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Harmsen, G. Jan

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Reactive distillation: The front-runner of industrial process intensification

A full review of commercial applications, research, scale-up, design and operation

G. Jan Harmsen^{a,b}

^a Shell Global Solutions, Shell Research and Technology Center Amsterdam, P.O. Box 38000, 1030 BN Amsterdam, The Netherlands

^b RijksUniversiteit Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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Abstract

Most industrial scale reactive distillations (presently more than 150), operated worldwide today at capacities of 100–3000 ktonnes/y, and are reported in this paper. Most of these plants started up less than 15 years ago. The drivers, processes, systems, scale-up methods and partner collaborations for this rapid invasion of a new process intensified technique are explained in this paper.

The business drivers are (a) economical (prosperity): variable cost, capital expenditure and energy requirement reduction. In all cases these are reduced by 20% or more, when compared to the classic set-up of a reactor followed by distillation. (b) Environmental (planet): lower emissions to the environment. In all cases carbon dioxide and diffusive emissions are reduced and (c) social (people): improvements on safety, health and society impact are obtained by lower reactive content, lower run away sensitivity and lower space occupation.

These industrial reactive distillation systems comprise homogeneous and heterogeneous catalysed, irreversible and reversible reactions, covering large ranges of reactions, notably hydrogenations, hydrodesulfurisation, esterifications and etherification. Various commercial methods for packing heterogeneous catalyst in columns are now available.

The systems comprise amongst others: multiple catalyst systems, gas and liquid internal recycle traffic over these catalyst systems, separation, mass flow, and enthalpy exchange. These are integrated optimally in a single vessel, a characteristic feature of process intensification.

The scale-up methods applied from pilot plants to commercial scale are brute force and modelling.

Technology providers CDTECH and Sulzer Chemtech have used these scale-up methods successfully. Barriers perceived and real have also been removed by these companies. Chemical manufacturing companies have also developed their own specific reactive distillations by their own research and development. These companies, both on their own and in consortia, also developed heuristic process synthesis rules and expert software to identify the attractiveness and technical feasibility of reactive distillation. Heuristic rules and expert software will be presented and supported by examples.

Academic research also produced design methods to identify the feasibility of reactive distillation, to determine the feed locations, to select packing types, to sequence columns optimally and also produced methods to design, optimise and control the columns with steady state and dynamic simulation models.

The rapid commercial scale implementation of reactive distillation by co-operation of partners in research, scale-up, design and reliable operation can also be seen as a model for rapid implementation of other process intensification techniques in the chemical industry.

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1. Introduction

Reactive distillation, also called catalytic distillation, can be considered as reaction and distillation combined into one new unit operation. Distillation itself is here considered in the wide sense, i.e. the separation by use of vapour–liquid composition

E-mail address: jan.harmsen@shell.com.

Table 1
Catalytic distillation in commercial operation in 2006, licensed from CDTECH [1]

Process	Number
Ethers: MTBE, TAME, ETBE	69
Hydrogenation of aromatics and light sulfur	50
Hydrodesulfurisation	21
Isobutylene production from C ₄ stream	3
Ethyl benzene production	3
Total	146

difference. So it includes distillation columns, flashers, strippers and condensers. The reactions in reactive distillation considered include heterogeneous catalysis reactions, homogeneous catalysis reactions, and thermal (non-catalyst) reactions. In nearly all cases reactions take place in the liquid phase, but reactions taking place in the gas phase and locate the catalyst in the vapour phase of the column is conceivable.

In this paper, we review the commercial scale reactive distillations on their application areas, advantages, scale-up and design methods and roles of various partners in the development to implementation. As reactive distillation is the most widely applied process intensification technique today, lessons learned for implementation of other process intensification techniques are derived.

1.1. Reactive distillation processes in commercial operation

CDTECH, the major commercial process technology provider, licensed up to now over 200 commercial scale processes. Of these 146 are in commercial operation at the end of 2006 [1]. The process applications are shown in Table 1. Mid 2005 this number was 121 [2] and in 2002 the number of 79 [3], so the rate of implementation is still increasing. Sulzer reports the following industrial commercial scale applications: synthesis of ethyl, butyl and methyl acetates, hydrolysis of methyl acetate, synthesis of methylal, removal of methanol from formaldehyde, formation of fatty acid esters [4] with their regional spread shown in as shown in Table 2. Sulzer does not disclose numbers.

