DEVELOPMENT OF FEASIBILITY CRITERIA FOR BATCH AND CONTINUOUS REACTIVE DISTILLATION

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Abstract

Recently, there has been increased interest in process intensification since huge potentials exist for economic savings and environmentally-benign effects. Process intensification usually aims at combining many operation units into the smallest number of units. Reactive distillation is a type of process intensification that combines reaction and V-L phase separation. There have been many publications about reactive distillation. However, no feasibility evaluation method has been available to determine the possibility of producing pure products given the simple information of reaction and phase equilibrium. This article addresses such a systematic feasibility evaluation for batch and continuous reactive distillation by using this simple information. Specifically, we use reaction equilibrium data and residue curve maps (RCMs) to estimate the composition trajectories of reactive feed drums in batch systems and the composition profiles of extractive sections and non-reactive rectifying sections in both batch and continuous systems.

Keywords

Feasibility criteria, reactive distillation, process intensification.

Introduction

Process intensification is the execution of two or more unit operations in one piece of equipment. Reactive distillation is an intensification of chemical reaction and vapor-liquid phase separation. Eastman Chemical's methyl acetate production system features a reactive distillation column and is one of the most successful large-scale commercial applications of process intensification (Agreda and Partin, 1984, Sirrola, 1995). Other commercial examples of process intensification include the synthesis of cumene (Shoemaker and Jones, 1987) and methylal (Masamoto and Matsuzaki, 1994), also by reactive distillation.

Process intensification can simplify many processes, circumvent non-ideal phase separation behavior, reduce energy use, and, in some cases, avoid the use of harmful extractive agents (Allen and Shonnard, 2002, Malone and Doherty, 2000, Taylor and Krishna, 2000).

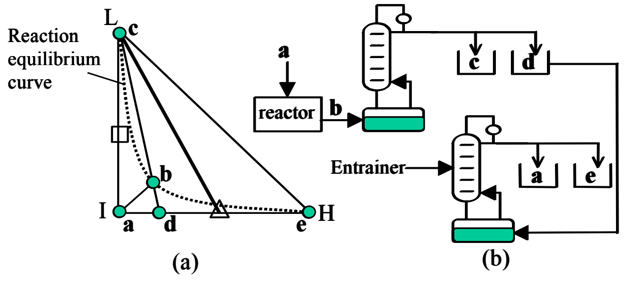


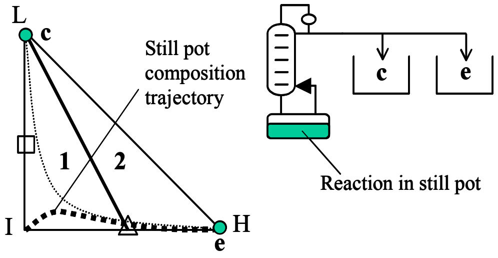
Figure 1. (a) RCM-320 with superimposed reaction equilibrium curve. (b) A conventional batch process flowsheet. Hereafter, the dotted curve denotes reaction equilibrium.

Consider the reaction I ↔ L + H where L, I, and H are the light, intermediate, and heavy-boiling components and

L and H are the desired products. The distillation boundary and reaction equilibrium curve for this system are shown in Fig. 1 (a). Fig. 1 (b) shows a conventional flowsheet for producing pure products from this reaction.

In the conventional process, the reactant (whose composition is marked “a” in Fig. 1) is fed to a reactor and is allowed to approach equilibrium. The reactor effluent (marked “b”) is then transferred to a batch rectifier where pure L (marked “c”) is removed at the top, leaving an I-H mixture in the still pot (marked “d”). This mixture is then distilled under a side-fed entrainer to break the I-H azeotrope and recover pure I (marked “a”) at the top. Then, the H-entrainer mixture is distilled to produce pure H (marked “e”).

However, if the reaction is conducted in the still pot of a batch reactive rectifier while the mixture is distilled, as shown in Fig. 2, then we find that the column composition profiles connect the still pot composition with the L vertex, so pure L is removed at the top of the column. Then, the forward reaction takes place in the still pot consuming more of the reactant, I. The still pot trajectory travels towards the H vertex as only pure H will remain in the still pot. Only one batch operation is needed to consume all of the reactant and separate the products.



(a) (b)

Figure 2. A batch reactive rectifier.

This paper will discuss the feasibility criteria of various intensified column configurations, both batch and continuous, and will then discuss the dynamic simulations used to verify these criteria.

Feasibility Criteria for Various Structures

We use residue curves (also called distillation lines) to estimate column composition profiles. A column section with enough stages will follow a residue curve to an unstable node or a stable node. So, residue curve maps (Hoffman, 1964, Doherty and Perkins, 1978) and reaction equilibrium are used to quickly determine feasibility for a system that combines a single reaction with vapor-liquid separation (Guo et al., 2003a,b, Guo and Lee, 2003).

