

## MULTIFUNCTIONAL REACTORS

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**Keywords:** Multifunctional reactor, integrated chemical processes, reactive separation processes, heat-integrated reactors, reactive distillation, reactive absorption, reactive adsorption, reactive extraction, chromatographic reactor, membrane reactor, reactive crystallization, reactive precipitation, reactive comminution, reactive extrusion, reactive filtration, fuel cell.

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## Summary

Multifunctional reactors integrate chemical reactions and physical operation units such as separational operations, mechanical operations and heat exchange in one apparatus. The integration gives rise to synergetic effects, which may enhance the performance of chemical reaction or/and physical effect. By suitable process design, an efficient and environmental-friendly process operation can be achieved, the general benefits of which include higher productivity, higher selectivity, reduced capital investment and energy consumption, improved operational safety, and improved ecological harmlessness.

Though multifunctional reactors are promising even many processes have been successfully applied, the process behaviors are very complicated due to the interaction of different effects in single units. Therefore, suitable method for the process design and control must be developed and applied, more experimental work should be carried out ensuring optimal and safe operation of the considered integrated process.

## 1. Introduction

Multifunctional reactors can be described as reactors combining at least one more function from unit operations such as separation, heat exchange, and mechanical unit operation, which conventionally would be performed in a separate piece of equipment. The processes are classified in Table 1. Multifunctional reactors are not new concepts. Numerous applications have been commercialized over the course of several decades. For example, reactive absorption has long been practiced for the removal of acid gases in the petroleum production and refining industries, and reactive distillation for purifying chemicals. However, the academia and industries have taken renewed interest in development and commercialization in recent years, which have caused the emergence of new industries and decline of existing technologies. In general, reactive separation processes are so far applied more widely and reactive distillation is the most in large scale applicable multifunctional reactor.

<b>Integrated effect</b>	<b>Multifunctional reactors</b>
Separation	<ul style="list-style-type: none"><li>• Reactive distillation</li><li>• Reactive absorption</li><li>• Reactive adsorption</li><li>• Simulated moving bed reactors/Reactive chromatography</li><li>• Reactive membrane separation/Membrane reactor</li><li>• Reactive extraction</li><li>• Reactive crystallization</li><li>• Reactive precipitation</li></ul>
Mechanics	<ul style="list-style-type: none"><li>• Reactive comminution</li><li>• Reactive filtration</li><li>• Reactive extrusion</li></ul>

Heat transfer	<ul style="list-style-type: none"> <li>• Heat-integrated reactors</li> <li>• Direct fuel cells</li> </ul>
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Table 1: Intensification of multifunctional reactors

The potential advantages of process intensification are numerous, as listed in Table 2. Some of these advantages are realized by using reaction to improve other effect especially separation, e.g. overcoming azeotropes or reacting away contaminants; others are realized by improved reaction efficiency, e.g. overcoming the reaction equilibrium limitation. The potential is greatest when both aspects are important. More excitingly, multifunctional reactor is sometimes the only way for special problems, which otherwise cannot be solved by the conventional methods, for example the separation of closely mixture by reactive distillation and the removal of diesel soot in car exhaust by reactive filtration. Moreover, multifunctional reactors are found in some areas to meet the requirements for green engineering and sustainable development with safe and environment-friendly processing. Despite all of these potential advantages and a number of successful commercial applications of multifunctional reactors, there are still several important barriers hindering their deeper development and commercialization in chemical industries, as given in Table 2. The lack of process simulation, early screening methods, and scale-up capability stimulate the scientific and industrial research.

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>• Enhanced reaction rate/conversion/selectivity/yield</li> <li>• Improved product quality</li> <li>• Increased catalyst life</li> <li>• Simplified process</li> <li>• Reduced operation costs</li> <li>• Reduced capital investment</li> <li>• Inherently safer unit</li> <li>• Heat integration benefits</li> </ul>	<ul style="list-style-type: none"> <li>• Relatively new technology</li> <li>• Complex process behavior</li> <li>• Limited applications window</li> <li>• Narrow operating window</li> <li>• Process design and modeling problems</li> <li>• Expensive development costs</li> <li>• Increased operational complexity</li> <li>• Scale-up risks</li> </ul>

Table 2: General advantages and disadvantages of multifunctional reactors

In this chapter, the principles and typical application examples of each type of multifunctional reactors are introduced. The reactive separation processes will be first emphasized by typical industrial applications; then the mechanical and heat-integrated processes will be briefly introduced.

