Netherlands Enterprise Agency

Wikisheet
Reactive Distillation

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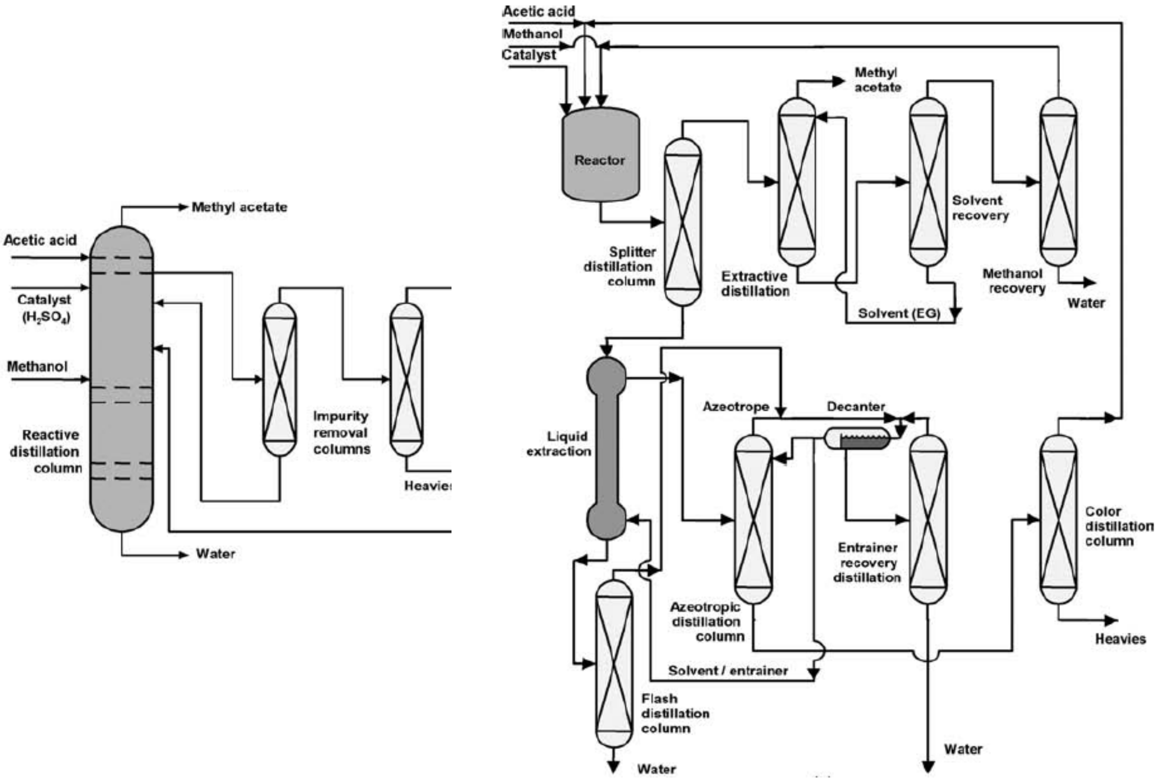
PIN-NL
Dutch Process Intensification Network

Wikisheet
Reactive Distillation

Methyl acetate production, reactive distillation and conventional process



From Kiss (2013) Chapter 13 – according to Jeffrey Siirola (1996)
In spite of the date, the lay-out of Siirola still represents the basics well.

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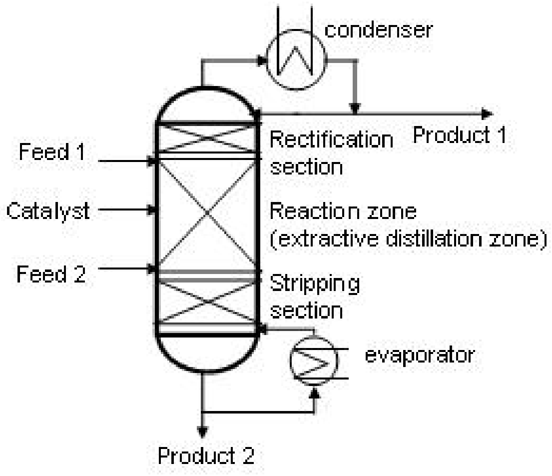
1. Description

From Schoenmakers (2007): Reactive distillation, as the name implies, refers to a distillation process which incorporates a reaction and a separation step within the distillation column arrangement. The most important advantage is that by separation of one of the products an equilibrium reaction may be affected in such a way that the reaction equilibrium can be overcome and an total or near total conversion can be reached. In addition the selectivities may be increased by separation of distinct components. An additional advantage is the possibility of equipment savings.

