

Reactive distillation: The front-runner of industrial process intensification

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

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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

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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

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