

Taking Reactive Distillation to the Next Level of Process Intensification

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Reactive distillation (RD) is an efficient process intensification technique that integrates catalytic chemical reaction and distillation in a single apparatus. The process is also known as catalytic distillation when a solid catalyst is used. RD technology has many key advantages such as reduced capital investment and significant energy savings, as it can surpass equilibrium limitations, simplify complex processes, increase product selectivity and improve the separation efficiency. But RD is also constrained by thermodynamic requirements (related to volatility differences and heat of reaction), overlapping of the reaction and distillation operating conditions, and the availability of catalysts that are active, selective and with sufficient longevity.

This paper is the first to provide insights into novel reactive distillation technologies that combine RD principles with other intensified distillation technologies – e.g. dividing-wall columns, cyclic distillation, HiGee distillation, and heat integrated distillation column – potentially leading to new processes and applications.

1. Introduction

Reactive distillation (RD) is one of the best success stories of process intensification technology – developed since the early 1920s – that made a strong positive impact in the chemical process industry (CPI). RD allows reaction and separation to take place simultaneously inside the column, thus providing a valuable synergistic effect that overcomes the equilibrium limitations of many reactions, e.g.: (trans-)esterification, etherification, hydrolysis, (de-)alkylation, (de-)hydrogenation, condensation, isomerization. RD is also used for fast reactions where the high concentration of one of the products or reactants may lead to undesired side reactions, hence the need to reduce their concentration in the reacting phase to minimal levels to hinder the undesired reaction. Figure 1 illustrates the main configurations of typical RD processes: conventional (for quaternary systems), azeotropic RD (column coupled with a decanter), and with pre-reactors and/or side-reactors (Kiss, 2013).

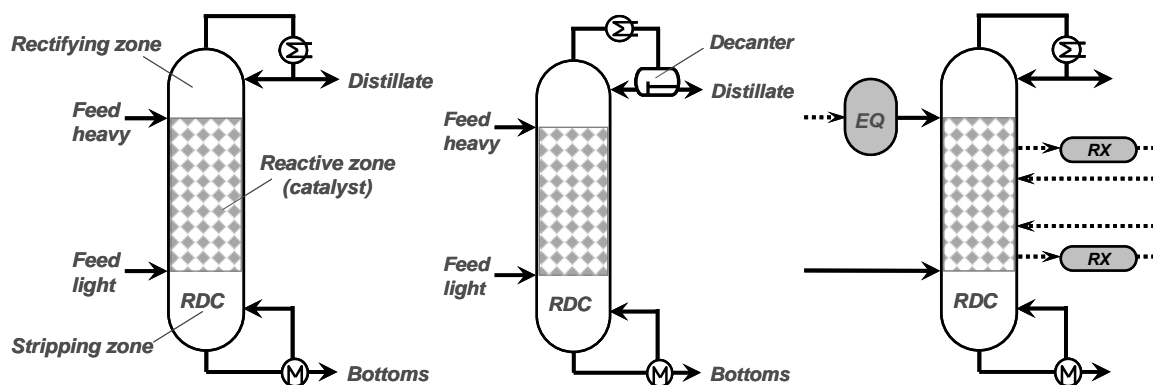


Figure 1: Configurations of reactive distillation (RD) processes: classic RD (left), azeotropic RD (middle), RD with pre-reactors and side-reactors (right).

Nonetheless, the range of classic RD applications is somewhat limited due to the requirement for overlapping operating conditions for reaction, distillation and equipment (Kiss, 2013). Taking RD to the next level of process intensification would require more advanced RD configurations, which allow an additional range of operating conditions (not available in classic RD setups). Other variations of RD may include: membrane-assisted RD, or microwave- or ultrasound-assisted reactive distillation (Lutze and Gorak, 2013). This paper aims to provide an insightful overview of recent novel RD technologies that combine the principles of reactive distillation with other intensified distillation technologies, leading to new RD processes such as:

- Reactive dividing-wall columns (R-DWC)
- Reactive cyclic distillation (R-CyDist)
- Reactive (internally) heat integrated distillation column (R-HIDiC)
- Reactive HiGee distillation (R-HiGee)

A comparison with classic RD processes and a pro/con analysis is made, considering process synthesis and design, controllability and operability, energy efficiency, key benefits and limitations, and the potential for practical adoption of these technologies by the CPI. We also pinpoint the most promising of these RD technologies, as well as the research challenges that lie ahead for adoption industrially.