In more detail the advantages of reactive distillation compared to a reaction step plus a separate distillation process are:

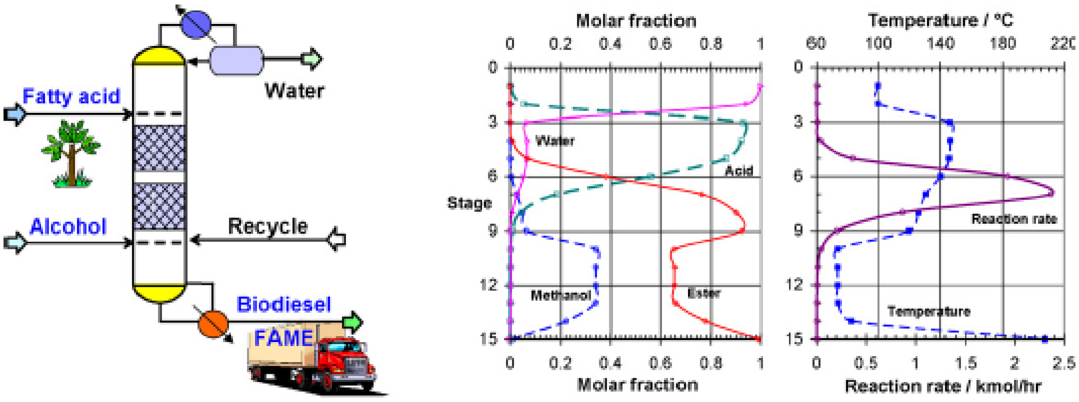
- An enhancement of conversion and selectivity,
- a reduction of investment,
- a simpler process,
- the use of the heat of reaction (if present) in situ,
- ease of control of the reaction temperature (evaporating system),
- and the possibility of overcoming azeotropes.

A typical reactive distillation set-up is depicted in the figure below from Schoenmakers (2007)



The high boiling reactant is fed as feed 1, the low boiling reactant as feed 2. Between the two feeds, there is the reaction zone. The low boiling product leaves the column at the top and the section between feed 1 and the reflux serves as a rectifying section. The high boiling product is withdrawn at the bottom, the section between feed 2 and the evaporator is known as the stripping section.

A nice illustration of temperature and concentration profiles, as well as reaction rate over the stages for fatty acids esterification can be found in the publication of Shah et al.(2012).



2. **Process envelope, including requirements** - from Kiss (2013)

RD is especially attractive in systems where certain chemical and phase equilibrium conditions co-exist. The reaction and distillation take place in the same zone of a distillation column, the reactants being converted with the simultaneous separation of the products and recycle of unused reactants. As the products must be separated from reactants by distillation, this implies that the products should be lighter and/or heavier than the reactants. The ideal case is when one product is the lightest and the other product is the heaviest, with the reactants being the intermediate boiling components (Luyben and Yu, 2008). Moreover, as both operations occur simultaneously in the same unit, there must be a proper match between the temperatures and pressures required for reaction and separation (Noeres, Kenig, and Gorak, 2003; Thery, Meyer, and Joulia, 2005) as clearly illustrated by Figure 10.2a. If there is no significant overlap of the operating conditions of reaction and separation, then the combination of reaction and distillation is not possible (e.g., a high pressure reaction cannot be combined with a vacuum distillation). Furthermore, one must also consider that working in the limited overlapping window of operating conditions is not always the optimal solution, but merely a trade-off (Thery, Meyer, and Joulia, 2005).