## 2. Reactive Separation Processes

The reactive separation processes involve the integration of chemical reaction into another separation operation such as distillation, absorption, adsorption, extraction and so forth. The additional degrees of freedom in the unit design offer the possibility to tailor the concentration profiles inside the unit in order to achieve better process performance (e.g. higher selectivity and higher yield). Especially the in-situ separation results in continuous removal of product, which not only generally overcomes the limitation of chemical equilibrium but also suppresses the side reactions for many cases.

However, due to the compatible operating conditions for both reaction and separation, the field of application is limited. Though many ways to carry out reactive separations for certain chemical reaction such as acid-catalyzed esterification by reactive distillation, reactive extraction, membrane reactor, and stimulated moving bed reactor, not all technologies are equally good due to their different process efficiency and economic consideration.

## 2.1. Reactive Distillation

### 2.1.1. Principle

Reactive distillation takes advantages of simultaneous reaction with multistage vapor-liquid separation. It is structured as a distillation column with partial section containing catalyst. The catalyst used for heterogeneous reactive distillation is usually incorporated into solid packing, which also provides liquid redistribution and vapor disengagement. For homogeneous case, the catalyst is in the same phase as the reacting species. The feeds are introduced into the column near the reactive section according to the volatilities of the involved components, of which with lower volatility to the lower part and higher volatility to the upper part. Chemicals are converted on the catalyst while reaction products are simultaneously and continuously separated by fractionation. Usually, the reaction takes place in the liquid phase.

Methyl acetate production from acetic acid and methanol, invented and practiced by Eastman Chemical company, is probably the best-known industrial application of reactive distillation. The biggest commercial application of reactive distillation is the production of ethers, such as methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE) and tert-amyl methyl ether (TAME), for blending into gasoline. Here reactive distillation for methyl acetate production is first illustrated to explain the principle. The working reaction is



Several factors make it quite difficult to produce high purity ester by conventional methods: (1) limitation of chemical equilibrium, (2) difficulty of separating acetic acid and water, and (3) presence of binary azeotropes between methyl acetate and water, and between methyl acetate and methanol. The conventional process is shown in Figure 1. The liquid-phase reactor, with large excess of one reactant to achieve high conversion of the other, is followed by eight distillation columns, one liquid-liquid extractor and a decanter. This process requires a large capital investment, high energy costs and a large inventory of solvents.

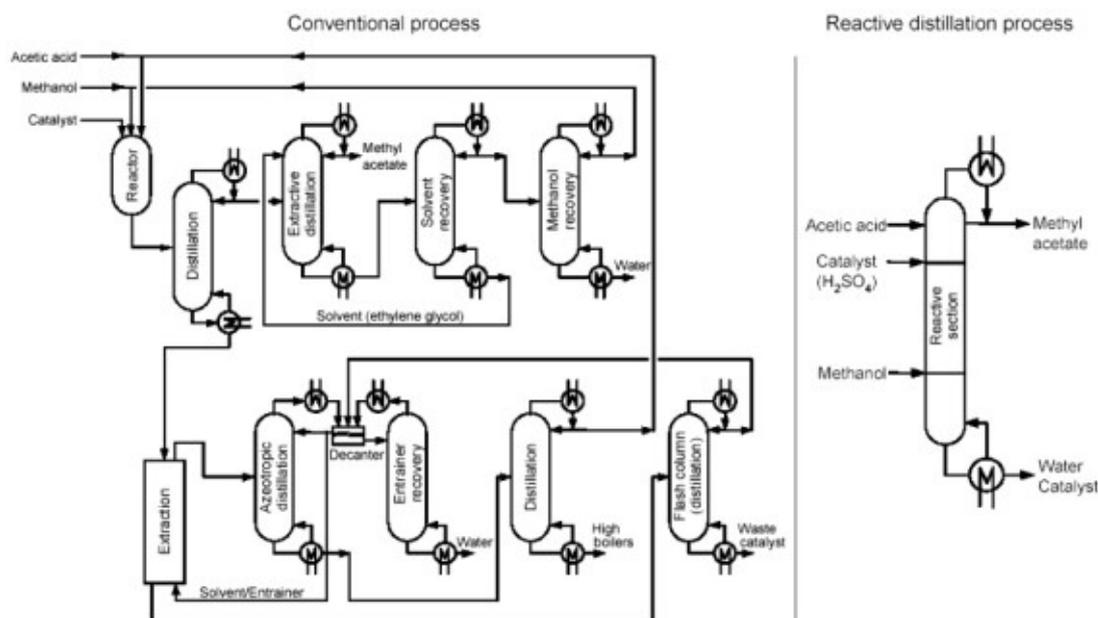


Figure 1: Schematic of traditional and reactive distillation technologies for the production of high-purity methyl acetate.