Feasibility of Batch Systems

A reactive batch rectifier (shown in Figs. 2(b) and 3(a)) consists of a distillation column above a reactive still pot. Because column profiles under very high reflux ratios follow the residue curves, the distillate composition at any given moment in time can be found by following the residue curve from the still pot composition through more volatile compositions to an unstable node. If that unstable node is a pure light product, then its removal in the distillate causes the still pot composition to move away from reaction equilibrium and to move to reactant-rich compositions, resulting in the consumption of more reactants. If the distillate composition remains that pure light product, then as the distillate product is removed, more of the reactants are consumed, and only the heavy product remains in the still pot at the end of the batch operation. *This therefore requires that the light product be an unstable node that is reachable (via simple distillation) from the still pot composition during the entire batch operation.* Since the reaction is equilibrium-limited and the light product is being removed, the still pot composition (as a function of time) follows the reaction equilibrium curve and the light product vertex should therefore be reachable from the reaction equilibrium curve.

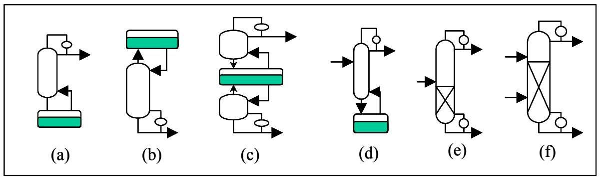


Figure 3. Various structures of reactive distillation columns.

A reactive batch stripper consists of a distillation column below a reactive still pot as shown in Fig. 3(b). Similarly to the reactive rectifier, column profiles under very high reboil also follow residue curves, except that they go through less volatile compositions while going down the column and lead to stable nodes. *Therefore, a batch reactive stripper is feasible if the pure heavy product is a stable node that is reachable from the still pot composition throughout the entire batch operation.* That is, it should be reachable from the reaction equilibrium curve.

In a batch middle vessel column, there is a distillation column both above and below the reactive still pot as shown in Fig. 3(c). Therefore, for a middle-vessel column to produce pure products, it is necessary to meet the requirements of both reactive rectifiers and reactive strippers. That is, the light product must be an unstable node, the heavy product must be a stable node, and both nodes must be reachable from the still pot composition by simple distillation. *In this case, the unstable and stable nodes are in the same distillation region as a piece of the reaction equilibrium curve.*

There are cases where the initial charge composition is in a different distillation region from the reaction equilibrium curve and that the light and/or heavy product is not reachable from any composition near the initial feed charge. In these cases, it is necessary merely to operate under total reflux/reboil until the still pot composition crosses any intervening distillation boundaries by reaction. Then, the pure product vertices become reachable and one can then switch to finite reflux/reboil.

If both of the products are saddles and there is a minimum-boiling azeotrope formed with one of the products, then it is necessary to conduct the reactive distillation under a side-fed entrainer. This is Batch Reactive Extractive Distillation (BRED) and is shown in Fig. 3(d).

Feasibility of Continuous Systems

In a continuous distillation column, there is no reactive still pot, so reaction takes place on some of the trays of the distillation column itself. In the reaction zone, the column profiles do not follow the residue curves. However, there are still non-reactive stages at the top and bottom of the column where the column section profiles still follow the residue curves. Since it is still desired to produce pure products, it is therefore still necessary for these profiles to reach the pure product vertices of composition space. So, in a single-feed reactive distillation column (shown in Fig. 3(e)), similar to the case of the batch middle-vessel column, *the light product must be an unstable node, the heavy product must be a stable node, and both must be in the same distillation region as the reaction equilibrium curve*.

If both products are saddles and there is an unstable node azeotrope between them, then a double-feed distillation column (where the upper feed is an extractive agent as shown in Fig. 3(f)) is needed to break the azeotrope and produce pure products.

Dynamic Simulations

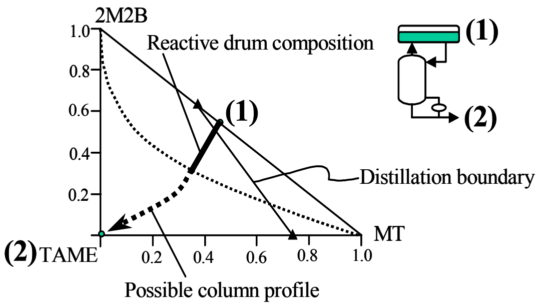


Figure 4. Flowsheet and composition diagram for TAME synthesis by batch reactive stripping at 8 atm. Equilibrium and kinetic data from Rihko and Krause (1995).

