Green Chemical Engineering Aspects of Reactive Distillation

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Reactive or catalytic distillation technology combines chemical synthesis steps with separations by distillation. This combination can lead to intensified, high-efficiency process systems with significant green engineering attributes. New applications and understanding have prompted growth in the use of reactive distillation for a variety of chemical syntheses, especially esterifications and etherifications involving oxygenated hydrocarbons. We describe several applications and the potential and tradeoffs for reactive distillation technology in the context of green engineering principles.

Introduction

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 (*1*). In designs for chemical routes to new molecules, alternative reaction schemes are frequently studied. New synthesis routes motivated by green chemistry principles offer the possibility for greater efficiency and inherently fewer byproducts. Green engineering can also have a major impact on byproduct formation as well as other factors identified in green engineering principles.

Green chemistry seeks molecular-level change in search of a high "atom efficiency". However, 100% atom efficiency is often elusive, and a particular chemical synthesis frequently cannot be made inherently free of byproduct formation. For example, even when a desired product can be made using a chemical transformation with 100% atom efficiency, undesired byproduct reactions may also be present. Green engineering can reduce the formation of these byproducts. In addition, chemical reaction equilibrium may be limiting, and separation and purification tasks are often critical for producing a final product, for deriving pure feed materials, and for recovering ingredients for recycle. These separations are often disconnected from the chemical transformations, both in conceiving the process and in implementing a technology. This may seem a natural division, but Principle 3 of green engineering emphasizes that separation should be considered early in the design. This goal and others, especially the need to "maximize mass energy, space and time efficiency" (Principle 4) and "output-pulled vs input-pushed" (Principle 5) are intimately related to a current emphasis on "process intensification" in chemical technology.

Processes can be made more "intense" in many ways. These include converting to continuous processes instead of batch operations (*2*) using high-intensity mixing in reactors or separators, combining chemical transformations with transport in pipelines, or using microreactors (*3*). Some intensification approaches that improve mixing not only improve overall rates and efficiencies but also reduce byproduct formation. Principles 2 and 4 of green engineering (preventing waste *and* maximizing efficiency) both favor this technology. The objectives of these two principles alone are both served, creating a "win−win" situation. However, other objectives may not be advanced when all green engineering principles are considered. For example, improved mixing may require substantial external energy input and process control, and these may be in opposition to green engineering Principles 1 and 5.

The existence of multiple objectives expressed or implied in green chemistry or engineering principles and tradeoffs among them requires a systems approach. For this, chemical and physical descriptions of the fundamental steps are necessary but not sufficient. Quantitative objectives for design are also needed. Because this may result in complex decisions where many variables must be balanced, mathematical models and optimization technology are invaluable.

Even simple models offer insight and improvements as long as they are systematic. For example, there are many continuous chemical processes that include the separation of byproducts and recycle of unconverted raw materials. Douglas (*4*) showed that designing for the maximum yield of a desired intermediate, a goal of many discovery studies in chemistry, often produces process technology that is far from optimal because it produces too much undesired byproduct. It is frequently far better to design for lower conversions where yield is low but selectivity is high and bear the expense of a larger and more costly separation system to recover and recycle unconverted ingredients. This increases energy use or investment in separations in order to reduce byproduct formation and is one important tradeoff between two objectives identified in the green engineering Principles 2 (prevention instead of treatment) and 3 (design for separation). This result often surprises those unfamiliar with a systems approach.

More complex phenomena involving larger systems, dynamics, and control and the engineering of micromixing patterns in reactors may be greatly advanced by sophisticated high-fidelity models. These are formulated for and solved effectively by advanced computational approaches. Increased knowledge and information technology reduce the cost of dealing with complexity and can therefore lead to greatly improved designs based on objectives that acknowledge green engineering principles. This offers the opportunity to make an explicit and quantitative treatment of factors in designs, which were previously underemphasized or ignored as too costly or time-consuming.

Reactive Distillation

Among several approaches to process intensification are hybrid combinations of separation and reaction for chemical synthesis. These combinations offer new process alternatives that may have greatly improved efficiencies (e.g., in reduced energy requirements, lower solvent use, reduced equipment investment, and greater selectivity). Many of these potential advantages are intimately linked to the principles and challenges for green engineering.