Eastman's first methyl acetate reactive distillation tower started up in 1980. It is more than 80 m tall with a diameter of about 4 m. The process (including condenser and reboiler)

Table 2
commercial reactive distillation applications with Katapak licensed from Sulzer Chemtech [4]

Process	Industrial column location
Acetate	
Synthesis of ethyl, butyl and methyl acetate	Europe
Hydrolysis of methyl acetate	Europe and Asia
Acetalisation	
Synthesis of methylal	Europe and Asia
Removal of methanol from formaldehyde	Europe
Fatty acid esters	Asia

is made of five different materials of construction (ranging to zirconium). It has an annual capacity significantly in excess of 200,000 metric tonnes per year methyl acetate [5]. The second plant, built 7 years later with the benefit of operating experience, is virtually identical (geometry, staging, dimensions, capacity) except for some sieve tray detail in the upper non-reactive zones [5]. It contains five functions in one column resulting in capital expenditure and energy reductions by a factor 5 relative to conventional unit operation design [6,7].

Except for the Eastman process the author knows of several other large-scale reactive distillations in the petrochemical industry, which are not disclosed to the public [8]. One was started up as early as 1953. Combining the reported commercial applications with these the total number of commercial applications exceeds 150.

1.2. Potential process applications

Sundmacher has a whole chapter containing over a 100 different industrial applications [9]. However, most of these stems from patents and little information is given on their industrial sta-

Table 3
CDTECH reactive distillations

CDHydro [®]	Selective hydrogenation using catalytic distillation: <ul style="list-style-type: none"> • MAPD reduction in mixed C₃s • C₄ diolefins reduction in mixed C₄s (hydroisomerisation option) • C₄ acetylenes reduction in mixed C₄s • C₅ diolefins reduction in mixed C₅s (hydroisomerisation option) • C₆ diolefins reduction in mixed C₆s • Benzene reduction in LSR and reformate streams • Mercaptan reduction in C₄/C₅/C₆ olefinic streams • Hydrogenation of benzene to produce cyclohexane
CDHDS [®] and CDHDS+ [®]	Desulfurisation using catalytic distillation: <ul style="list-style-type: none"> • FCC gasoline • Jet fuel/kerosene
HDSlect [®]	Selective desulfurisation of mid catalytic naphtha
CDSelect SM	Low cost desulfurisation of low sulfur catalytic naphtha
CDAlky SM	Sulfuric acid alkylation of olefins
CDMtbe [®]	MTBE production from mixed C ₄ s and methanol
CDEtbe [®]	ETBE production from mixed C ₄ s and ethanol
CDTame [®]	TAME production from mixed C ₅ s and methanol
CDTae [®]	TAAE production from mixed C ₅ s and ethanol
CDEthers [®]	Co-production of ethers from mixed C ₄ –C ₇ s and methanol
CDEtherol [®]	Selective hydrogenation of diolefins within ether processes above
ISOMPLUS [®]	Isomerisation of <i>n</i> -olefins to iso-olefins
Dimer ₈ SM	Dimerisation of iso-olefins in C ₄ streams
CDCumene [®]	Alkylation of benzene with propylene
CDIB [®]	Decomposition of MTBE to high-purity isobutylene
CDTECH EB [®]	Alkylation of benzene with ethylene
BASF SELOP	Selective hydrogenation of C ₄ s and C ₅ s for diolefin reduction
CDAcrylamide SM	Hydration of acrylonitrile to acrylamide
Sulzer Butene-1	Superfractionation of mixed C ₄ s to produce high-purity butene-1

tus. Table 3 shows the process applications CDTECH presently offers for licensing.