2. Reactive dividing-wall columns

Dividing wall column (DWC) technology is expanding its use to azeotropic separations (Kiss et al., 2013) and reactive distillation (Kiss, 2013). Hence RD in a DWC was a logical next step waiting to be developed in academia and applied industrially. Literature reports range from rate-based modeling and simulation of R-DWC processes (Mueller and Kenig, 2007), to broad analysis of the R-DWC, its minimum energy demand and the potential for energy savings (Schröder et al., 2016) and more recently a comprehensive review on R-DWC (Weinfeld et al., 2018). The R-DWC has been modeled using rate-based approaches and the performance of R-DWC units was theoretically studied for different chemical systems. Some research groups investigated R-DWC using standard routines available in commercial process simulators (e.g. Aspen Plus), but experimental investigations of R-DWC are still very scarce. The advantages demonstrated by this highly integrated process are: high conversion, increased selectivity and product purity, significant energy and cost savings.

Figure 2 illustrates the typical configuration of an R-DWC as well as an application to the dimethyl ether process (Kiss, 2013). R-DWC applications have been reported (mostly as simulation studies) for the production of various chemicals e.g. methyl acetate (An et al., 2015), dimethyl ether (Kiss and Suszwalak, 2012), fatty acid methyl esters (Kiss et al., 2012), biodiesel (Ignat and Kiss, 2013), diethyl carbonate (Zheng et al., 2017), and other industrial applications (Kiss et al., 2009).

R-DWC technology has been an active area of research during the past decade, with many studies concluding that the technology is industrially feasible and ready for implementation at commercial scales. The main challenges to the commercialization of R-DWC are the lack of experimental results (currently limited to only 5 chemical systems, 2 lab-scale and 2 industrial scale units), uncertainties in R-DWC modeling and simulation, lack of demonstration of (complex) control schemes (e.g. model predictive control), need for improvement of dynamic models and shortcut design. Nonetheless, R-DWC technology can add significant value to new chemical processes, with a strong potential to improve production yields, to save 15-75% in energy usage and over 20% in capital cost, as compared to conventional processes (Weinfeld et al., 2018). The design and control of R-DWC can draw on the extensive experience of RD and DWC, respectively. The limitations of R-DWC relate to: catalyst formulation, hold-up & residence time, pressure drop & flooding, equal pressure needed in a DWC. Main applications are for reversible reactions with suitable boiling point characteristics.

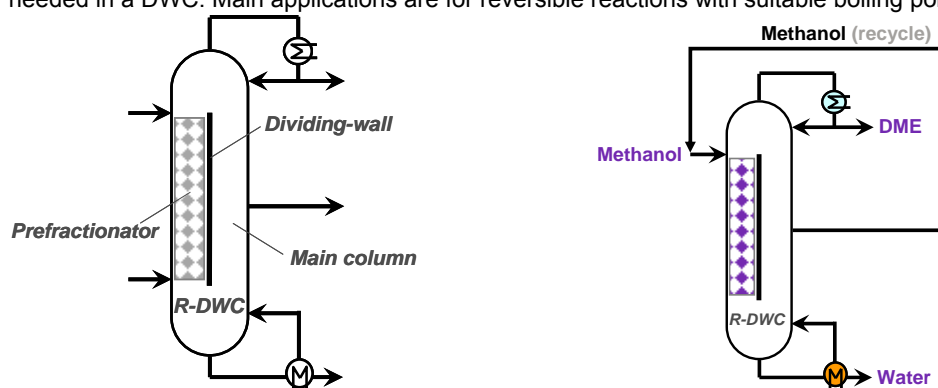


Figure 2: Reactive dividing-wall column: generic configuration (left), specific setup for DME synthesis (right)

3. Catalytic cyclic distillation

Cyclic distillation is as a new contender in fluid separations due to an innovative way of thinking in contacting the liquid and vapor phases (Kiss, 2013). Unlike conventional operation, cyclic distillation uses separate phase movement (SPM) that can be achieved with technology-specific internals and a periodic operation mode (Kiss and Bildea, 2015). One operating cycle consists of two key parts: a *vapor flow period* (when the thrust of rising vapor prevents liquid downflow) followed by a *liquid flow period* (when the liquid flows down the column, dropping by gravity from one tray to the tray below). This cyclic mode of operation leads to key advantages, compared to conventional trayed columns: high throughput and equipment productivity, high separation efficiencies (140-200% Murphree efficiency), reduced energy requirements (20-35% savings), and increased quality of the products. The pilot scale CCD implementation of the technology from MaletaCD is expected to be valuable for demonstration of technology-readiness.

