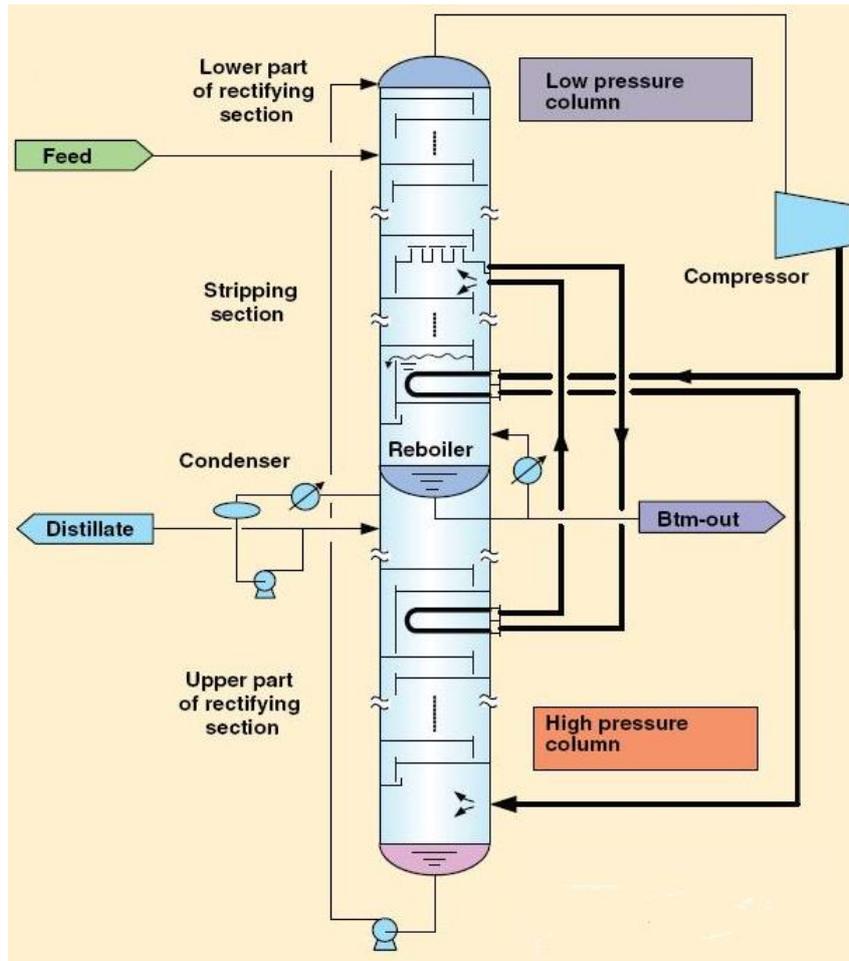
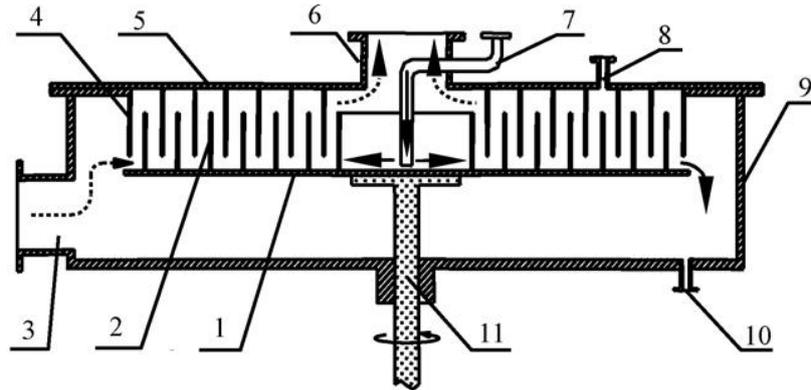


Figure 5. Schematic diagram of a SuperHIDiC configuration [38].