1.3. Operation experiences

No major operational problems are reported on these processes. Given the complex phenomena occurring in the columns this is remarkable. The designers, knowing the complexity, were paying extra attention to all critical details, to ensure robust controllable operation. For instance in the Eastman methyl acetate process the reactants flows are exactly controlled on stoichiometry. If this would not be precisely controlled either methanol will contaminate the product or acetic acid will contaminate the co-product water. The process has no back-up ability to recover from these kinds of errors [5].

1.4. Triple P (profit, planet, people) business drivers

1.4.1. Economic advantages

Present reactive distillation applications in general are showing large savings in capital cost and energy over conventional set-ups between 15 and 80% [3,6,7,10–12]. Moreover, industrial presenters often mention the higher reliability of the system, due to less rotating equipment in particular and due to less equipment in general, requiring less maintenance.

For hydrogenations the following specific advantages appeared [3]:

- (1) Lower capital expenditure due to no recycle compressor H₂.
- (2) Lower capital expenditure due to integrated heat removal.
- (3) Lower capital expenditure due to lower H₂ pressure (5–15 bar i.s.o. 25–40 bar).
- (4) Lower feedstock cost due to higher selectivity by product to vapour by lower temperature across reaction zone.
- (5) Longer catalyst life due to (a) washing with cleans reflux, (b) reduced oligomer formation, because dimer goes to bottom none-reacting zone.

1.4.2. Environmental advantages

Because reactive distillation reduces the number of equipment and the number of connections between equipment it will have less diffusive gas emissions. Because it requires less energy it will also reduce carbon dioxide emissions.

1.4.3. Social acceptance

In reactive distillation the heat of reaction is removed by evaporation. A higher reaction rate means a higher evaporation rate, but the reaction temperature changes very little. Runaway behaviour of a reactive distillation is therefore in general less severe than a conventional reactor. This means that reactive distillations in general require less safety precaution measures. Safety of chemical processes is the key critical factor for social acceptance; so reactive distillation implementation is likely to help in achieving social acceptance.

A sustainable development assessment for industrial cases of process intensification, including reactive distillation is available [12].

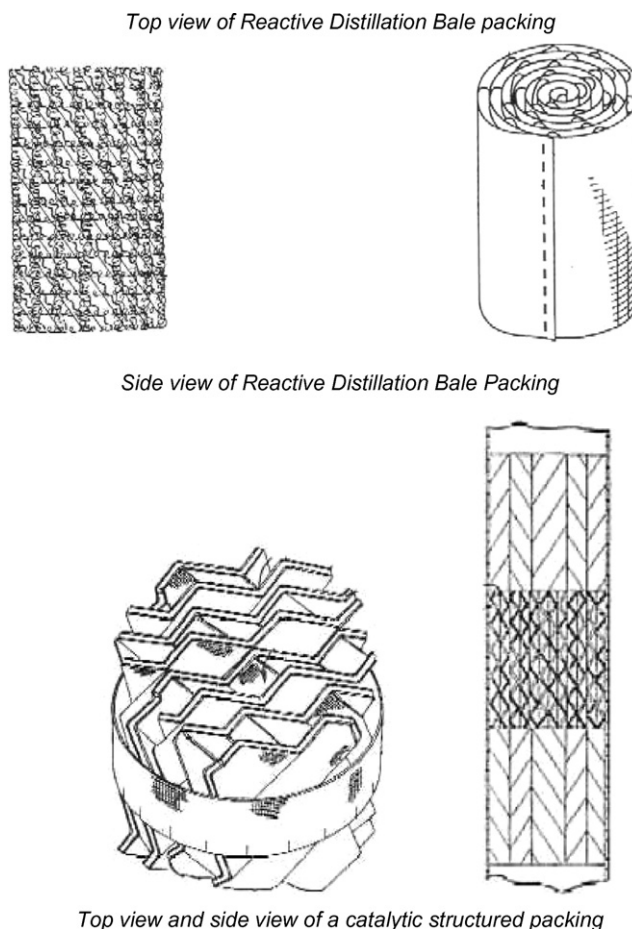


Fig. 1. Packing types in a reactive distillation column.