We focus exclusively on combinations of chemical reactions with vapor−liquid separations based on distillation

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FIGURE 1. Schematic of (a) conventional and (b) reactive distillation technologies for the production of high-purity methyl acetate (*11*).

because "reactive distillation" (RD) and "catalytic distillation" (CD) show significant growth in both patents and journal papers (*5*). (Note that other combinations of chemical transformations with separations can also be thought of in this context (e.g., in situ product removal in fermentations, or reaction−extraction systems for bioproduct recovery; *6*). These offer many similar advantages when conditions of vapor−liquid boiling temperatures and pressures are impractical for the materials or catalysts under consideration.)

Complexity and the need for a systems approach also arise from the interactions of chemical reaction rates and equilibria and the vapor−liquid or liquid−liquid phase behavior of multicomponent mixtures. New conceptual design methods and simulation approaches are described elsewhere (*7*) along with details on equipment and related open issues (*8*). We focus below on key examples and potential for further advances linked to the principles of green engineering.

Examples

Methyl acetate production from acetic acid and methanol, invented and practiced by Eastman Chemical Company, is probably the best-known example of reactive distillation in the literature (*9*−*11*). Figure 1 shows a schematic of the conventional technology (with 11 major units) as compared with a single hybrid unit for reactive distillation. Reactive distillation lowers the investment as well as the energy use to one-fifth of the conventional technology; furthermore, the use of two solvents is eliminated. These benefits are obtained not only by overcoming limitations due to chemical reaction equilibrium but also by avoiding or overcoming difficult separations. Although there are no published numbers, the inventory of materials in reactive distillation is presumably substantially smaller. These are all advantages according to several of the principles of green engineering.

Reactive distillation systems are a challenge to design and control, and the resulting process equipment may be difficult to reuse for another purpose if and when the original process is no longer commercially viable. These would seem unfavorable aspects according to green engineering Principles 6 and 11.

It is difficult to conduct the reverse reaction and hydrolyze methyl acetate via RD due to the large volatility of the ester. However, RD at different conditions can be used for ester hydrolysis to produce dimethyl ether (DME) rather than methanol (*12*). Design for separation (Principle 3) is interpreted by Anastas and Zimmerman (*1*, 97A) not only to promote advanced planning for the separation of desired products from undesired materials but also to the final products' ultimate recycle or disassembly. This suggests that we assess in a design whether a reactive distillation process can also be used either to reverse the reaction to "disassemble" the original product molecule into the original ingredients or into another useful material.

This example also illustrates some of the tradeoffs among the goals implied in the principles of green engineering. Except when a design favors all aspects of green engineering principles, the relative effects on each must be balanced by design decisions. However, it is likely that for a wide variety of weights that might be assigned, the reactive distillation technology is superior according to the principles of green engineering.

Etherification reactions for the production of fuel ethers such as MTBE were among the first reaction−separation technologies developed and implemented to use heterogeneous catalysts (*13*). Interestingly, CD can also be used for deetherification in certain cases (*14*), and CD is under study for a technology to destroy MTBE in light of new understanding and data on its environmental impact. More details on the MTBE example and on other fuel ethers such as ETBE and TAME can be found in the some of the references cited above (*7*, *8*) and elsewhere.

