

## REACTIVE DISTILLATION TECHNOLOGY FOR CLEANER PRODUCTION OF CHEMICALS ON INDUSTRIAL SCALE

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### ABSTRACT

*Considerable progress was made by the chemical industry in the development and implementation of cleaner production processes via Reactive Distillation (RD) technology. The main challenge for reactor engineering is to ascertain the scientifically based cleaner technologies necessary for meeting the future energy, environmental, and materials needs of the world. Minimisation of direct or indirect CO<sub>2</sub> emission for energy intensive processes is precedence for reducing their environmental impact. For distillation, this issue is observed in redesigning the separation processes to improve the energy efficiency.*

*In this paper a new methodology is presented for assessing for cleaner production of chemicals economically. We present here the potential applications of RD technology for cleaner production of industrial chemicals by illustrating case studies. This paper presents the principles of green technology, with case studies of greener technologies, reactive distillation and highlights the economic benefits of adopting environmentally friendly processes. We also describe the positive and negative aspects of typical RD technology and the potential and tradeoffs for RD technology in the context of green engineering principles.*

### 1. INTRODUCTION

Green Chemical Engineering (GCE) involves alternative more environmental - friendly synthetic processes, and was another area for production of chemicals on industrial scale with the mantra – 'Think Green'. [1,2,17] Traditionally chemical engineers have been more concerned about selectivity than conversion. Green technologies explore alternate reaction conditions, alternate (solvent free) media and even alternate energy sources. These technologies aimed for the design of chemical products and processes that reduces or eliminates the use and generation of hazardous substances, which is the most fundamental approach to pollution prevention. [17]

Green technology addresses the need to produce the goods and services that society depends on in a more environmentally benign manner. Life-saving pharmaceuticals can be produced while minimizing the amount of waste generated, plastics that biodegrade can be synthesized from plants, and

reactions can be run in water rather than in traditional organic solvents by applying GCE principles to chemical products and processes. [5,11] Elimination/minimisation of waste, improvement in safety, enhancement of security, and saving industry money are the few dividends of these technologies.

### 2. NEED FOR NOVEL TECHNOLOGIES

Rapid globalization of the industries, economic and political changes in the world order, environmentally driven governmental regulations and social pressures, declining reserves of some raw materials, and increasing competition and overcapacity are the circumstances wherein companies are fighting for their future existence. As a response, the chemical and petroleum industries are slowly realizing the significance of new technologies - compared to incremental improvements in the existing processes - as a means of producing products more competitively while simultaneously protecting the environment. The need for more

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efficient and environmentally 'cleaner' processes has led to a growing interest in novel processes and hybrid process systems, which combine conventional and non-conventional processes.[11]

The demands from the society for '*cleaner*' technologies rather '*clean-up*' technologies, the emergence of 'performance chemicals and materials' etc., is driving the profession towards achieving symbiotic relationship with other disciplines.[2,11] The need for more efficient and environmentally '*cleaner*' processes has led to a growing interest in novel processes and hybrid process systems, which combine conventional and non-conventional processes. A drive towards '*Process Intensification*' is leading to the search of novel reactor configurations, which will enhance selectivity as well as productivity. Emerging equipment, processing techniques, and operational methods promise amazing improvements in process plants, noticeably shrinking their size and significantly boosting their efficiency. These developments may consequence in the disappearance of some traditional types of equipment, if not whole unit operations. [12]

Today, we are witnessing important new developments that go beyond "traditional" chemical engineering. Modern industries are looking for novel equipment and techniques that potentially transform concept of chemical plants and lead to compact, safe, energy-efficient, and environment-friendly sustainable processes. Process intensification consists of the development of novel apparatuses brings dramatic improvements in manufacturing and processing, substantially decreasing equipment-size/production-capacity ratio, energy consumption, or waste production, and ultimately resulting in cheaper, sustainable technologies.[2,3]

### **3. CLEANER TECHNOLOGY AND/OR CLEANER PRODUCTION CONCEPTS AND BENEFITS**

Cleaner Production is generally defined as "*the continuous application of an integrated preventive environmental strategy to processes, products, and services to increase eco-efficiency and reduce risks*

*to humans and the environment*" [15, 16]. Cleaner production aims at progressive reductions of the environmental impacts of processes, products and services, through preventative approaches rather than control and management of pollutants and wastes once these have been created. It is an integrated approach, since it includes all relevant environmental aspects and impacts, and is not confined to one environmental impact category like most end-of-pipe technologies. Cleaner technology is a manufacturing process which by its nature or intrinsically:

- ✓ Reduces effluent and other waste production;
- ✓ Maximizes product quality;
- ✓ Maximizes raw materials and energy and any other input use.