1.5. Available commercial catalytic packings and homogeneous internals

Catalyst particles as such cannot be used directly as distillation packing because they form too compact a mass for the upward flow of the vapour and downward flow of liquid. Therefore, the catalyst particles are placed in various ways in the column as shown in Fig. 1. A short description will follow for each packing type.

In bale packing the catalyst particles are placed in pockets in a cloth belt and these are supported in a distillation column reactor with the help of open mesh knitted stainless steel wire so that the requisite flow of the vapour and liquid can be ensured. This type of a structure prevents the loss of catalyst, it allows for the swelling of the catalyst particles and it also prevents the breakage of the catalyst particles due to mechanical attrition [13]. This packing structure was the first commercially used packing for reactive distillation applications for MTBE production. The cloth containers that hold the catalyst particle should be inert to the reactants and products and to the conditions in the reaction system. Cotton, polyester, nylon and the like can be used for the cloth containers, but fiberglass has been reported to be the most widely used [13,9, p. 179].

The bales are placed on trays, so that they can be easily replaced. The technology is licensed by CDTECH. The hydro-

dynamics and mass transfer characteristics are published. For references see Refs. [22–26] in Ref. [9, p. 188]. These bale packings have been used for a long time in the reactive distillation processes and they provide good performance in terms of reduced pressure drop and reduced channelling within the distillation column. But it has been reported that they fail to achieve the distillation performance achieved with many types of other packings [14]. Also as the catalyst containers are intimately associated with the support structure; both the catalyst containers and the support structure must be dismantled and replaced when the catalyst is spent. This can lead to a significant loss in the operating time even when the catalysts have a cycle life of several months.

Catalyst particles sandwiched between corrugated sheets of wire gauze are licensed from Sulzer (KataPak) and Koch-Glitsch (Katamax). Information on fluid dynamics, mixing and mass transfer is available (Refs. [30–34] in Ref. [9, p. 188,].

In these catalytic structured packing the catalyst bed is formed by sandwiching a layer of solid, particulate catalyst between pairs of corrugated plates. Preferably the plates are comprised of wire gauze or metal screen material but other types of materials, such as plastic gauze and ceramics are also utilised. The top view and the side view of such a type of packing are shown here. It is important to note here that a class of catalytic distillation packings, known as the M-series packings, have been developed by CDTECH which belong to the class of ‘structured packing’ but whose configuration is markedly different from that mentioned previously. The M-series packing has a higher catalyst packing density than their ‘conventional’ counterparts.

Sulzer Chemtech has extended their product line with KATAPAK-SP (SP for separation performance), which alternates catalyst bags with conventional distillation layers. With this modular concept separation efficiency and catalyst volume fraction can be varied to perfectly fit the requirements of each specific process [15].

1.6. Homogeneous reaction column internals

For homogeneous reactions taking place in the liquid phase multi-tray columns are commercially used, because the liquid hold-up can be adjusted to achieve the required residence time for reaction [9, p. 169]. In the methyl acetate column of Eastman for instance trays with bubble caps of 25 cm high are used [5]. In cases of fast reactions packings could be used [9, p. 169].

1.7. Multi-function integrated design

Reactive distillation can also be considered as a result of functional integration design rather than just a new unit operation. The classic example is the methyl acetate process by Eastman Chemical, which combines five functions into one column. Another example is the hydrodesulfurisation of crude mercaptan and olefin containing gasoline process from CDTECH. The column contains two different catalytic reaction sections. The feed enters below these two sections. Mercaptan and diolefins go up as vapour to the top section, where they react in the liquid phase to di-alkyl-sulfides. This component goes down to the second

reaction section where it is hydrogenated to H₂S and hydrocarbons. The H₂S and clean light naphtha leave the column at the top; the heavy naphtha leaves the column at the bottom. The heat of reaction is directly used inside the column for evaporation. The recycle mass flow of sulfur containing species is obtained by vapour and liquid countercurrent flow without requiring a pump or compressor [2].