CD technology has also been developed for a number of other chemical routes such as isomerizations and alkylations and for the manufacture of acetals. The proper placement of catalyst among and between column sections that have
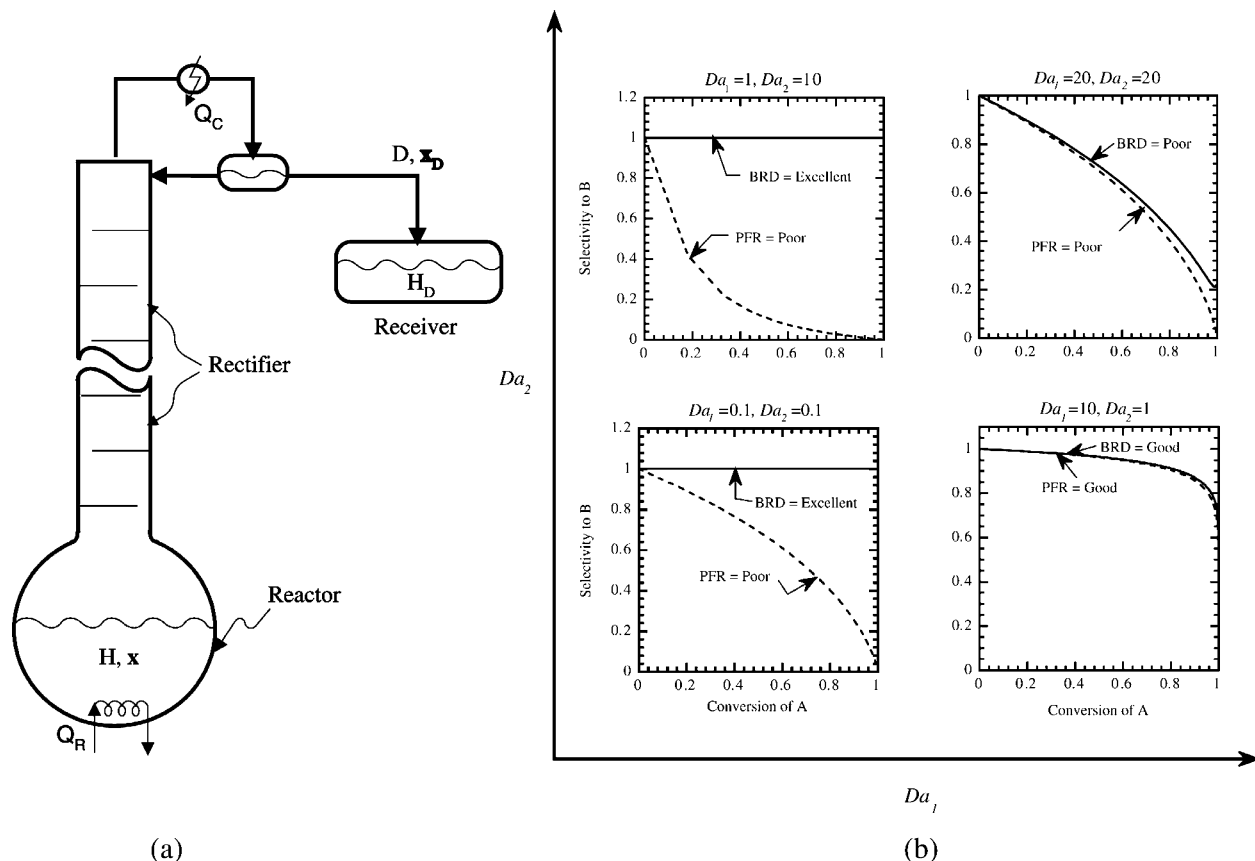
FIGURE 2. Batch reaction with distillation (BRD) (25). The plots in panel b show the selectivity for the formation of *B* as a function of the fractional conversion for *A*. The solid line corresponds to BRD in panel a, and the dashed line corresponds to the batch reactor without distillation, which is the same as the plug flow reactor (PFR).

no reactions as well as the level of catalyst and the method of fixing the catalyst within the equipment for effective contacting offers many alternatives and is an active area of study (15).

The proper contact time relative to the residence time in reactive or catalytic distillation can be a critical issue. For example, short contact times for very fast reactions may be required to reduce byproduct formation (16). Methods for scaling up the results from small-scale tests and for understanding the control and regulation of catalytic distillation systems are less well-developed but important to the effective use of catalytic distillation technology.

More recent but less well-studied examples of reactive or catalytic distillation include hybridization of catalytic distillation with membrane pervaporiation (17) (a further process intensification) and a novel application to hydrogen storage and transportation (18). It is unknown if these areas will lead to a commercial application, but it is interesting to note the breadth of studies.

