EUROPEAN ROADMAP OF PROCESS INTENSIFICATION

- TECHNOLOGY REPORT -

TECHNOLOGY:
Reactive Distillation

TECHNOLOGY CODE:
2.2.8

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1. Technology

1.1 Description of technology / working principle

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 influenced 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 that equipment savings are possible.

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 Fig. 1.

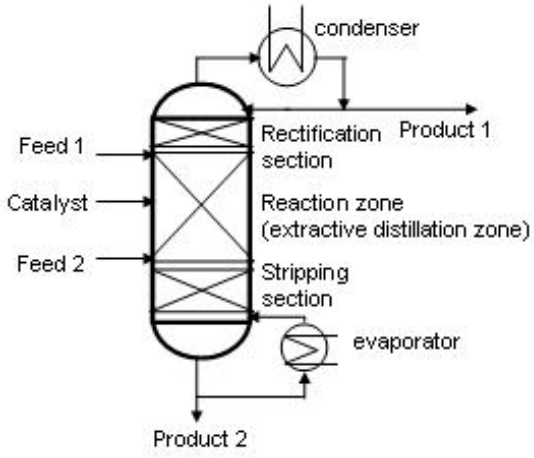

Figure 1. The basic elements of a reactive distillation column.

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 The high boiling product is withdrawn at the bottom, the section between feed 2 and the evaporator is known as the stripping section. As a special application, feed 1 can serve as an extractive agent, e.g. in the case of the production of methyl acetate, acetic acid serves as an entrainer for the binary azeotropic mixture methanol and methyl acetate.This ensemble is then a reactive extractive distillation column, a configuration still more complex than a reactive distillation.

The technique offers a key opportunity for improving the structure of a process. It is a so-called hybrid process, i.e. it merges two different unit operations in a single apparatus, namely reaction and distillation. But the combination of distillation and reactions is possible only if the conditions of both unit operations can be combined.

This means that the reactions have to show reasonable data for conversions at pressure and temperature levels that are compatible with distillation conditions. 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. The chemical equilibrium constant is one basis for the design of reactive distillation process, it determines the separation efficiency that has to be installed in the column to get the desired conversion. Because of the limited hold-up in a distillation column, those reactions having a conversion half-time of 10 minutes are preferred if the reaction runs within the column. If it is in the bottom or in special residence time internals these times may be shifted to about 30 minutes. So, the design of a reactive distillation process is dominated by the interdependence between the relative volatilities and the reaction velocity and as a consequence every such process is a special solution for a given set of parameters.

1.2 Types and "versions"

In reactive distillation the type of the catalysis is important. Autocatalysis is advantageous and used if possible but in many cases the reaction velocity is not fast enough so that catalytic support is necessary. Homogeneous catalysis is possible in many cases but needs a separation step to recycle the catalyst. This can be avoided in heterogeneous catalysis, but here the catalyst has to be fixed in the reaction zone.
So, two different technologies are in use:
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. The standard equipment for distillation columns can normally be used in general. Nevertheless special constructions of residence time trays for slower reaction velocities exist. As a special version the reaction may run only in the bottom of the column if the separation needs a rectifying section alone. This configuration is frequently used in batch reactive distillations.
In heterogeneous catalysis the equipment has to offer separation efficiency and on the other hand has to keep the catalyst in place. So specialised constructions are necessary and realized: The technical basis may be a distillation tray with catalyst bags placed on these trays, a solution used in industrial scale for the production of fuel ethers or a structured packing in which cage layers containing the catalyst are included, see figure 2.

Figure 2. Structured packing with catalyst layers, laboratory scale (SULZER Chemtech)

There are other suggestions for technical solutions, for example to fill the catalyst in the downcomers or to keep it on the trays as fluidized bed but these solutions are not

realized in a technical scale or like the fluidized bed constellation they are property of one single company and thus not generally available.

Reactive distillation of every type can be combined with a pervaporation step to a again more complex process configuration. Here the pervaporation cell is used to separate the overhead vapor stream in a similar way as it can be done after condensation if phase splitting occurs. The advantage is that such a separation step is possible without liquid phase splitting and in principle applicable in more cases. But nevertheless this alternative is not yet realized in a technical scale.