A full description of a general method of functional design is provided by Sirola [6]. A summary is provided by Harmsen [11]. An embracing systematic investigation of ‘functional integration’ is facilitated by a software package called ‘SYNTHESISER’ [16]. The software is developed by the company Process Design Center (PDC) and is used to support their process synthesis services in the area of reactive distillation. The tool offers several benefits: commencing with limited, easily accessible information concerning the reaction system and basic thermodynamic data the ‘SYNTHESISER’ (and its successor) is capable of developing catalytic and reactive distillation processes systematically. Besides non-catalytic reactions heterogeneous or homogeneous catalysis can also be investigated.

The ‘SYNTHESISER’ applies a hybrid, so called heuristic numeric approach. This sophisticated approach combines the accuracy of numerical results with the versatility of heuristic knowledge. The advantage of this approach is obvious: the decisions taken are based on numeric calculation. Heuristic knowledge bases support the generation of these results by:

- Transforming qualitative information into quantitative data.
- Predicting lacking parameter by conclusion of analogy.
- A rejection of unsuited processes in an early phase of the investigation.
- Shortening numerical calculations by the generation of feasible initial values.

Summarizing the author’s experience with PDC, four cooperative studies were carried out at Shell, revealing that the service of Process Design Center is useful in identifying feasible and attractive opportunities and also in rejecting non-feasible or not-attractive options.

Processing companies have developed their own methods for quickly assessing the feasibility and attractiveness for particular cases. BASF for instance provides a rapid way of identifying reactive distillation as a feasible and attractive option is by using a qualitative graphical method provided by Schoenmakers [17] and shown in Fig. 2.

For rapidly assessing the economic attractiveness and technical feasibility of cases the author has developed a set of 15 guidelines for Shell. Here are a few of those rules. Reactive distillation is attractive:

- If the reaction is so exothermic that cooling in the conventional reactor is required.
- If there is an undesired consecutive reaction and the product is a light boiler.
- If the conventional separation is expensive due to azeotrope formation and by reaction the azeotrope is prevented.

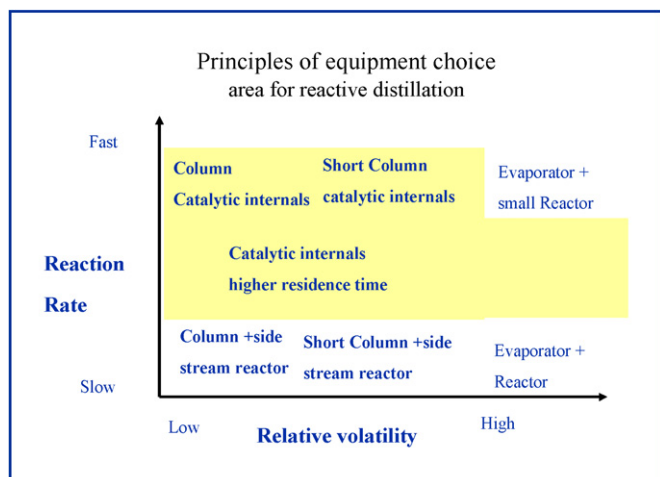


Fig. 2. Principles of equipment choice reactor and distillation from Ref. [17].

For design and optimisation the book *Reactive Distillation* by Sundmacher [9] is available. A chapter on reactive distillation in a book by Doherty [18] is very useful for insight and educational purposes. Frey provides a method for testing the occurrence of a reactive azeotrope [19,20].

Several commercially available computer packages are available for dynamic and steady state flow sheet modeling of reactive distillation. Due to the limited time for preparing this paper a comprehensive overview was not possible.

1.8. Column internals selection and design

Column design requires relations for reaction kinetics, mass transfer, heat transfer and impulse transfer in relation to the required performance. A large European project INTENT (Intelligent Column Internals for Reactive Separations) aimed at principle improvement of column internals and their fitting to particular reactive separation processes. The results are found in a special issue of *Chemical Engineering and Processing* [21]. The key theoretical innovation has been the application of Computational fluid Dynamics programming in combination with rigorous, rate based process simulation. The project resulted in a software tool for internal pre-selection ADVISER [22], a software tool for the fluid flow and reaction simulation CFX-INTENT [21] and a rate based flow simulator, PROFILER [23]. All models were verified for five reactions in pilot plants [21].