Conversely, in a conventional multiunit flow sheet, the reactors can be operated at their optimum parameters that are most favorable for the chemical kinetics while the distillation columns can be operated at their optimal pressures and temperatures that are most favorable for the vapor–liquid equilibrium (VLE) properties (Luyben and Yu, 2008). In this respect, the residue curve maps (RCMs) are an invaluable tool for the initial screening and flowsheet development of RD.
The pressure and temperature effects are much more pronounced in RD than in conventional distillation as these parameters affect both the phase equilibrium and chemical kinetics (Stichlmair and Fair, 1998; Doherty and Malone, 2001; Schmidt-Traub and Gorak, 2006; Luyben and Yu, 2008). A low temperature that gives high relative volatilities may give small reaction rates that require large amounts of catalyst or liquid holdups to achieve the required conversion. In contrast, a high temperature may promote undesirable side reactions or give a low equilibrium constant that makes it difficult to drive the reaction to completion (Luyben and Yu, 2008; Thery, Meyer, and Joulia, 2005).

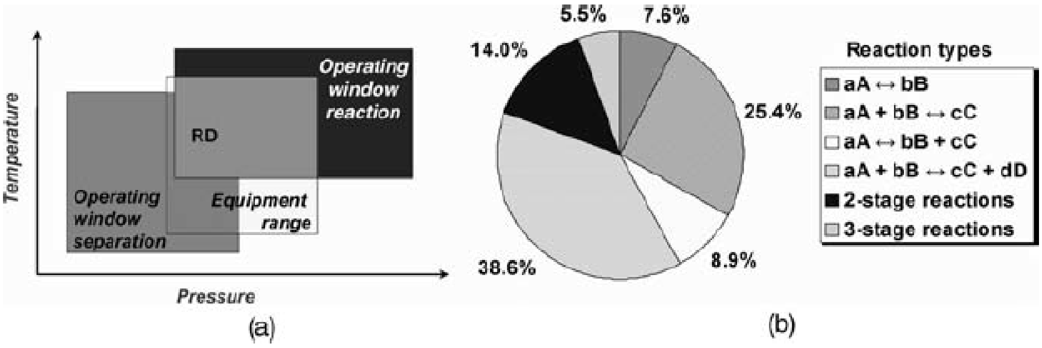


Figure 10.2 Overlapping of operating windows for reaction, separation, and equipment (a); reaction types used in reactive distillation (b)

RD is typically applied to equilibrium reactions, such as esterification, etherification, hydrolysis, and alkylation. Remarkably, over 1100 articles and 800 US patents on RD were published during the past 40 years, covering in total over 235 reaction systems (Luyben and Yu, 2008). Figure 10.2b provides a convenient overview of these systems classified into various reaction types. Most of the reactions types belong to the aA + bB ↔ cC + dD or aA + B ↔ cC or aA ↔ bB + cC class, with the rest of them falling into other categories of two- or three-stage reaction (Luyben and Yu, 2008).
Note: The references given in the Kiss (2013) book chapter have been left in the copy above. This shows the extensive basis of the statements.
Besides the homogeneously catalyzed systems as in the methyl acetate case, we can distinguish heterogeneously catalyzed systems. Schoenmakers (2007): Processes with autocatalysis or homogeneous catalysis may be designed like a normal distillation column but the internals have to be chosen with respect to the residence time needed to reach the desired conversion. In heterogeneous catalysis the equipment has to offer separation efficiency and on the other hand has to keep the catalyst in place. Early development of heterogeneous RD was reported in a patent by Hunter (1968) and in the PhD studies of Van den Berg (1973).

Schoenmakers (2007) concluded: "There is no general rule for the detail design of a reactive distillation process, the volatilities of educts and products are decisive for the feasibility of such a process together with the reaction parameters." Schoenmakers states that the use of mini/pilot plants is needed for scale-up.

3. Avantages and limitations

Advantages and limitations have already been mentioned in previous sections to explain the basics of reactive distillation. Summarized:

- Combination of reaction and distillation can positively influence equilibrium and/or conversion, heat efficiency and costs by removing products directly after formation
- As reaction and distillative separation operations occur simultaneously in the same unit, there must be a proper match between the temperatures and pressures required for reaction and separation. Residence times of the fluids in the column must also match kinetics.