The reactive distillation column for the manufacture of high-purity and ultra-high-purity methyl acetate consists of three sections (Figure 1). The lighter reactant methanol is fed at the lower section and the heavier acetic acid at the upper section. The reaction takes predominately in the middle reactive section. The bottom section serves to strip off methanol from water and return it to the reaction section. The vapor leaving the reactive section consists of methyl acetate-methanol azeotrope which is broken in the rectifying section by addition of acetic acid that plays as entrainer. The remarkable fact is that, in spite of the reaction having an unfavorable equilibrium, a high-purity product is obtained using stoichiometrically balanced feeds. The whole process is integrated in a single column eliminating the need for a complex distillation column system and recycling of the methyl acetate-methanol azeotrope. Consequently, the investment has been significantly reduced and the energy is only about one-fifth of the conventional technology.

### 2.1.2 Application Examples

Reactive distillation can, not only improve reaction performance by the distillation effect but also solve difficult separation problems by reaction. The motives of applying reactive distillation and typical examples are listed in Table 3 according to the potential benefits.

	Motives	Examples
Reaction	Overcoming limitations of chemical equilibrium	$\text{methanol} + \text{acetic acid} \rightleftharpoons \text{methyl acetate} + \text{water}$ $\text{methanol} + \text{isobutene} \rightleftharpoons \text{methyl tert-butyl ether}$ $\text{formaldehyde} + 2\text{methanol} \rightleftharpoons \text{methylal} + \text{water}$

	Increasing selectivity	chlorohydrins → propylene oxide + water → propylene glycol 2acetone → diacetone alcohol → mesityl oxide + water isobutane + 1-butene → isooctane + 1-butene → C <sub>12</sub> H <sub>24</sub>
	Utilizing heat of reaction	propene + benzene → cumene ethylene oxide + water → ethylene glycol
Separation	Separation of closely boiling mixtures	m-xylene / p-xylene (reactive entrainer: Na-p-xylene) 1-butene / isobutene (reactive entrainer: methanol / water) cyclohexene / cyclohexane (reactive entrainer: formic acid)
	Break of azeotropes	methyl acetate / water; methyl acetate / methanol (entrainer: acetic acid)
	High purity separation	hexamethylene diamine / water (in nylon-6,6 process) (reactive entrainer: adipic acid)

Table 3: Motives for application of reactive distillation

According to the types of chemical reactions, reactive distillation is widely potential beyond the classic esterification and etherification reactions, which mainly includes:

- Esterification, e.g. acetic acid with *n*-butanol, isobutyl alcohol, amyl alcohol and hexanol, and high boiling fatty acids
- Transesterification, e.g. production of butyl acetate and oxalates
- Hydrolysis of esters
- Etherification, e.g. production of MTBE, TAME, ETBE and higher ethers; and separation of isobutene from hydrocarbon mixture
- Hydrogenation, e.g. production of cyclohexane from benzene, cyclopentane from cyclopentadiene, isooctane from isobutene; removal of methyl acetylene/propadiene from hydrocarbon streams; hydrodesulphurization
- Dehydrogenation, e.g. decalin to naphthalene
- Alkylation and trans-alkylation, e.g. ethylbenzene from ethylene and benzene, cumene from propylene and benzene, alkylation of isobutane with normal butene for gasoline blending
- Hydration, e.g. cyclohexanol from cyclohexene, tert-butanol from isobutene
- Dehydrations, e.g. tetrahydrofuran from 1,4-butandiol
- Isomerization, of 1- and 2-butene, α- and β-isophorone, and *n*- and iso-pataffin
- Dimerization of C<sub>4</sub> iso-olefin and oligomerization of linear butenes
- Decomposition of ethers to high-purity olefins
- C<sub>1</sub> chemistry reactions
- Chiral separation, e.g. mixture of propylene oxide and propylene glycol