1.3 Potency for Process Intensification: possible benefits

The magnitude of potential savings count for the part of the process where reactive distillation is applied instead of a sequential sequence of reaction and distillation, in general not for the process as a whole. One exception is, if the whole process is influenced like it could be in the case of a simpler process avoiding additional separation steps, entrainers, etc.
In general it has to be stated that reactive distillation has certain ranges of applicability, it is not a general intensification technology.

Table 1: Documented and expected benefits resulting from technology application

Benefit	Magnitude	Remarks
Shift of conversion over the equilibrium value	Savings in investment and energy may be up to 60%	Applicability of reactive distillation depends from the specific case. The volatilities of the components have to be in the right order for separating one of the products and the reaction velocities have to be such that residence times in internals are sufficient.
Increase of selectivity	Savings may be up to 50%	Applicable again only in specific cases, where the separation of the "right" component may enhance the selectivity
Reduction of investment	Savings typically in the range of 30%	Reaction and separation in a column instead of reaction in a reactor and separation in a column
Simpler process	Savings in investment and energy for the whole process may be up to 60%	Reactive distillation may avoid additional separation steps by overcoming azeotropes, entrainers may be avoided, difficult separations may be simplified. But process development to get these advantages is a crucial step.
Use of the heat of reaction	Savings in investment of 10%	Avoids additional heat exchangers.
Ease of control of the reaction conditions	Savings in investment of 10%	Controlling a boiling system by keeping the pressure constant is easier than controlling the temperatures by separate heat exchangers.
Reactive distillation combined with pervaporation	Investment and energy savings may be up to 30%	Additional separation steps for breaking azeotropes including entrainers may be avoided.

1.4 Stage of development

Process synthesis:

The first step is well understood, the method of reactive distillation lines to judge the feasibility of a combination of reaction and distillation is introduced and generally known, methods for a pre screening or short cut design like rectification bodies have been developed, process simulation tools that allow for reactions including kinetic parameters in distillation simulations are available.
The following step, the detailed design of a reactive distillation process needs a clearance of the type of catalysis. That step can't be done without experiments. Efficiency and life cycle time of the catalyst have to be tested carefully under process conditions. Normally a miniplant is needed to do that, in some cases even pilot plants are necessary. The results determine the configuration of the process and the choice of equipment suitable to fulfill the demands of reaction and separation efficiency. So, the overall expenditure to develop a reactive distillation process is much higher than the development of the single separate steps of reaction and distillation.
Nevertheless it is possible and state of the art for experts.

Equipment development:

Homogeneous catalysis:
A catalyst that is soluble in the reaction mixture offers the advantage that the equipment introduced for distillation applications is suitable for a reactive distillation process. The residence time has to be adopted to the reaction velocity but this can be overcome at least partly by enhancing the concentration of the catalyst. Special constructions of trays with a high hold up may be necessary but offer no real design problems. So it can be stated that for homogeneous catalysis not only the process design but although the choice and scale up of the equipment is known and again state of the art for experts.

Heterogeneous catalysis:
As stated above in heterogeneous catalysis special equipment is necessary to keep the catalyst in place. Different technical solutions are offered by equipment vendors or by engineering companies that offer the equipment only together with a license for the process as a whole.
Column internals available on the market are structured packings with catalyst bags included in the packing structure. In these packings the possible loading factors are lower than in normal structured packings but construction and operation of columns equipped with such packings are comparable to normal distillation columns. Internals that are licensed together with processes are bags filled with catalyst that are placed on trays. They show only little separation efficiency and reduce the maximum loading factors but they are technically feasible and introduced in industrial scales. Another technical solution offered by an engineering company keeps the catalyst on the distillation trays in a fluidized bed. The construction is complicated in detail but allows to change the catalyst during operation of the column, a possibility offered by no other technique for a reactive distillation with heterogeneous catalysis.
In general the design of the equipment for heterogeneous catalysis is much more complicated compared to homogeneous catalysis. One of the main problems is the scale up from the experimental to the industrial scale. That problem is not yet completely solved, there are deviations in many cases. The only way to a design that meets the specifications is to refer to a process in industrial scale. So the first industrial realization of a new process including the scale up step may lead to a process that has to be corrected or at least optimized after start up. Expert knowledge is necessary to a large extend.

Plant operation and control

The control equipment and the operation of a reactive distillation process are not more complicated than in a non-hybrid process. The only difference is that the residence time in a reactive distillation column has to be kept constant independent of load changes in order to get the desired conversion. That may lead to different control strategies compared to a normal process but all these steps are well understood as state of the art.