Cleaner Production stands for a proactive and preventive approach to industrial environmental management and aims for process- and/or product-integrated solutions that are both environmentally and economically efficient ('eco-efficiency'). Cleaner Production in the process industry is not a new concept [15]. It has essentially been practiced since the first chemical processes were utilized in our industrial society. Initially, the industry focused on issues such as yield improvement rather than specifically preventing pollution from entering the environment. However, the consequence of both activities was the same: less material constituting waste streams entering the environment. The application of cleaner production technologies and practices has already enabled the process industry to reduce and better manage pollution risks associated with wastes and other releases. Industry is now tasked with addressing emerging environmental issues, including the emissions of greenhouse gases, and providing a positive contribution to sustainable development in general. Further and renewed application of the cleaner production approach can provide a competitive edge for process industries while addressing those emerging environmental concerns.

Cleaner Production is related to several other environmental management concepts [16].

- a) *Environmental impact categories* covered, in particular whether only one environmental impact category is targeted ('single media') or several ('multi media');
- b) Primary *motivation* driving the respective environmental management strategy: a division is made between environmental regulation or corporate self-responsibility as the key drivers;
- c) *Reactive versus preventive* approaches; whether the environmental strategy addresses waste and pollution once it has been generated or aims to avoid waste and emissions in the first place;
- d) *Focus*: whether the environmental management concept centres on waste streams, production facilities or product life cycle.

Cleaner Production aims at making more efficient use of natural resources (raw materials, energy and water) and reducing the generation of wastes and emissions at the source. This can be achieved in various ways. A division in five prevention practices is most common. [e.g. 17].

- a) *Product modifications* change the product characteristics, such as shape and material composition. The lifetime of the new product is, for instance, expanded, the product is easier to repair, or the manufacturing of the product is less polluting. Changes in product packaging are generally also regarded as product modifications.
- b) *Input substitution* refers to the use of less polluting raw and adjunct materials and the use of process auxiliaries (such as lubricants and coolants) with a longer service lifetime.
- c) *Technology modifications* include for instance improved process automation, process optimization, equipment redesign and process substitution.

- d) *Good housekeeping* refers to changes in operational procedures and management in order to eliminate waste and emission generation. Examples are spill prevention, improved instruction of workers and training.
- e) *On-site recycling* refers to the useful application of waste materials or pollutants at the company where these have been generated. This could take place through re-use as raw material, recovery of materials or useful application.

#### 4. GREEN CHEMICAL ENGINEERING PRINCIPLES

The chemical process industry aims particularly at energy, capital expenditure and variable feedstock cost savings due to fierce global competition and requirements for sustainable development. Increasingly novel processes are used in the industry to achieve these aims.[1,6] They are used in:

- a) Existing processes to renew parts;
- b) Process re-designs based on existing feed stocks and catalysts;
- c) Innovative processes (new feed stocks, new catalysts, new process routes, new multifunctional equipment).

GCE is much more than a method for addressing environmental problems. It offers a framework for achieving innovation. It is a way to not only improve the environment but also positively impact the client's bottom line. Avoiding the generation of waste (including energy) or pollutants can often be more cost-effective than controlling or disposing of pollutants once formed.

##### 4.1 Twelve Principles of Green Engineering

###### 1. *Inherent Rather Than Circumstantial*

Designers need to strive to ensure that all materials and energy inputs and outputs are as inherently nonhazardous as possible.

## **2. Prevention Instead of Treatment**

It is better to prevent waste than to treat or clean up waste after it is formed.

## **3. Designs for Separation**

Separation and purification operations should be designed to minimize energy consumption and materials use.

## **4. Maximize Efficiency**

Products, processes, and systems should be designed to maximize mass, energy, space, and time efficiency.

## **5. Output-Pulled Versus Input-Pushed**

Products, processes, and systems should be "output pulled" rather than "input pushed" through the use of energy and materials.

## **6. Conserve Complexity**

Embedded entropy and complexity must be viewed as an investment when making design choices on recycle, reuse, or beneficial disposition.

## **7. Durability Rather Than Immortality**

Targeted durability, not immortality, should be a design goal.

## **8. Meet Need, Minimize Excess**

Design for unnecessary capacity or capability (e.g., "one size fits all") solutions should be considered a design flaw.

## **9. Minimize Material Diversity**

Material diversity in multicomponent products should be minimized to promote disassembly and value retention.

## **10. Integrate Material and Energy Flows**

Design of products, processes, and systems must include integration and interconnectivity with available energy and materials flows.

## **11. Design for Commercial "Afterlife"**

Products, processes, and systems should be designed for performance in a commercial "afterlife".

## **12. Renewable Rather Than Depleting**

Material and energy inputs should be renewable rather than depleting.