Reaction kinetics in the end leads to the required catalyst hold-up. Special attention should be paid to the feasible catalyst hold-up in the column. Reported data about catalyst amounts applied in commercial reactive distillation (RD) processes are scarce, since these data are regarded as proprietary information. A large amount of open literature on RD deals with etherification reactions for which mostly an ion exchange resin catalyst as Amberlyst is used. This catalyst is typically used as spherical particles with particle size ranging between 0.5 and 0.84 mm. From various publications on MTBE RD-modeling it is estimated that the amount of catalyst in a commercial RD-column is in the range of 7–10 tonnes [24].

Table 4
CDTECH pilot plant scale reactive distillation columns [30,2]

Diameter (in.)	Height feet	Number	Comment
1	30	>1	Exp. dev. units
3	50	5	Com dev. units CDU
3	50	2	Top sections CDU
4	50	2	Bottom sections CDU

2. Process development in pilot plants

CDTECH is a very successful developer of reactive distillation technologies. Their first commercial implementation was a MTBE plant at Charter Oil, Houston, TX USA in 1981. Since then they have implemented 123 commercial units [2].

This rapid development and reliable commercial implementation is probably due to their large pilot plant facilities and their connection with the engineering contractor ABB/Lummus. Table 4 summarises their main experimental facilities.

Sulzer Chemtech has pilot plant facilities for testing and contractor engineering capability for commercial scale design. As part of the European consortium project INTINT comprehensive testing of reactive packings was carried out and for the study two processes pilot plants were build [25]. Currently more than 20 industrial processes are in pilot testing phase [4].

So far all companies seem to use pilot plants to validate their designs. BASF has a reactive distillation pilot plant facility obtained from Sulzer Chemtech in Ludwigshaven with Sulzer Katapak-S packing [25]. Shell Global Solutions has currently several reactive distillation pilot plants in operation. Eastman developed their first methyl acetate plant without the benefit of commercial reactive distillation codes at that time (1980). Internal dynamic simulation software and piloting at several scales (up to 20-cm diameter) were then used to prove the concept. The second plant, built 7 years later with the benefit of operating experience, is virtually identical (geometry, staging, dimensions, capacity) except for some sieve detail in the upper non-reactive zones [5].

2.1. Scale-up methods

For reliable scale-up from pilot plant facilities two scale-up methods are typically taken into consideration:

- Brute force;
- Rate model.

In the “Brute force” method all critical parameters in the pilot plant are kept equal to the commercial scale design, so only the diameter and the feed flow rates are scale down. Care is taken that the catalytic distillation packing is fitted correctly to the wall, to avoid wall flow. The “Brute force” method is very reliable, but relatively costly.

In the Rate model method an elaborate model of mass transfer and reactions is made for the commercial scale and for the pilot plant scale. In the commercial scale and in the pilot plant packings are applied for which the mass transfer performances are

Table 5
Scale-up methods

Commercial scale	Pilot plant “Brute force”	Pilot plant + models
Feed quality	Same	Same
Diameter	Smaller	Smaller
Height	Same	Smaller
Packing	Same	Smaller
Velocities	Same	Smaller
Feed locations	Same	Same model location
Good distribution gas and liquid	Avoid wall flow	Avoid wall flow

known. The elaborate model is then validated in the pilot plant in which also care is taken that the catalytic distillation packing is fitted correctly to the wall, to avoid wall flow. This scale-up solution, is suggested by Schoenmakers in Ref. [9, p. 38]. Table 5 summarises the key features of both scale-up methods.

2.2. Barriers to commercial implementation

The barriers (real and perceived) are:

- Complex design.
- Complex control design with less degrees of freedom.
- Expensive pilot plant development is needed.
- Validated scale-up knowledge is needed.
- Difficult to start-up and to operate.

Let us briefly discuss these barriers and ways (including research) to reduce them.