2. Applications

2.1 Existing technology (currently used)

A conventional process including reaction and distillation separates the two unit operations. The reaction is made in a reactor specially designed and optimized for the reaction parameters, the separation train is the downstream process specially adopted to the parameters vapor pressures and relative volatilities.

One known technology is to arrange the reactor(s) in side stream pumparound(s) at a column. The results may be very similar to a reactive distillation arrangement with the reaction in the column or in the bottom, but the technical expenditure is higher. Some industrial applications are known.

2.2 Known commercial applications

Table 2. Industrial-scale applications of the Technology (existing and under realization)

Sector	Company - Process/Product name/type	Short characteristic of application	Production capacity /Plant size	Year of application	Reported effects
Large volume chemicals	Fuel ethers (MTBE, TAME), process offered by CD Tech and others	Continuous process, reaction in the rectifying part of the column, heterogeneous catalysis	Typically 50000 – 200000 t/y	After 1980	the reactive distillation process is not the only but the leading technology
	Methyl acetate, process by Eastman Chemicals	Continuous process, homogeneous catalysis	Range of 100000 t/y	After 1980	Reactive distillation replaces a complicated distillation train with azeotropes, entrainers etc.
	Plasticizers (phthalic esters) by BASF and others	Reaction in the bottom of a column, homogeneous catalysis, process conti or batch	20000 – 300000 t/y	After 1965	Leading technology

Specialty chemicals	Esterifications	Water is separated as overhead product	500 – 10000 t/y	After 1921	Technology introduced

More examples may be seen in paper Harmsen, G.J., 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 (2007) in print (doi:10.1016/j)

2.3 Known demonstration projects

Table 3. Demonstration projects related to the technology (existing and under realization)

Sector	Who is carrying out the project	Short characteristic of application investigated, including product name/type	Aimed year of application	Reported effects
Large volume chemicals	EU supported, BASF, Degussa, Enichem, DSM and others from the industrial side	3 successive projects (Reactive Distillation, INTINT and INSERT), products mainly esters	Last project finished 2007	Research projects, topics development methods, equipment design, simulation techniques

2.4 Potential applications discussed in literature

The technique is possible for all applications where chemical reactions need a downstream separation step in the fluid phase. The limitation to reactions with components in a range of vapor pressures that can be combined with distillation is a restriction to reactants between C1 and C10 approximately. The most suitable reactions are esterification, etherification, hydrolysis, isomerisation, alcylation, hydration. The favorable field of application seems to be petrochemicals and chemicals, not so much specialty chemicals and pharma. The technique may be combined with other hybrid techniques like dividing wall columns or HiDiC columns. The combination with a pervaporation step is an option to enlarge the application range.

3. What are the development and application issues?

3.1 Technology development issues

Table 4. Technology development issues

Issue	Description	How and by whom should be addressed?
Heterogeneous catalysis: scale up procedure	Problem to represent the separation efficiency, the catalyst hold up and the residence time distribution of a technical column in a laboratory scale column	Research should be done in collecting, analyzing and evaluating available data in different scales (work mainly for universities)

Description of flow characteristics	Simulation of hydrodynamics including residence time distribution in countercurrent operation: CFD modeling seems suitable	Universities together with CFD companies
Heterogeneous catalysis: support arrangements for the catalyst	Alternative arrangements should be developed, for example catalyst in the downcomers or fluidized bed constructions.	Equipment providers, universities
Heterogeneous catalysis: thin layer catalyst	Thin layer catalysts may be a solution advantageous for fast reactions because normal equipment could be coated. Selectivities may be influenced positively.	Equipment providers, universities