Adding a catalyst on the trays leads to catalytic cyclic distillation (CCD) that is as novel process intensification approach in reactive separations (Patrut et al., 2014). Figure 3 illustrates the internals used for cyclic distillation, without and with solid catalyst on trays. Such a setup has the ability to control the amount of liquid on the tray, and thus the reaction time. As the liquid holdup and the amount of catalyst per tray can be significantly greater than in conventional RD systems, applications to slower reactions become feasible as well, thus extending the range of applicability of RD.

In terms of design and control, dynamic models are needed with multiple degrees of freedom to optimize. Key challenges include: moving parts (especially in the presence of catalyst particles); obtaining good mixing and turbulence in liquid phase for enhancing reaction but potentially damaging to catalyst particles. Adding structured catalytic packing / catalytic internals on the tray may overcome this challenge. Just as with RD technology, CCD is also limited to liquid-phase reactions (i.e. to relatively low temperatures). Nonetheless, CCD has a good utilization of the column shell (high ratio of catalyst volume and liquid hold-up to space for vapour flow); potentially good range of application (e.g. for slower reactions); but there is also a need for development and validation of sophisticated process models for design and optimization purposes.

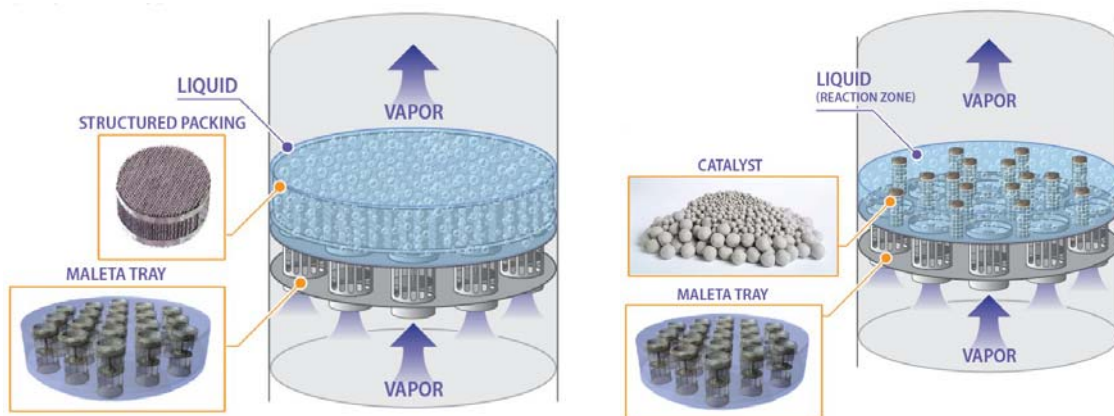


Figure 3: Schematics of cyclic distillation internals: Maleta trays and packing (left) or trays with solid catalyst (right) – photos courtesy of Maleta Cyclic Distillation (www.maletacd.com).

4. Reactive heat integrated distillation column

HIDiC is a radical approach of heat pump assisted distillation which uses internal heat integration: the whole rectifying section of a column is the heat source, while the stripping part acts as a heat sink (Kiss, 2013). As shown in Figure 4, heat is transferred from the rectifying section (operated at high pressure) to the stripping section. The heat required for evaporation in the stripping section is thus obtained from the rectifying section, reducing the heat duty of the reboiler (but work is needed for the compressor). Overall, HIDiC can achieve primary energy savings of up to 70-90% (Kiss, 2013). The industrial implementation of HIDiC (SuperHIDiC by Toyo Engineering Corporation) is serving as a valuable demonstrator that could significantly increase the confidence of industry in the HIDiC technology (Kiss and Olujić, 2014).