Systematic Methods and Design Targets

RD is feasible and advantageous in several applications, as discussed above. However, based on our current understanding, reactive or catalytic distillation is not always desirable—or at least a desirable configuration—and conditions are not always apparent. Feasible process configurations generally combine both reactive and nonreactive distillation components. These can depend in a sensitive manner on the combined effects of phase behavior, reaction chemistry, reaction equilibria, and catalysts. For instance, the process in Figure 1b provides chemical reaction in the entire lower part of the column/reactor below the feed point for the homogeneous catalyst and a nonreactive section above. In

contrast, catalytic distillation for MTBE is implemented with a nonreactive stripping section below a section packed with (heterogeneous) catalyst.

This is not to say that reactive or catalytic distillation cannot be used in a particular case, but only that these systems require study on an individual basis. Fortunately, new theories and modeling tools for the design of reactive distillation systems provide tools for rapidly assessing feasibility in many cases as well as for more detailed simulations and optimizations. One class of such tools is based on "geometric methods" that provide a global picture of the constraints on feasible products and conversions in reactive distillation. These use a systematic classification of the critical points in models for the simultaneous reaction and distillation.

When the reaction rates can be made large enough (e.g., by sufficient catalyst or residence time), the limits for reactive distillation are determined by simultaneous phase and reaction equilibrium. Surprisingly, the addition of chemical reaction can sometimes induce the formation of a mixture which, in an isobaric experiment, boils and reacts at constant temperature and composition containing many or all of the chemical components in the mixture. Such a "reactive azeotrope" (19) is evident in the esterification of acetic acid to isopropyl acetate (20), although absent for methyl acetate (21). At conditions far from this equilibrium limit, reaction kinetics are an important factor, and these can be systematically studied by using bifurcation theory to classify the nature of critical points and parameter values where they occur (22, 23).

Important but less well-studied issues arise in cases with multiple chemical reactions where only some of the reactions are desirable. Green chemistry studies have the objective of

TABLE 1. Positive and Negative Aspects of Typical Reactive Distillation Technology with Respect to Green Engineering Principles[a]

green engineering principles	reduced no. of process units	more specialized equipment	complex design & control	enhance overall rates	overcome unfavorable 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 & energy flows	+	+						+	
11 design for a commercial afterlife	+	−							
12 renewable rather than depleting	+								

[a] Blank entries indicate no known advantage or disadvantage.

discovering synthesis schemes and/or catalysts for which undesired reactions are absent. For cases where such schemes are unknown, selectivity losses can nevertheless be reduced; this is a goal of green chemical engineering (Principle 2, waste prevention). There are a number of predictions from the methods mentioned above suggesting cases where reactive or catalytic distillation can have a major impact on waste prevention.

For instance, consider a simple conceptual case of serial reactions [also see Allen and Shonnard (24, p 263 ff.)]:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$
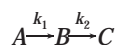
The desired component (B) is the lowest-boiling, the undesired byproduct (C) is highest-boiling, and the mixture follows a simple ideal phase equilibrium description. The ratios of process time to reaction times for each step (Da_1 and Da_2) are key parameters (25). Predictions of selectivity for an isobaric batch reactor−rectifier (Figure 2a) are shown in Figure 2b.

If the process time is long as compared to the characteristic time for the first reaction, the selectivity is hardly influenced by simultaneous distillation. It is relatively poor when the reactions have comparable rates (Figure 2b, upper right; $Da_1 = Da_2 = 20$) or relatively good when the second reaction is slower than the first (Figure 2b, lower right; $Da_1 = 10$, $Da_2 = 1$). However, when the process time is comparable to or smaller than the characteristic time for the first reaction, the impact of distillation on the selectivity can be dramatic. The rate for the second reaction is 10 times larger than the first in Figure 2b (upper left, $Da_1 = 1$, $Da_2 = 10$) or equal to it in Figure 2b (lower left, $Da_1 = 0.1$, $Da_2 = 0.1$). In the latter two cases, extremely high selectivity and very low byproduct production is feasible via reactive distillation. The economies of achieving this depend on the particular mixture, equipment costs, energy, etc. and should be determined with an optimization. These results show that bench-scale experiments producing poor selectivity due to byproduct reactions can sometimes be greatly improved using RD technology.