4. Commercial status / TRL level

In 2007 Harmsen published an overview of RD development and application. Kiss (2013) traced 12 classes of application of RD: Alkylation, Amination, Carbonylation, Condensation, Esterification, Etherification, Hydrogenation/dehydrogenation, Hydrolysis, Isomerization, Nitration, Transesterification. Kiss reports: CDTECH—the major commercial provider of RD technology—has licensed to date over 200 commercial-scale processes operated worldwide at capacities of 100–3000 ktpy for the production of ethers (MTBE, TAME, ETBE), hydrogenation of aromatics and light sulfur hydro-desulfurization (HDS), and ethylbenzene and isobutylene production (Harmsen, 2007). Sulzer ChemTech has also reported several industrial-scale applications, such as synthesis of ethyl, butyl, and methyl acetates, hydrolysis of methyl acetate, synthesis of methylal (dimethoxymethane), methanol removal from formaldehyde, and production of fatty acid esters (Harmsen, 2007).
The development of RD is still ongoing, but considering the applications, we consider RD as having a high TRL, 9.

5. Examples of application

The basis has already been given in the previous section. Schoenmakers (2007) documented four product and reactions systems. Harmsen (2007) traced 150 applications. Kiss (2013) extended the progress of applications.
Vendor information provides additional applications. See e.g. Sulzer, CDTech (now part of CB&I), Koch-Glitsch.

6. Technology and developments

Since several publications indicate that development is an ongoing issue. In the book of Kiss (2013) we see that progress has been made for: basic design, modelling, plant operation and control.
A technology review of membrane-assisted reactive-distillation has been prepared by Hoffmann (2007),
A relatively new development is the use of a divided wall column in combination reactive distillation, see e.g. Kang and Lee (2015).
Segovia-Hernadez et al. (2015) review optimal design using deterministic and stochastic techniques. They analyze 15 published cases and state: Despite the recent advances, it can be claimed the complexity in the design of reactive distillation. One important reason is the difficulty associated with the modeling and nonlinear and multivariable equation systems of these processes and the parametric uncertainty of the model parameters. As a result, reliable and consistent models (for property prediction, reaction kinetics, and process simulation) are not available, and the dependence of the model parameters is unknown. Stochastic optimization algorithms are capable of solving, robustly and efficiently, the challenging multi-modal optimization problem, and they appear to be a suitable alternative for the design and optimization of complex separation schemes taking into account one or several objective functions.

7. Potential for industrial branches

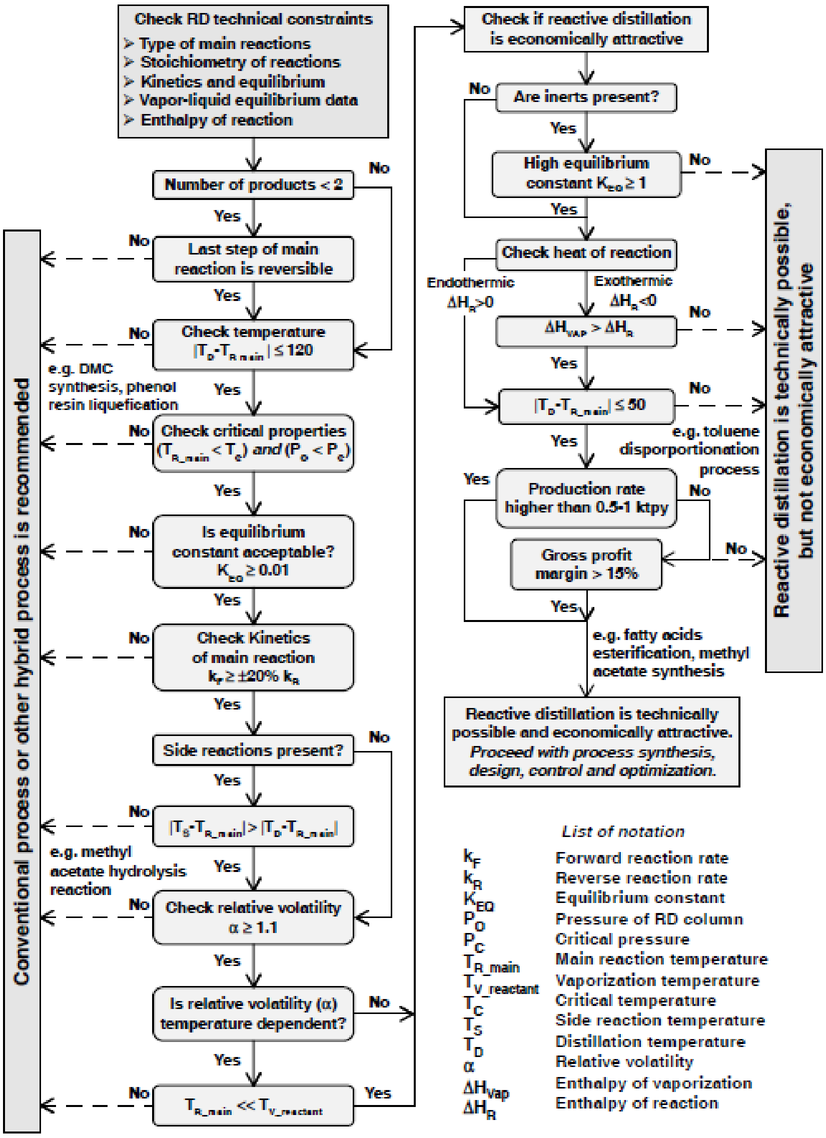
- Chemical process industries (MJA3 + MEE)
- Oil and gas producing industry (MJA3)
- Refineries (MEE)
- Animal Food industry (MJA3)
- Soda water and fruit drinks industry (MJA3)
- Margarine, Oil and Fat industry (MJA3)
- Dairy industries (MJA3)]