Combining HIDiC with RD in a single unit leads to a reactive system (R-HIDiC) with potential for industrial applications. Savings would be expected in capital and energy costs. In addition, R-HIDiC has potential to be applied to azeotrope-forming mixtures as reaction can consume the azeotropes. The simulation of this new

technology was reported for tert-amyl meth ether production (Pulido et al., 2011; Vanaki and Eslamloueyan, 2012) and for ethyl acetate synthesis from acetic acid (Leon-Pulido et al., 2017). However, to date, only simulation studies have been reported and experimental validation of the process concept is lacking. Design and control can benefit in practice from the ‘simplicity’ of the SuperHIDiC concept using two discrete heat exchangers - a good compromise that provides high energy savings at low investment costs, in an operable configuration. The outlook for R-HIDiC is positive, as the high energy savings of HIDiC provide strong incentives - although the initial R-HIDiC studies showed up to 22% savings as compared to classic RD. The range of applicability (beneficial to equilibrium-limited reactions) is likely to be narrower than that for conventional RD, i.e. close-boiling mixtures (to avoid high pressure ratio in rectifying and stripping sections).

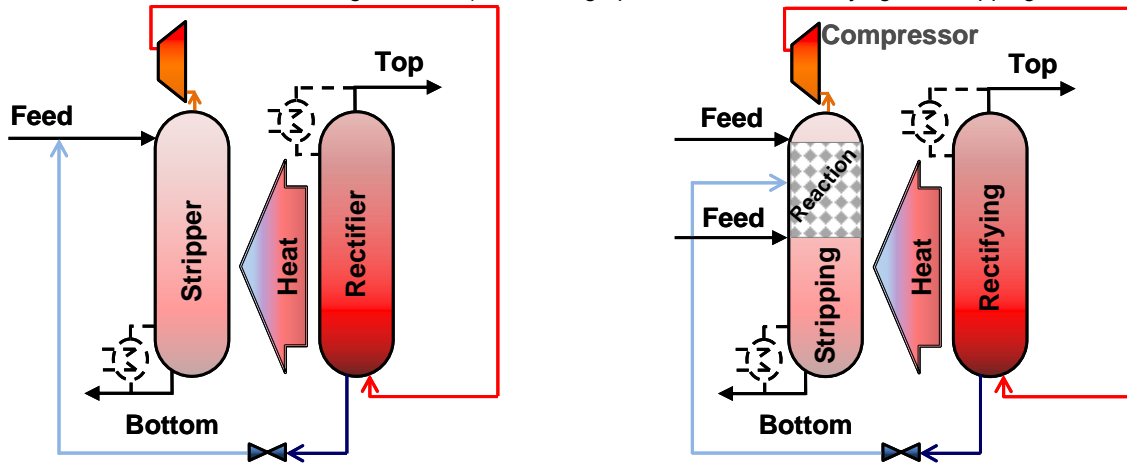


Figure 4: Heat integrated distillation column (left) and reactive HiDIC configuration (right)

5. Reactive HiGee distillation

High gravity (HiGee) technology replaces the usual gravitational field by a centrifugal field achieved in a specially shaped rotating device. The high gravity field (100-1000 g) shifts the flooding limit and allows the use of dense packing materials with a high interfacial area. For rotating packed beds (as illustrated in Figure 5), HETP values as low as 2-8 cm have been reported, while for rotating zig-zag beds (RZB), a volume reduction of a factor 4-7 is claimed for certain distillations as compared to classic columns (Cortes Garcia et al., 2017). In this case, one could also add a catalyst to convert the system into a reactive HiGee distillation. The two-stage counter-current rotating packed bed (RPB, an upgraded version of RZB) combines the benefits of the RZB with the capability to use packing and it has been assessed (together with conventional RPB) to be the most appropriate equipment to perform RD among all HiGee contactors available (Cortes Garcia et al., 2017).

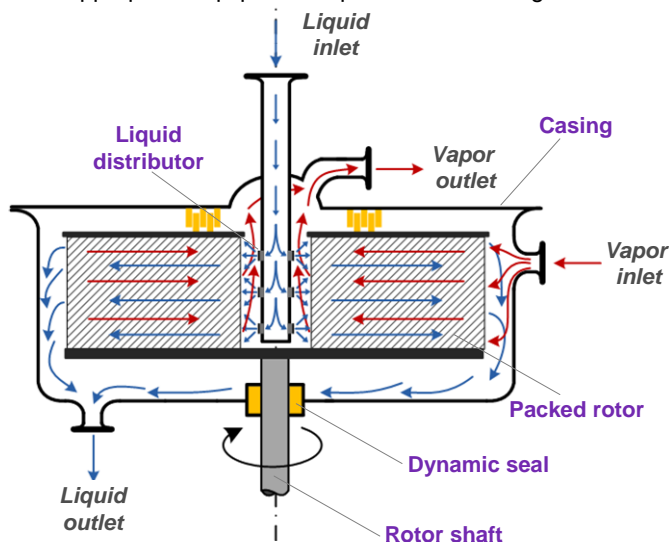


Figure 5: Rotating packed-bed for (reactive) HiGee distillation (adaptation from TU Dortmund; Kiss, 2014)

