Review on Reactive Distillation and Recent Applications

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Abstract—Reactive distillation columns can render great advantages in capital investment and operating cost over the conventional reactor/separatory/recycle systems for some simple reaction operation and separation operation. In the case of the separations of some complicated reacting mixtures including multiple step reactions, a train of reactive distillation columns is frequently needed. Although such kind of systems can still present superior performance in comparison with their conventional counterparts, it is likely to go further in seeking the potential of process intensification. It is noted that in addition to multiple condensers and reboilers, outlet and inlet streams, and possible recycle streams, each reactive distillation column involved carries out only one reaction operation and separation operation. These points remind us of arranging multiple reaction and separation operations in a single reactive distillation column and this leads to a reactive distillation column with multiple reaction zones.

Keywords—Reactive distillation, Application, Reaction, Operation, Biodiesel.

1. Introduction

Reactive Distillation (RD) is a process where the reaction and distillation both the processes taken place in a single column. Separation of the product from the reaction mixture does not need a separate distillation step, which saves energy (for heating) and materials. This Technique was invented in 1921, but the industrial application of reactive distillation (RD) taken place after the 1980s [6]. This technique is especially useful for equilibrium-limited reactions such as esterification and transesterification reactions. Conversion can be raised far beyond what is expected by the equilibrium due to the continuous removal of reaction products from the reaction zone [3]. Reactive distillation (RD) is used with reversible, liquid phase reactions. For many reversible reactions the equilibrium point lies far to the left and little product is formed, however, if one or more of the products are removed more of the product will be formed because of Le Chatlier's Principle, Removing one or more of the products is one of the principles behind reactive distillation (RD) [14].

The term catalytic distillation is also used for such Systems where a catalyst (homogeneous or heterogeneous) is used to accelerate the reaction [12]. Being a relatively new field, research on various aspects such as modeling and simulation, process synthesis, column hardware design, non-linear dynamics and control is in progress. The suitability of reactive distillation (RD) for a particular reaction depends on various factors such as volatilities of reactants and products along with the feasible reaction and distillation temperature. Hence, the use of reactive distillation (RD) for every reaction may not be feasible. Exploring the candidate reactions for reactive distillation (RD), it is an area that needs considerable attention to expand the domain of reactive distillation (RD) processes.

Figure 1: The basic elements of a reactive distillation column [15].

The high boiling reactant is fed as feed 1 and the low boiling reactant as feed 2. Between the two feeds, there is the reaction zone [15].
2. Theory

Reactive distillation (RD) often shows complex behavior such as steady state multiplicity, process gain sign changes and strong interactions between process variables, this results in that reactive distillation (RD) processes are often non-linear in nature. This presents a strong challenge for the construction of a working control structure. Even though an increasing number of papers on reactive distillation columns have been published in the past years, still there is a gap in the market regarding a systematic plant-wide control procedure with focus on optimization [5].

Reduction of energy and equipment cost is possible by thermally coupled distillation sequences as they allow interconnecting vapor and liquid flows between the two columns to eliminate the reboiler or condenser or both. Thermally-coupled side-rectifier, side stripper, and Petlyuk columns are the three well-known configurations. Petlyuk configuration is restricted due to bidirectional vapor and liquid flows. The side-rectifier and side-stripper configurations tend to be the most efficient ones [8].

Reactive distillation (RD) column with the two reaction zones is also in practice. In terms of thermodynamic characteristics of reaction operation and separation operation involved, a reactive distillation (RD) column with two reaction zones is proposed for the production of cyclohexanol by indirect hydration of cyclohexene. The arrangement of two separate reaction zones not only allows the careful coordination of the two reaction operations involved, but also provides additional degrees of freedom for the reinforcement of internal mass integration and/or internal energy integration between the reaction operations and the separation operation involved [16].

Through deep comparison between the reactive distillation (RD) column with two reaction zones and the coupled reactive distillation (RD) columns, it is demonstrated that the former could lead to reduced total annual cost in comparison with the latter. The reactive distillation (RD) column with two reaction zones should therefore be considered as a competitive alternative to the coupled reactive distillation (RD) columns for the production of cyclohexanol by indirect hydration of cyclohexene [16].

A. 2.1. Reactive distillation (RD) has many applications which are as follows –

- 2.1.1. Reactive distillation (RD) process for Methyl Valerate, Methyl valerate (VAME), also known as methyl pentanoate, is a methyl ester of pentanoic acid (valeric acid). Methyl valerate (VAME) is usually used as a fragrance in the production of beauty care, soap, and laundry detergents. High purity methyl valerate (VAME) can also be used as a kind of plasticizer. A reactive distillation (RD) column is used in the production process to overcome equilibrium limitation of the esterification reaction. Products, methyl valerate (VAME) and water are withdrawn from the distillate of reactive distillation (RD) column and then can be separated by two strippers and a decanter. A thermally coupled design is then developed to reduce the remixing effect in the rectifying section of the reactive distillation (RD) column. The simulation results show that 30% energy saving can be achieved by using the proposed thermally coupled configuration, but only 17% of total annual costs can be saved due to the use of a compressor.[2]