3.2 Challenges in developing processes based on the technology

Table 5. Challenges in developing processes based on the technology

Challenge	**Description**	**How and by whom should the challenge be addressed?**
Reaction kinetics	Kinetic data for main and side reactions are needed for a proper design of such a process, simulation models absolutely need a kinetic model for the reaction. Heterogeneous catalysis up to now cannot be modeled exactly.	Work for laboratories for the data and for experts for formulation of a kinetic model
Simulation depth	Different simulation models are available, either an equilibrium stage based model or a more complicated rate based model, decision what to take is not trivial. The reaction has to be described with a kinetic model in any case.	Experts for process simulation
Scale up from the laboratory scale for homogeneous catalysis	Separation efficiency, residence time and residence time distribution are decisive for scaling up. These parameters are different in laboratory scale and in technical scale. In homogeneous catalysis changing the concentration of the solved catalyst allows a correction if the predicted conversions and selectivities are not reached.	Experience in such procedures is important, data in technical scale device are useful. Experts in industry may have that knowledge.
Scale up from the laboratory scale for heterogeneous catalysis	Separation efficiency, residence time and residence time distribution are decisive for scale up. These parameters are different in laboratory scale and in technical scale, specially for heterogeneous catalysis. The prediction of conversion and selectivity thus is difficult, corrections in the technical scale are not possible.	Experience in such procedures is important, data in technical scale device are very useful. Experts in industry may have that knowledge.
Catalyst lifetime (heterogeneous catalysis)	In column internals that are technically introduced an eventual change of the catalyst is difficult and expensive because a shut down of tha plant or of parts of the plant is necessary. Here new ideas are needed how to improve that.	Suppliers of internals together with universities

4. Where can information be found?

4.1 Key publications

Table 6. Key publications on the technology

Publication	Publication type (research paper/review/book/ report)	Remarks
Sundmacher,K., Kienle, A., (Eds.), Reactive Distillation, Status and Future Directions, Wiley-VCH, Weinheim, 2003	Book	Comprehensive overview
Gorak, A., (Ed.), Chemical Engineering and Processing, vol. 42, issue 3, 2003	Special Issue Reactive Separations	Good overview for all reactive separations
Tuchlenski, A., Beckmann, A., Reusch, D., Düssel., R., Weidlich, U., Janowsky, R., Reactive distillation – industrial applications, process design & scale up, Chemical Engineering Science 56 (2001) 387-394	Review	Industrial experience
Schoenmakers, H.G., Bessling, B., Reactive and Catalytic distillation from an industrial perspective, Chemical Engineering and Processing, 42 (2003) 145-155	Review	Industrial experience
Harmsen, G.J., 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 (2007) in print (doi:10.1016/j)	Review	Actual overview
Taylor, R., Krishna, R., Modeling reactive distillation, Chemical Engineering Science 55 (2000) 5183-5229	Review	Modeling aspects
Almeida-Rivera, D.P., Swinkels, P.L.J., Grievink, J., Designing reactive distillation processes: present and future, Computers and Chemical Engineering 28 (2004) 1997-2020	Review	Process design aspects
Chadda, N., Malone, M., Doherty, M.F., Feasible Products for kinetically controlled reactive distillation of ternary mixtures, AIChE Journal 46 (2000) 5, 923-936	Research paper	Process synthesis
Huss., R.S., Chen, F., Malone, M.F., Doherty, M.F., Reactive distillation for methyl acetate production, Computers and Chemical Engineering 27 (2003) 1855-1866	Research paper	Process synthesis for a special application
Sanchez Dasa, O., Perez-Cisneros, E.S., Bek-Pedersen, E., Gani, R., Graphical and stage to stage methods for reactive distillation column design, AIChE Journal 49 (2003) 11, 2822-2841	Research paper	Process synthesis
Blagov, S., Bessling, B., Schoenmakers, H., Hasse, H., Feasibility and multiplicity in reaction-distillation processes for systems with competing irreversible reactions, Chemical Engineering Science 55 (2000) 5421-5436	Research paper	Process synthesis in the case of irreversible reactions
Schoenmakers, H., Buehler, W.K., Distillation column with external reactors – an alternative to the reaction column, German Chemical Engineering 5 (1982) 292.296	Research paper	Side reactors as alternative

Baur, R., Krishna, R., Distillation column with reactive pumparounds: an alternative to reactive distillation	Research paper	Side reactors as alternative
Steinigeweg, S., Gmehling, J., Transesterification processes by combination of reactive distillation and pervaporation, , Chemical Engineering and Processing, 423 (2004) 447-456	Research paper	Combination of reactive distillation and pervaporation