As early as 1999, Dow Chemicals successfully introduced one of the first commercial applications of RPBs, namely the reactive stripping of hypochlorous acid (Cortes Garcia et al., 2017). A model of a novel reactive HiGee distillation was developed and applied for analysis (Krishna et al., 2012), and for optimization of a reactive HiGee stripper-membrane process for methyl lactate hydrolysis (Krishna et al., 2013). Also the solid-catalyzed reactive stripping for the production of octyl-hexanoate with simultaneous water removal from the reaction zone has been reported (Gudena et al., 2012).

While few studies have included solid catalysts in the (wire mesh) packing, published results showed the potential of HiGee for solid-catalyzed gas-liquid reactions and even for RD. This potential mainly results from the intensified gas-liquid mass transfer rates and the good catalyst wetting at high gravity. But prolonged operation at high gravity also results in erosion of the catalyst entrapped in the internals (e.g. wire mesh). An important limitation is the very low liquid holdup of RPBs, and the correspondingly low residence times that limit application of RPBs to reactive systems with very high reaction rates. Therefore, reactive HiGee technologies need more research to enhance packing design in order to achieve higher liquid-phase residence times and thus to extend the range of applicability of RPBs (Cortes Garcia et al., 2017). For now the range of applicability is limited to liquid-phase reactions only and includes fast reactions with competing serial reactions, to achieve enhanced selectivity and ensure low yield losses.

6. Comparison of RD processes

Table 1 provides a convenient comparison of the RD processes discussed in the previous sections. This analysis is based on industrial and academic experience, as well as on the information available in literature. This summary captures only qualitatively the current situation, which is expected to change in the coming years in view of novel research developments and applications.

While all these new RD technologies are quite promising, they are in different stages of development with various niche applications driving the research. Especially R-DWC (building on the success of DWC) and CCD (pushing cyclic distillation further) have a high potential for industrial implementation. R-HiDiC is in principle also promising, but has yet to build on the success of SuperHiDiC for industrial applications. Reactive HiGee could drastically reduce equipment sizes, but it does not offer any significant energy savings while its range of applicability is limited to fast reactions.

Table 1. Comparison of RD processes combined with other PI technologies

	RD	R-DWC	CCD	R-HiDiC	R-HiGee
Process design & simulation (availability of methods & tools)	+++	+++	++	++	+
Process dynamics and control (availability of methods & tools)	+++	++	++	+	+
Practical challenges (ease of implementation)	+++	++	++	+	+
Range of applicability (variety of chemical reactions)	+++	++	++	+	+
Technology-readiness (pilot & industrial experience)	+++	++	+	n/a	n/a
Energy savings range (compared to classic processes)	15-80%	15-75%	20-35%	50-90%	n/a
Capital savings (compared to classic processes)	+++	+++	+++	n/a	+++

7. Conclusions

Novel reactive distillation technologies that combine the principles of RD with other intensified distillation technologies can lead to promising new RD processes for resource-, energy- and capital-efficient production of chemicals. The potential benefits offered by these novel intensified technologies is significant and motivates accelerated research efforts, especially experimental and pilot-scale studies, as well as advanced dynamic and/or rate-based modeling techniques and methodologies of design and optimization.