Next, consider the more complex scheme of reversible reactions:

$$A + B \rightleftharpoons C + D$$

$$B + C \rightleftharpoons E$$
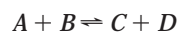
where C is the desired product and E is an undesired byproduct. D is an unavoidable byproduct, and if this cannot be used beneficially then there is less than 100% atom
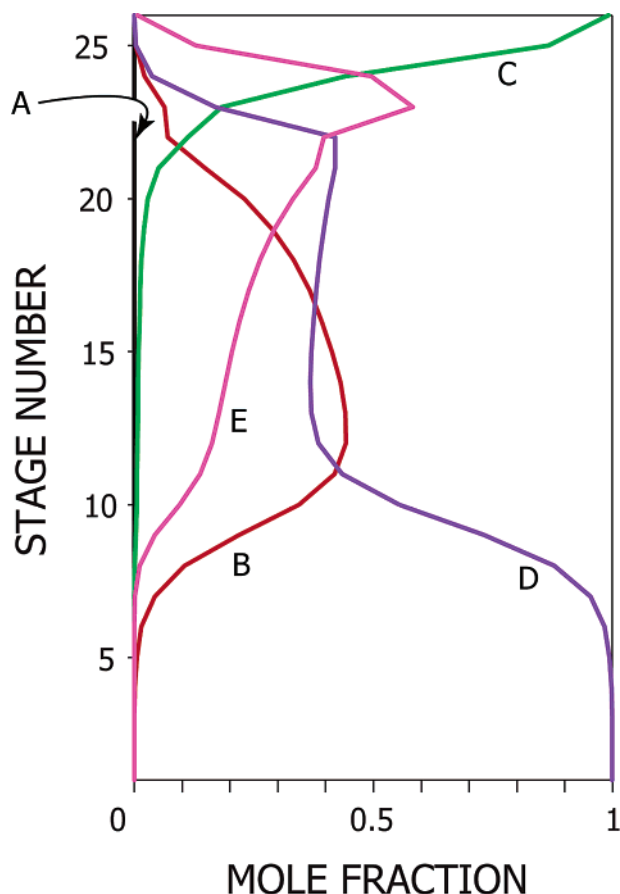

FIGURE 3. Stage-to-stage composition profiles for a reactive distillation that contains a reversible byproduct (E). Ingredient A is also contained along with a slight excess of B that is fed in this particular design. This design depends on continuous monitoring and control of the system, and therefore sacrifices inherency (Principle 1) to achieve waste prevention (Principle 2).

efficiency in the first reaction, and a green chemistry solution for an alternative synthesis route should also be considered. The relative boiling points are C < A < B < E < D. Geometric methods for feasibility and design predict that RD can be used to contain the second reaction completely, leading to very large selectivity.

One set of predicted composition profiles within a RD column is shown in Figure 3. Essentially, the RD device recycles component E internally until it reaches a sufficient

level to attain reaction equilibrium with compounds *B* and *C*. Further reaction leads to a net production of only *C* and *D*, which appear as high-purity distillate and bottom products, respectively. It is well-known that the recycle of a reversible byproduct can greatly reduce or nearly eliminate byproduct formation in systems where reaction and separation are sequential (*4, 24*); the results shown in Figure 3 are the RD analogue. It should be possible to greatly reduce the cost of recycle for reversible byproducts in some cases using RD or CD.

We emphasize that the predictions in these examples have not yet been demonstrated, although the example in Figure 3 is under study. These examples are meant to illustrate the power of recent modeling approaches to set targets for new technologies that have the potential to dramatically reduce waste or achieve other green engineering objectives via RD or CD.

Discussion

RD or CD offers process improvements or "intensifications" that have some clear benefits relative to the principles of green engineering. For instance, the number of process units is greatly reduced, offering improvements desirable by Principles 6, 8, and 10−12. Other aspects of RD offset parts of these advantages, [e.g., the "reactive−extractive" distillation for methyl acetate production has several different materials of construction (undesirable by Principles 7, 9 and 11) and requires an active control system (undesirable by Principles 1 and 6)]. Tradeoffs are also found in other aspects as described above; a summary is given in Table 1. Further studies on the formulation of green engineering principles into quantitative objectives and their use to find optimal designs in the general area of process intensification is a promising direction for research.

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