- 1-rotational disc 2-rotational baffle 3-gas inlet 4-stationary baffle
5-stationary disc 6-gas outlet 7-liquid inlet 8-middle feed 9-liquid outlet
10- casing 11-shaft

Figure 6. Simplified sketch of the RZB and its rotor [40].

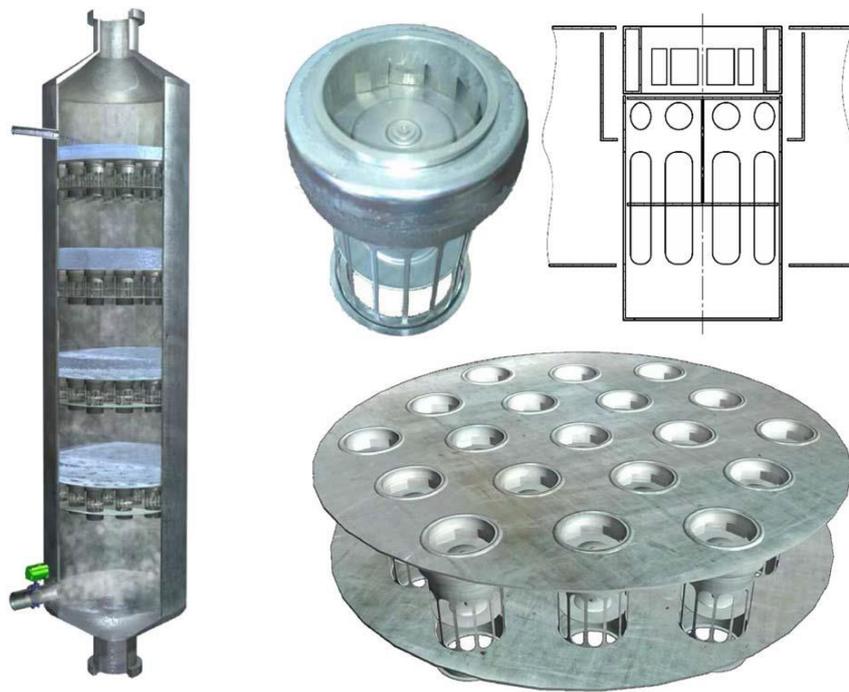
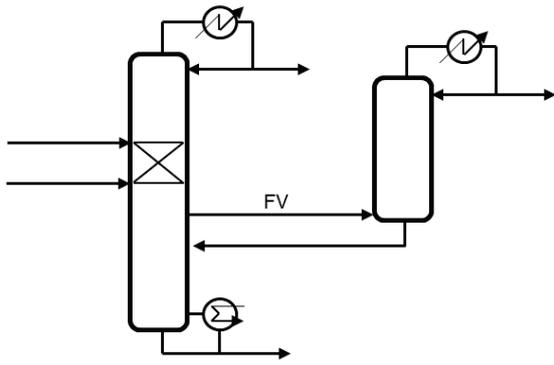


Figure 7. Cross-section of a cyclic distillation and specific internals [47].

(a)



(b)

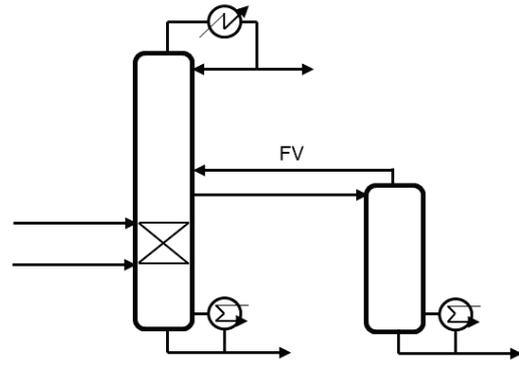
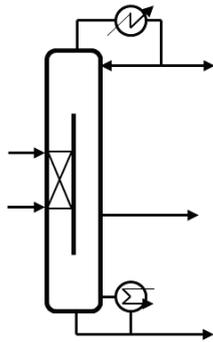
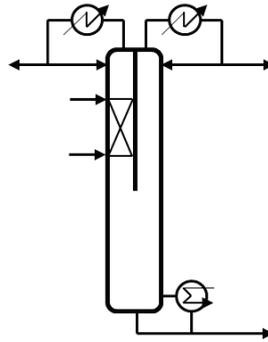


Figure 8. Schematic diagram of the TCRDC with (a) side rectifier and (b) side stripper.