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References

- An D., Cai W., Xia M., Zhang X., Wang F., 2015, Design and control of reactive dividing-wall column for the production of methyl acetate, *Chemical Engineering and Processing*, 92, 45-60.
- Bildea C.S., Patrut C., Jorgensen S.B., Abildskov J., Kiss A.A., 2016, Cyclic distillation technology - A mini-review, *Journal of Chemical Technology and Biotechnology*, 91, 1215-1223.
- Cortes Garcia G.E., van der Schaaf J., Kiss A.A., 2017, A review on process intensification in HiGee distillation, *Journal of Chemical Technology and Biotechnology*, 92, 1136-1156.
- Gudena K., Rangaiah G.P., Lakshminarayanan S., 2012, Modeling and analysis of solid catalyzed reactive HiGee stripping, *Chemical Engineering Science*, 80, 242-252.
- Ignat R.M., Kiss A.A., 2013, Optimal design, dynamics and control of a reactive DWC for biodiesel production, *Chemical Engineering Research and Design*, 91, 1760-1767.
- Kiss A.A., 2013, *Advanced distillation technologies - Design, control and applications*, Wiley-Blackwell, Chichester, UK.
- Kiss A.A., 2014, Distillation technology - Still young and full of breakthrough opportunities, *Journal of Chemical Technology and Biotechnology*, 89, 479-498.
- Kiss A.A., Pragt J.J., van Strien C.J.G., 2009, Reactive dividing-wall columns - How to get more with less resources?, *Chemical Engineering Communications*, 196(11), 1366-1374.
- Kiss A.A., Segovia-Hernandez J.G., Bildea C.S., Miranda-Galindo E.Y., Hernandez S., 2012, Reactive DWC leading the way to FAME and fortune, *Fuel*, 95, 352-359.
- Kiss A.A., Suszwalak D.J-P.C., 2012, Innovative dimethyl ether synthesis in a reactive dividing-wall column, *Computers & Chemical Engineering*, 38, 74-81.
- Kiss A.A., Suszwalak D.J-P.C., Ignat R.M., 2013, Breaking azeotropes by azeotropic and extractive distillation in a dividing-wall column, *Chemical Engineering Transactions*, 35, 1279-1284.
- Kiss A.A., Olujic Z., 2014, A review on process intensification in internally heat-integrated distillation columns, *Chemical Engineering and Processing*, 86, 125-144.
- Krishna G., Min T.H., Rangaiah G.P., 2012, Modeling and analysis of novel reactive HiGee distillation, *Computer Aided Chemical Engineering*, 31, 1201-1205.
- Krishna G., Rangaiah G.P., Samavedham L., 2013, Modeling and optimization of reactive HiGee stripper-membrane process for methyl lactate hydrolysis, *Industrial & Engineering Chemistry Research*, 52, 7795-7802.
- Leon-Pulido J.L., Martinez Arias E.L., Wolf Maciel M.R., Maciel Filho R., 2011, Heat integrated reactive distillation column (r-HiDiC): Implementing a new technology distillation, *Chemical Engineering Transactions*, 24, 1303-1308.
- Lutze P., Gorak A., 2013, Reactive and membrane-assisted distillation: Recent developments and perspective, *Chemical Engineering Research and Design*, 91, 1978-1997.
- Mueller I., Kenig E.Y., 2007, Reactive distillation in a dividing wall column: Rate-based modeling and simulation, *Industrial & Engineering Chemistry Research*, 46 (11), 3709-3719.
- Patrut C., Bildea C.S., Kiss A.A., 2014, Catalytic cyclic distillation - A novel process intensification approach in reactive separations, *Chemical Engineering and Processing*, 81, 1-12.
- Pulido J.L., Sarmiento M.P., Garzon D.M., Hernandez M.A., Gonzalez A.D., Peralta-Ruiz Y.Y., Duran M., 2017, Energy study of Reactive-HiDiC simulation for ethyl acetate synthesis from acetic acid, *Chemical Engineering Transactions*, 58, 547-552.
- Schröder M., Ehlers C., Fieg G., 2016, A comprehensive analysis on the reactive dividing-wall column, its minimum energy demand, and energy-saving potential, *Chemical Engineering & Technology*, 39, 2323-2338.
- Vanaki A., Eslamloueyan R., 2012, Steady-state simulation of a reactive internally heat integrated distillation column (R-HiDiC) for synthesis of tertiary-amyl methyl ether (TAME), *Chemical Engineering and Processing*, 52, 21-27.
- Weinfeld J.A., Owens S.A., Eldridge R.B., 2018, Reactive dividing wall columns: A comprehensive review, *Chemical Engineering and Processing*, 123, 20-33.
- Zheng L., Cai W., Zhang X., Wang Y., 2017, Design and control of reactive dividing-wall column for the synthesis of diethyl carbonate, *Chemical Engineering and Processing*, 111, 127-140.