- 2.1.2. Reactive distillation (RD) for production of Furfural using solid acid catalyst, In this process reactive distillation (RD) uses solid acid catalysts for producing furfural from synthetic and real (pre-hydrolysate liquor (PHL) from wood chip digestion) feeds containing xylose. The reactive distillation (RD) process provides a unique advantage of immediate furfural separation from the reaction zone as it is formed, thus minimizing the formation of undesired by-products (e.g., oligomers of furfural/humins) from subsequent furfural condensation reactions. An in situ catalyst regeneration method was demonstrated successfully and resulted in achieving extended catalyst lifetime and furfural yield, similar to that obtained with synthetic xylose feeds.[9]

- 2.1.3. Reactive distillation (RD) process for the production of fluorinated alkenes, The preparation of suitable chlorofluorocarbon and hydro chlorofluorocarbon materials or chlorofluorocarbon and hydro chlorofluorocarbon alkene and alkyne intermediates which serve as useful feedstock for fluorination and reduction to cis-1,1,1,4,4,4-hexafluoro-2-butene. Also, a continuous process for the production of cis-1,1,1,4,4,4-hexafluoro-2-butene from the alkene and alkyne intermediates.[1]
2.1.4. Reactive Distillation (RD) of Biodiesel, With global increased energy demands, the continued depletion of fossil fuels and problems associated with global warming and emissions, it is necessary to focus research on development of renewable fuel alternatives. Biodiesel is a carbon-neutral alternative which can be used in most automotive engines without need for modification. Reactive distillation (RD) is an integrated reactive and separation unit which offers several potential benefits; less waste processing, higher yield of product, better separation and large savings on both OPEX and CAPEX [5].

2.1.5. Biodiesel production using thermally coupled reactive distillation (RD), Production of ethyl dodecanoate (biodiesel) using lauric acid and methanol with a solid acid catalyst of sulfated zirconia is studied by using two distillation sequences. In the first sequence, the methanol recovery column follows the reactive distillation (RD) column. In the second sequence, the reactive distillation (RD) and methanol recovery columns are thermally coupled. Thermally coupled distillation sequences may consume less energy by allowing interconnecting vapor and liquid streams between the two columns to eliminate reboiler or condenser or both. [8].

2.1.6. Transesterification process by combination of reactive distillation (RD) and pervaporation, the development of a reactive distillation process for the production of n-butyl acetate by transesterification of methyl acetate with n-butanol [13].

B. 2.2. PROS OF REACTIVE DISTILLATION (RD)-
C. Some of the benefits of reactive distillation (RD) are –
• 2.2.1. Increased speed.
• 2.2.2. Lower costs – reduced equipment use, energy use and handling.
• 2.2.3. Less waste and fewer byproducts.
• 2.2.4. Improved product quality- reducing opportunity for degradation because of less heat.

E. 2.3 CONS OF REACTIVE DISTILLATION (RD)-
F. As everything has pros and cons of its own, reactive distillation (RD) also have its own complications that are as follows:
• 2.3.1. The conditions in the reactive column are suboptimal both as a chemical reactor and as a distillation column, since the reactive column combines these.

• 2.3.2. The introduction of an in situ separation process in the reaction zone or vice versa leads to complex interactions between vapor-liquid equilibrium, mass transfer rates, diffusion and chemical kinetics, which poses a great challenge for design and synthesis of these systems.
• 2.3.3. Side reactors, where separate columns feeds a reactor and vice versa, are better for some reactions, if the optimal conditions of distillation and reaction differ too much.

H. 2.4 PUBLICATIONS OF PAPERS AND RESEARCH WORKS-
Last few years have seen a dramatic rise in the number of applications of reactive distillation (RD). This useful technology is now being applied for any scale of operation- from manufacture of fine chemicals to that of bulk chemicals. Reactive distillation (RD) has been successfully used and investigated in the past for several reactions such as etherification, esterification, hydrogenation, hydrodesulphurization and polymerization. Various reviews have been published on this aspect [4-10-12-7]. However, even after the recent review by Sharma and Mahajani (2003) that was presented in the first international workshop on reactive distillation (RD) held at Magdeburg, Germany in 2001, an increasing number of articles have appeared in the last couple of years. An updated version of the recently published statistics [4], shows that there are around 180 papers and 100 patents published in the last two years on reactive distillation (RD) alone. This clearly reveals the increasing interest in this area. Apart from the theoretical aspects of reactive distillation (RD), we see the research being performed mainly in two different directions, firstly, in improving the performance of reactive distillation (RD) for the existing applications and secondly, in exploring new applications. Hence, considering the growing rate of publications, we felt it necessary to review this voluminous information shortly after the gap of about 2-3 years. The present article is intended to serve as a supplement to the review by Sharma and Mahajani (2003) which we feel the reader to go through as well, in order to get an idea of the entire spectrum of reactions that comes under the umbrella of reactive distillation.

3. Conclusion
Reactive distillation (RD) has major impact on economy of industries, and also with the developing world new technologies replacing the conventional one, in this sense reactive distillation (RD) is the perfect example. Time is money and and reduction in manufacturing time plays a major role for any of the developing industries. New implementations in the
design of reactive distillation (RD) column leading to the great reduction in the capital cost and energy cost. One of the important aspects of reactive distillation (RD) is that it has low impact on environmental conditions and also proving to be the safe and reliable process. Reactive distillation (RD) has set up its application as the unit operation in the process technology. In nutshell we can say that reactive distillation (RD) is becoming the front-runner in the field of process intensification.

4. References