(a)



(b)



(c)

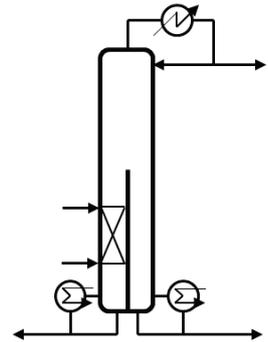


Figure 9. Schematic diagram of the (a) conventional reactive dividing wall column, (b) top reactive dividing wall column, and (c) bottom reactive dividing wall column.

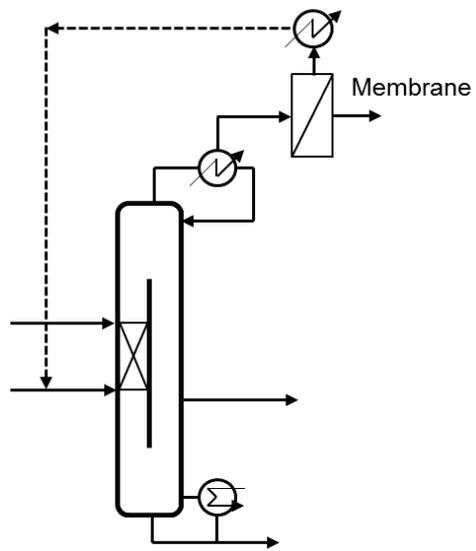


Figure 10. Schematic diagram of the hybrid membrane-RDWC systems.

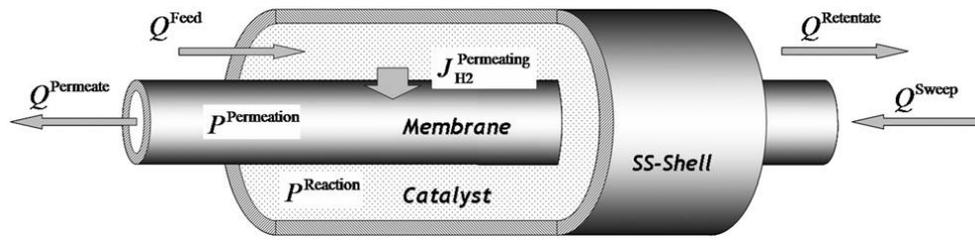


Figure 11. A membrane reactor scheme [2].

Table 1. Summary of other selected separation processes intensification technologies

Process type	Equipment type (or name)	Intensification technique (or mechanism)	Main remarks	Ref.
Absorption	HiGee	Rotating packed bed	Significant volume reduction can be achieved using HiGee over conventional packed beds.	[48]
	Reactive absorption (RA)	Integrating of reaction and absorption in one single equipment	The most common use of RA is for the separation of a gas mixture (e.g., CO ₂ , H ₂ S, NO _x and SO _x) in a solvent. The extensive efforts in CO ₂ capture and storage mainly stimulate the current growth of RA processes. Owing to the large chance for enhancing the regeneration of the solvent, which is responsible of up to 70–80% of the operating costs, most current research had focused mainly on development of new solvents.	[49]
Adsorption	Temperature swing adsorption (TSA)	The molecules are strongly adsorbed at low temperatures, and the molecular sieves are regenerated at high	The CO ₂ capture from flue gases can consider TSA as an interesting option. A gap between the emerging works aimed at determining quantitative structure property relationships of adsorbents and the actual process performance still remains.	[50]