## **5. GREEN CHEMICAL ENGINEERING ASPECTS OF REACTIVE DISTILLATION**

Green engineering principles have been described recently in the context of design, both for manufacturing molecules in chemical processes and for more general products and systems. Green engineering can also have a major impact on by-product formation as well as other factors identified in green engineering principles. Reactive distillation has been used as a "clean technology" for chemical synthesis in the industry because of advantages like saving of energy cost and capital cost. Reactive distillation has been used as a "clean technology" for chemical synthesis in the industry because of advantages like saving of energy cost and capital cost.[6]

## **6. PRINCIPLES OF REACTIVE DISTILLATION TECHNOLOGY**

### **6.1 Reactive Distillation Process:**

With ever-growing environmental concerns, petrochemical and fine chemical industries face a ubiquitous issue in recovering dilute acetic acid from its aqueous solutions. Reactive distillation (RD) holds dominance over conventional physical separation methods such as distillation and extraction. Distillation is associated with the high costs involved in vaporizing the more volatile water that exists in high proportions and possesses a high latent heat of vaporization. Extraction is limited in view of the distribution of the components in the reacting system. The execution of RD reduces capital and operating costs, and allows for a wider range of operating conditions. RD is receiving increasing attention and holds a huge potential for the recovery of acetic acid in many industrial processes. [9, 13]

RD is the combination of chemical reaction and distillative product separation in single piece of equipment, offers several dividends over conventional

processes in which the reaction and the product separation are done in series, especially for reactions limited by equilibrium constraints. Improved selectivity, increased conversion, better heat control, effective utilization of reaction heat, scope for difficult separations and the avoidance of azeotrope are a few of the advantages that RD offers. [4] As the products in RD are continuously separated from the reaction zone, no limiting chemical equilibrium can be established and thus the reaction velocity is maintained at a high rate, resulting in greater yields.

Other benefits of RD can include the minimization of side reactions and the utilization of the heat of reaction for the mass transfer within the same column. Therefore the capital investment and operating costs are significantly lower with RD than for conventional processes. Examples for successful applications of RD have, among others, been reported for esterifications, etherifications, alkylations and isomerizations [16, 17]. Sulzer Chemtech has developed special structured catalytic packings for Reactive distillation columns, see Figure 1. [12, 17]

RD is a potentially important method of separation for the recovery of dilute acetic acid from its aqueous streams. Moreover, a value added product in the form of isoamyl acetate is produced during the recovery of acetic acid by esterification with Isoamyl alcohol. An additional column will be required for the complete separation of Isoamyl alcohol and Isoamyl acetate. The energy costs for the additional column would be minimized as the water content of the top organic product is kept to a minimal [18].

## 6.2 Continuous fatty acid esterification Processes

The following section describes the basic principles and suggests a possible process set-up for RD process. In this example, the esterification of acetic acid with Isoamyl alcohol is described.

In principle, RD column consists of three different sections; middle one reactive section, bottom one stripping section and top one rectifying section. The reaction and distillation (separation) takes place in middle section; i.e. reactive section. A peristaltic pump was being used to introduce feed to the column. Two peristaltic pumps were used for two feeds. A double-coiled condenser was used and it has been ensured that the condensation is complete.

The experimental setup of a laboratory scale reactive distillation consists of 3 m tall distillation column of inside diameter 50 mm that operates at atmospheric pressure is used. The reboiler (2 lit) is heated with the help of a heating mantle (2KW), provided in the reboiler. The non-reactive rectifying and stripping sections are packed with wire mesh packing. (Evergreen Technologies, Mumbai) The middle reactive zone is packed with structured packing (Fenix Technologies, Pune) embedded with TULSION<sup>®</sup>-T-63 MP (Courtesy Thermax India Ltd.), ion exchange resins as a catalyst. The stripping section is 1 m tall, reactive section 1 m, and rectification section 1 m tall in height respectively. A proper insulation (with asbestos) with external wall heating arrangement is provided to minimize the heat losses to the surrounding.