4.2 Relevant patents and patent holders

Table 7. Relevant patents

Patent	Patent holder	Remarks, including names/types of products targeted by the patent
US Patent 1,400,849 (1921)	Backhaus, A.A.	First patent for RD, homogeneous catalysis
US Patent 4.435.595 (1984)	Agreda, V.H., Partin, L.R.	First continuous process patent, homogeneous catalysis
German Patent DBP 1075613 (1957)	Keller, R. et al.	Heterogeneous catalysis, first patent
European Patent EP 0396650 (1992)	Shelden, R.,Stringaro, J.-P	Equipment for heterogeneous catalysis
European Patent 461855 (1991)	Jones	Equipment for heterogeneous catalysis
German Patent DE 19701045A1 (1997)	Gorak, A., Kreul, L.-U.	Equipment for homogeneous catalysis
German Patent 1933538 (1974)	Scharfe, G. et al.	External reactors
World patent 94/08679	Yeoman, N. et al.	Concurrent operation
US Patent 5,907,065 (1999)	Krill, S. et al.	Isomerisation catalyst
European Patent EP0726241 (1995)	Sakuth, M., Peters, U.	Endothermic reactions

4.3 Institutes/companies working on the technology

Table 8. Institutes and companies working on the technology

Institute/Company	Country	Remarks
BASF	Germany	Design and operation knowledge
Degussa	Germany	Design and operation knowledge
Bayer Technical Services	Germany	Design knowledge, operation knowledge in Bayer companies
Shell Global Solutions	The Netherlands	Design knowledge, operation knowledge in Shell companies
DSM	The Netherlands	Design and operation knowledge
Uhde (Thyssen Krupp)	Germany	Design and construction knowledge

Enichem Technologie	Italy	Design and operation knowledge
ABB Lummus, CD Tech	USA	Design, construction and operation knowledge
University Dortmund, Prof. Gorak	Germany	Synthesis and Design Knowledge for RD and RD + pervaporation
University Stuttgart, Prof. Hasse	Germany	Synthesis and Design Knowledge
RWTH Aachen, Prof. Marquardt	Germany	Process Synthesis Knowledge
University Twente, Prof. Krishna	The Netherlands	Process Synthesis Knowledge
Technical University of Denmark, Lyngby, Prof. Gani	Denmark	Process Synthesis Knowledge
University of Manchester, Prof. Jobson	United Kingdom	Process Synthesis Knowledge
University of Massachusetts, Amherst, Prof. Malone	USA	Process Synthesis Knowledge
PDC, Process Design Center	The Netherlands	Process Synthesis Knowledge
Max Planck Institut für Dynamik komplexer Systeme, Prof. Sundmacher	Germany, Magdeburg	Process Synthesis Knowledge

5. Stakeholders

5.1 Suppliers and developers

Table 9. Supplier and developers

Institute/Company	Country	Remarks
Homogeneous catalysis		
All suppliers of column systems	Nearly all countries	Traditional distillation equipment is used
Heterogeneous catalysis		
Sulzer Chemtech	Switzerland	Supplies columns with internals for heterogeneous catalysis, sells processes with reactive distillation steps
ABB Lummus (CDTECH)	USA	Sells processes and constructs plants with reactive distillation
Davy Process Technology	United Kingdom	Sells processes and constructs plants with reactive distillation steps
Uhde (Thyssen Krupp)	Germany	Sells processes and constructs plants with reactive distillation steps

5.2 End users

Every user of a chemical plant even if it is only for purification of internal recycles, for the production of additives or intermediate components could use the technique of reactive distillation. That is not really known in those companies because the chemical plant is not in the center of the production and experts for the synthesis of

chemical processes are not part of the staff. Companies of that type may be producers of

- pulp and paper
- fine chemicals for end user products
- pharmaceutical chemicals
- fibers
- polymers.

Petrochemicals are another possible end user group. But in that field the standardization of the plant components is on a level that an open atmosphere for introducing new technologies is difficult to reach. Reactive distillation seems not applicable because normally no reactions occur downstream. Nevertheless RD-technology may be used to facilitate difficult separations by introducing helpful reactions, for example. Therefore that big part of the chemical business should be adressed and included in the circle of users.

6. Expert's brief final judgment on the technology

Reactive distillation is a technology showing a big potential where it is applicable. The technology is well introduced, the challenges of designing such a process are known and experts are able to keep the risk low. The problem is that the applicability of the technology is taken into account only in industrial fields where experts are part of the staff. Widening the application range to users from other parts of the industry therefore is an important task to make use of the possible advantages.