### 2.1.3. Process Design Issues

The integration of reaction and the in-situ separation in the reactive zone or vice versa often leads to more complex interaction between vapor-liquid equilibrium, mass transfer, and chemical kinetics, which poses complex dynamic and steady-state operational behavior. The suitability of reactive distillation for a particular reaction depends on various factors such as volatilities of reactants and products, reaction and distillation temperatures, etc., which make reactive distillation not always advantageous

and even not feasible. Therefore, reliable tools for the conceptual design and process synthesis, and suitable strategies for process control have to be developed. Moreover, in order to provide better conditions for reactions, liquid holdup should be increased, which requires careful hardware design of packing. An effective way of decomposing the design and development of reactive distillation involves four stages:

- (1) Feasibility and alternatives. The feasible product compositions from a reactive distillation are determined for a given feed, operating pressure, and reaction conditions. In this step, knowledge of the involved chemical reaction and the phase equilibrium is vital. Currently, geometric methods are being pioneered, e.g. residue curve maps, bifurcation analysis of singular points and attainable region methods. However, no approach is completely satisfactory for application of realistic column configurations for any number of components and reactions. Results from the feasibility studies are used to identify and organize alternative column sequences.
- (2) Conceptual design and evaluation. Conceptual design methods estimate process configurations, i.e., equipment sizes (numbers of reactive and non-reactive stages, and column diameter), feed flows and locations, heating and cooling loads, catalyst concentrations, and liquid holdups. This provides the basis for an economic evaluation and ranking of the process alternatives from step (1). Some geometric and mathematic modeling methods are presented, which at this moment have the upper hand for finding designs of realistic complexity.
- (3) Hardware design. Since most processes are heterogeneously catalyzed, hardware design poses considerably challenges for large-scale reactive distillation column. The catalyst particle sizes are usually in the range of 1 to 3 mm. Larger particle sizes lead to intra-particle diffusion limitation. To overcome the limitation of flooding the catalyst particles have to be enveloped within wire gauze envelopes, for example catalyst bales and catalyst sandwiches (with 20-25 vol% catalyst loading), of which the pressure drop is low. This underlines the non-compatibility of requirements of chemical reaction (small particle size and high catalyst loading), separation (large interfacial area between vapor and liquid phases) and pressure drop (higher area for vapor and liquid flow).
- (4) Operability and control. A key issue is to check the robustness of the design, i.e. the ability to maintain product purities and conversion in desired range in the face of disturbances in production rate, feed composition, and other connections to the environment. This is because the strongly non-linear process behaviors caused by the integration of reaction and distillation effects. Therefore, suitable control strategies should be presented to ensure that disturbances in operating parameters do not change the feasible split, especially for the systems with steady state multiplicity which has been predicted and measured in some cases.

#### **2.1.4. Future Directions**

Currently, numerous studies in the field of design, modeling, control and column internals for reactive distillation are in progress. Further research activities will focus on development of new catalyst, which could broaden the feasible operation windows of

reactive distillation. Moreover, coupling of two or more reactions in one reactive distillation column with different catalysts or bifunctional catalyst is of high interest. The suitable example can be the dimerization of isobutene to isooctene with subsequent hydrogenation to produce isooctane.

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### Biographical Sketches

**Prof. Dr.-Ing Kai Sundmacher** studied mechanical and chemical engineering at the Universities of Hannover, Braunschweig and Clausthal, Germany. After gaining his Ph.D. in 1995 and his lecturing qualification in 1998 from the TU Clausthal, he was a postdoctoral researcher at the University of Newcastle upon-Tyne, UK. In 1999 he became a full professor for Process Systems Engineering at the Otto-von-Guericke University Magdeburg, Germany. Since 2001 he has also been the Director for Process Engineering at the Max-Planck Institute for Dynamics of Complex Technical Systems in Magdeburg. Professor Sundmacher's current research interests include integrated chemical processes, dynamics of particulate processes as well as dynamics of fuel cell systems.

**Dr. Zhiwen Qi** received his Ph.D. in Chemical Engineering from East China University of Science and Technology, Shanghai, in 1999. Afterward he worked as a postdoctoral research associate at the Max-Planck Institute for Dynamics of Complex Technical Systems Magdeburg, Germany. Dr. Qi's research areas encompass the synthesis and dynamics of integrated processes, discrete systems, microprocesses and bioenergy.

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