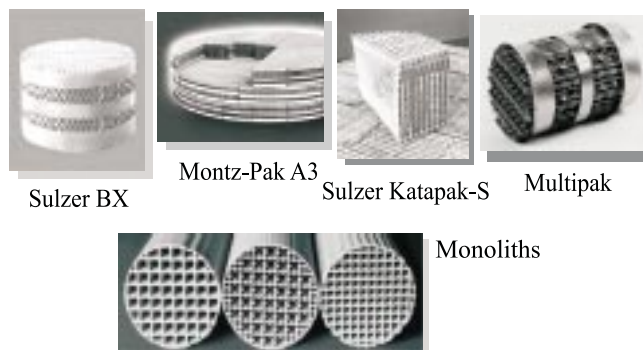
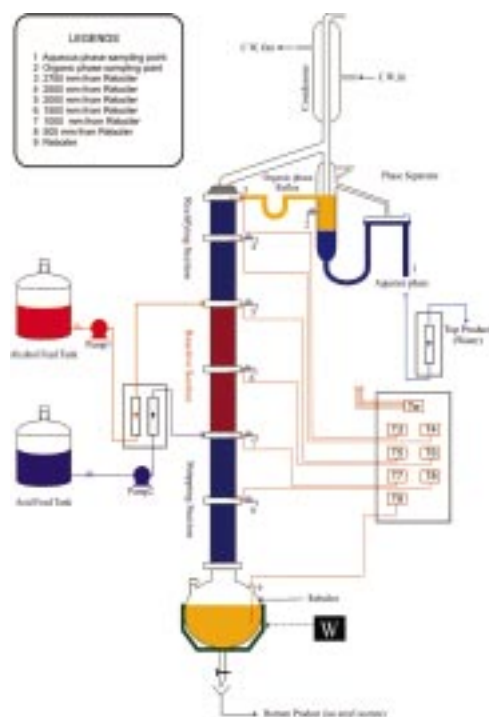


Figure 1 : RD column Internals

Green Engineering Principles	Reduced no. of process units	More specialized equipment	Complex design and control	Enhance overall rates	Overcome unfavourable equilibria	Avoid difficult separations	Improve selectivity	Reduce energy	Reduce solvents
1. Inherent rather than circumstantial			-						
2. Prevention instead of treatment									
3. Design for separation					+		+		+
4. Maximize efficiency				+	+	+			+
5. Output-pulled vs input-pushed					+	+	+	+	+
6. Conserve complexity	+		-		+				
7. Durability rather than immortality		-							
8. Meet need, minimize excess	+			+					
9. Minimize material diversity		-							
10. Integrate local material and energy flows	+	+							
11. Design for a commercial afterlife	+	-						+	
12. Renewable rather than depleting	+								

\* Blank entries indicate no known advantage or disadvantage.

**Table 1 : Positive and negative aspects of typical RD technology with respect to green engineering principles\*[5]**



**Figure 2 : Continuous RD process for production of Industrial Chemicals**

The reaction mixture consisting of acetic acid, alcohol is fed continuously to the column. An electronically driven metering pump is used to transfer the liquid from the feed tank to the column. The boil-up rate is an important parameter in RD processes. As the reflux ratio is fixed, the boil-up is the only operating parameter that can be efficiently changed to obtain the better performance. Hence it is possible to operate the column over a wide range of boil-up rates to study its effect. A wattmeter is used to measure the wattage power supplied to the heating mantle. The continuous process scheme for RD process on Laboratory scale is shown in Figure 2.

In the condenser, two immiscible phases are formed, an aqueous phase i.e. almost pure water and an organic phase containing water, amyl alcohol and amyl acetate. Phase separator with the condenser is used to provide reflux to the column and to continuously withdraw water formed during the reaction. Thermometer wells are provided at different locations in the column to measure these temperatures (Position 1- Position 8)

The conventional separation methods such as distillation and extraction suffer from several drawbacks and are very expensive in terms of time, energy and chemicals. RD is a method of separation that holds huge potential in the recovery of acetic acid from aqueous streams. Through the application of RD via the reaction of acetic acid with an aliphatic alcohol (e.g. Isoamyl alcohol), a useful ester in the form of (e.g. Iso amyl acetate) was produced. The esters of acetic acid, namely, Iso amyl acetate, n-butyl acetate, n-hexyl acetate, have a wide range of industrial applications. [7, 13, 14]

### 6.3 Advantages of the Reactive Distillation Process

The combination of reaction and separation by distillation in one unit allows a continuous production, with reduced processing time. This leads to constant high product quality and at the same time simpler maintenance and process control, which is especially worthwhile for larger production capacities. Well-defined and narrow residence time at gentle conditions throughout the whole plant minimizes degradation of the fatty acids and fatty acid esters. No neutralization, separation or recycling of catalyst is necessary. There is no necessity of emptying and cleaning the equipment, reducing the waste streams to the absolute minimum. The energy consumption of the RD process is only half of the conventional batch one. Also the size of the plant could be drastically reduced [16].

### 7. CONCLUSION

It is important to have an efficient and sustainable technology for the separation/recovery of acetic acids from the wastewater stream from the points of view of pollution control and recovery of useful materials. Several conventional separation techniques discussed in this paper have been employed to remove carboxylic acids from aqueous solution. Some of these techniques are not environment friendly and others are not cost effective. RD process allows the operation to run continuously, leading to a consistently high product quality. RD has been

proposed as a promising technique for separation/recovery of acetic acids from wastewater.

Moreover, a value added product in the form of acetate is produced during recovery of acetic acid by esterification with alcohol. Finally we conclude that RD process is cleaner technology and front-runner in recovery/separation and production of chemicals on industrial scale. [12]

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