	temperatures		
Pressure swing adsorption (PSA)	The molecules are strongly adsorbed at high pressures, and the molecular sieves are regenerated at low pressures	PSA is normally preferred over TSA because of its lower operating cost	[51]
Electro-thermal swing adsorption (ESA)	Passing electricity through the saturated adsorbent and the heat generated by Joule effect facilitates the release of gas	This technology proposed for CO ₂ capture can potentially be more energy effective than conventional TSA and PSA, thus reduces the CO ₂ capture cost.	[52]
Centrifugal adsorption technology (CAT)	Centrifugal force	CAT can lead to very good separation efficiencies but it requires very compact adsorption equipment with high capacity	[53]
Reactive adsorption	Integrating the mechanism of reaction and adsorption	This technology still needs to be applied commercially even though it is well proven on the laboratory scale,	[54]

in one single unit

Extraction	Podbielniak extractor	Centrifugal force	Intense contact between the two liquids and generation of an interfacial surface area for mass transfer	[55]
		Electric field	2 to 6-10 factor in the transfer rate rise can be achieved compared to the no-field case.	[56]
		Ultrasound	The yield and mass transfer in many solid–liquid extraction processes can be enhanced	[57]
	Reactive extraction (RE)	Integration of reaction and adsorption in one single equipment	Most studies in the literature are focused on equilibrium, kinetics and application of RE. The supercritical reactive extraction (SRE) process was also suggested for biodiesel production to obtain a fast rate. However, large fundamental research and development are needed before this relatively new technology can be used on a commercial scale.	[58-59]
Membrane	Membrane distillation	Vapor pressure difference between membrane surfaces	Most studies deal with the operating conditions based on lab scale experimentation. This is still rarely employed for commercial applications and is an interesting field for process intensification.	[60]

Membrane absorption/stripping	<p>Selective transportation of gaseous component through a membrane while the component is dissolved in the absorbing liquid. In membrane stripping, selected components are separated from the liquid phase using a stripping gas.</p>	<p>Most of the literature deals with a variety of membranes and membrane materials at different pressures and temperatures of operation using different classes of absorbents. The most important industrial application area is the capture of CO₂ from flue gas with a significant reductions of up to 70–75% and 65% in terms of the weight and size of equipment, respectively. This can be advanced for offshore technology.</p>	[61-62]
Membrane chromatography	<p>This is characterized by the absence of pore diffusion, which is the main transport resistance in conventional column chromatography using porous particles.</p>	<p>Membrane chromatography offers a process-intensive choice for different chemical processes, such as ion exchange, metal affinity, protein and reverse phase chromatography. Until now, the literature mostly discusses the approximate solutions neglecting dispersion and kinetic aspects. In the future, the complex modeling, considering the scale up, of membrane chromatography needs to be assessed.</p>	[63]

Membrane extraction	The treated solution and the solvent are separated from each other using solid or liquid membrane.	On the commercial scale, hollow fiber membrane solvent extraction units are mostly based. Hydrophobic hollow fibers with higher solvent resistance are required for most industrial applications. Hydrophilic hollow fibers with aqueous phase in the pores are needed for processes that involve organic solvent extraction.	[64]
Membrane crystallization	A modified form of membrane distillation that combines the principle of membrane and crystallization to achieve separation	The study of a membrane crystallizer is a response to the high market demand of high-value-added products. Moreover, it also allows control of the crystal shape, enhances crystal growth and achieves selective crystallization. These advantages over conventional separation techniques make it an interesting process in the field of process intensification.	[62]
Membrane reactors (MRs)	Integration of the reaction and membrane in a single unit	The recent development of catalytic membranes and membrane reactors, together with the membrane contactors units, might present crucial opportunities for the redesign of industrial processes based on integrated membrane systems. On the other hand, the implementation of commercial scale membrane reactors	[54]

is quite limited. Therefore, the development of very thin, flawless membranes° that can withstand high pressure and high temperature conditions is needed.