Reactive distillations are more complex to design than a reactor or a distillation column. However, methods and software facilitating the design are becoming increasingly more sophisticated. The large number of commercial applications shows that the design problems have been solved. For irreversible reactions no methods and little information are available in the open literature for conceptual design. Academic research in this area would be very useful.

Reactive distillations have indeed less degrees of freedom, but for all cases reported so far sufficient variables for control appear to be available. The design of the control is, according to CDTECH Lummus/ABB in their commercial applications, not complex. In other cases this may be the case and dynamic simulation to determine a feasible control design is needed. However, if the column design and the control design are done in an integral way, additional cost savings and increased robustness are achievable [26].

Extensive pilot plant development appeared to be needed for the Eastman process developed in the nineteen seventies [5]. However, this is about the most complex process (five functions in one column) imaginable and at that time no comprehensive simulation packages were available. Presently pilot plants of modest sizes and scale-up knowledge on mass transfer and pressure drop are sufficient to reduce the risk to normal levels. In general the pilot plants applied by CDTECH, Sulzer Chemtech and others have a small diameter of typically 5 cm, so small feed flows. So pilot plant cost are low.

Validated scale-up knowledge is needed. However, the scale-up methods, as indicated by the author, are available and also many commercial scale applications, whose results can be used for validation of models.

Difficult start-up and operations are not reported. From my own experience at a manufacturing site operation of the three-phase reactive distillation column was not particularly difficult. It is likely that the increased attention and focus in the design phase in fact reduces the operational difficulty, by a robust controllable design.

2.3. From reactive distillation to process intensification

Due to increased worldwide competition, increased fuel prices and more stringent emission limits, the benefits of applying reactive distillation and process intensification will increase. Moreover, due to increased knowledge by industrial experience and by academic research, the barriers for implementing reactive distillation and process intensification will be further reduced.

Design and simulation tools need to be developed that include reactions, residence time distribution, mass transfer, heat transfer and impulse transfer. In the long-term Computational Fluid Dynamic modelling packages integrated with reaction will facilitate virtual prototyping of reactive distillation column internals [21]. The same approach can be applied to process intensification in general.

The longer term forecast for the application of catalytic (reactive) distillation in the petrochemical industry, is that many reactions, homogeneous and heterogeneously catalysed, equilibrium and irreversible, will be implemented commercially. Moreover, in some separations, selective reversible chemical reactions will be applied in reactive extractive distillation set-ups to replace expensive distillations [27]. Barriers to commercial implementations are lowered, due to pilot plant testing and available scale-up knowledge on mass transfer and impulse transfer (pressure drop).

Integral design, optimisation, control by dynamic simulation show large cost savings [26].

Exergy loss minimisation should be included in conceptual design computer packages to include a more even spread of driving forces, causing lower exergy losses for reactive distillation in particular [28] and process intensification in general.

Design knowledge is being developed for novel combinations of reaction and separation, like reactive extractive distillation [27] and catalytic reaction in dividing wall distillation columns [29]. So this shows that the field of reactive distillation is being extended.

Reactive distillation can also be seen as the forerunner in the field of process intensification. The general lessons for rapid implementation are operation of pilot plants designed with scale-up in mind. Either by brute force or via model validation.

3. Conclusions

Reactive distillation for many different processes has been rapidly implemented in more than 150 commercial operations of the petrochemical and chemical industry.

These implementations show large capital and energy cost reductions, a lower environmental impact and safe and reliable operation.

Reliable scale-up from pilot plant facilities without intermediate demonstration scale seems to have been obtained in all cases. In most cases the scale-up is carried out by the major technology providers CDTECH and Sulzer Chemtech.

Academic research has led to methods and tools to identify design and optimise new applications, however all for reversible reactions only.

The present status seems to warrant the conclusion that reactive distillation is now an established unit operation in process technology.

Reactive distillation can also be seen as the front-runner in the field of process intensification.

4. Recommendations

Process synthesis heuristics on feasibility and attractiveness are typically recommended to be developed for irreversible reactions in reactive distillation.

Scale-up based on pilot plants with the brute force or by model validation method are recommended for process intensification technologies in general.

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