8. Self assessment for application

Kiss (2013) provides a Framework for checking if reactive distillation is an attractive option or not. Basic variables to be examined are:

- Temperature ranges required for reaction and distillation
- Chemical equilibrium, kinetic rates and heat effects

For modelling commercial simulators can be used.



9. Tags

Process intensification, combination of reaction and distillation having a positive influence on equilibrium and/or conversion, heat efficiency and costs by removing products directly after formation.

10. References

Hartmut Schoenmakers, “European Roadmap of Process Intensification, Technology report 2.2.8 Reactive Distillation” (2007)

A.A. Kiss, “Advanced Distillation Technologies: Design, Control and Applications”, Wiley-Blackwell, ISBN 978-1-1199-9361-2 (2013), Chapter 10 Reactive Distillation

G. Jan Harmsen, “Reactive distillation: The front-runner of industrial process intensification
A full review of commercial applications, research, scale-up, design and operation”,
Chemical Engineering and Processing 46 (2007) 774–780

Mayank Shah, Anton A. Kiss, Edwin Zondervan, André B. de Haan, “A systematic framework for the feasibility and technical evaluation of reactive distillation processes”, Chemical Engineering and Processing 60 (2012) 55–64

Achim Hoffmann, “European Roadmap of Process Intensification, Technology report 2.2.8.2 Membrane-assisted reactive distillation” (2007)

U.S. patent 3,366,457, January 30, 1968, W.K. Hunter (Universal Oil Products Company)

H. van den Berg, “Some aspects of the chlorination of benzene”, PhD dissertation, 1973, State University of Groningen, The Netherlands.

D. Kang and Jae W. Lee, “Graphical Design of Integrated Reaction and Distillation in Dividing Wall Columns”, Ind. Eng. Chem. Res. 2015, 54, 3175−3185 DOI: 10.1021/ie5047957

Juan Gabriel Segovia-Hernández, Salvador Hernández, Adrian Bonilla Petriciolet,
“Reactive distillation: A review of optimal design using deterministic and stochastic techniques”, Chemical Engineering and Processing 97 (2015) 134–143

Vendor info:

Sulzer: https://www.sulzer.com/en/Products-and-Services/Process-Technology/Reaction-Technology/Reactive-Distillation-Technology , visited 8/2/17

CDTech technology is now part of CB&I, http://www.cbi.com/ , visited 8/2/17

Koch-Glitsch: http://www.koch-glitsch.com/masstransfer/pages/Applications.aspx , visited 8/2/17

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