Tert-amyl methyl ether (TAME) is synthesized from methanol and 2-methyl-2-butene (2M2B) by the reaction MT + 2M2B ↔ TAME. In this system, there is a minimum-boiling unstable node azeotrope between methanol and 2M2B and a saddle azeotrope between 2M2B and TAME. 2M2B is a saddle and TAME and MT are stable nodes. A distillation boundary is formed between the two azeotropes such that TAME is the least volatile composition in only one of the distillation boundaries. Consequently, TAME is not reachable from everywhere in composition space. However, most of the reaction equilibrium curve lies on the TAME side of the distillation boundary, so if an equimolar mixture of methanol and 2M2B is allowed to approach equilibrium, then the resulting composition will lie on the TAME side of the distillation boundary and the mixture may be stripped to yield pure TAME, thus making the system feasible in a batch reactive stripper. Fig. 4 shows the results of a dynamic simulation that was conducted to verify the feasibility of the TAME synthesis system in a batch reactive stripper. Here, the initial feed charge composition (an equimolar mixture of 2M2B and MT) is on the MT side of the distillation boundary and the TAME vertex is not reachable by simple distillation. So, the drum mixture is allowed to react under total reboil, causing it to approach the reaction equilibrium curve and cross the distillation boundary. Once across the distillation boundary, the column composition profiles can reach the TAME vertex from the drum composition. Since the product TAME shares the same distillation region with the reaction equilibrium curve, a continuous single-feed reactive distillation column can also produce pure TAME at the bottom.

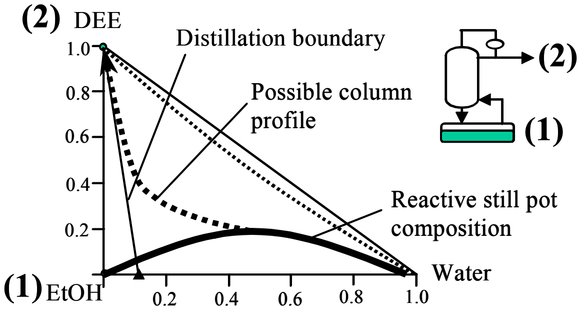


Figure 5. Flowsheet and composition diagram for DEE synthesis by batch reactive rectification at 1 atm. Equilibrium data from Aspen Plus^{TM}.

Diethyl ether (DEE) is produced by the dehydration of ethanol. 2 EtOH ↔ DEE + Water. In this system, there is only one azeotrope, a minimum-boiling saddle between ethanol and water. DEE is an unstable node and ethanol and water are stable nodes. A distillation boundary is formed between DEE and the ethanol-water azeotrope. Because DEE is an unstable node that is reachable from both distillation regions, this system is feasible in a batch reactive rectifier. Fig. 5 shows the results of a dynamic simulation that confirms the feasibility of the DEE system in a batch reactive rectifier. Here, the initial feed charge is pure EtOH. As the still pot mixture reacts, the still pot composition approaches the reaction equilibrium curve. The column composition profiles can reach the DEE vertex from any still pot composition, so DEE is removed from the still pot and the still pot trajectory approaches the water vertex. Only water remains in the still pot at the end of the batch operation. A continuous single-feed reactive distillation column can also produce pure DEE and water since they are unstable and stable nodes that lie in the same distillation region as the reaction equilibrium curve.

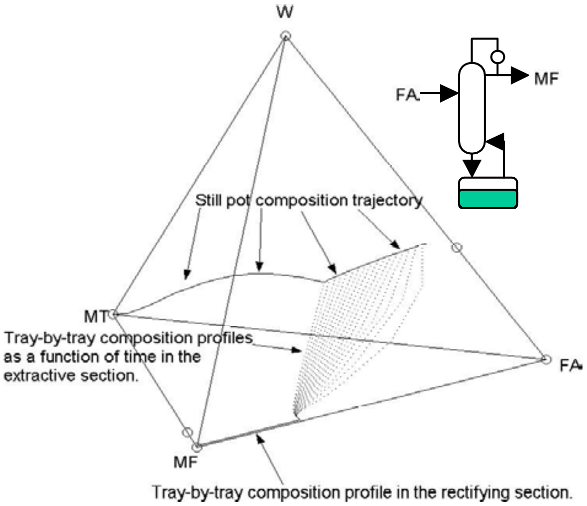


Figure 6. Dynamic simulation of MF synthesis by BRED at 3 bar. Equilibrium data from Bessling et al. (1997).

Methyl Formate (MF) is produced from the reaction of formic acid (FA) and methanol (MT). FA + MT ↔ MF + Water. The system contains a minimum-boiling unstable node azeotrope between MT and MF and a maximum-boiling stable node azeotrope between FA and water. All the pure components are saddles and no distillation boundary is formed. Because the products MF and water are both saddles and MF forms an unstable node azeotrope with MT, neither a batch reactive rectifier nor a batch reactive stripper can produce pure products from this reaction. However, FA, besides being a reactant, can also be used as an extractive agent to break the MT-MF azeotrope. With MT extracted, MF becomes an unstable node. So, a BRED column can be used to produce pure MF. Fig. 6 shows the results of a dynamic simulation that was conducted to verify the feasibility of producing pure MF in a BRED column. Here, the initial feed charge is pure MT. FA is fed into the column under total reflux to being producing MF in the still pot. Then, the mixture is simultaneously reacted and distilled under finite reflux while continuing the feed of FA as an extractive agent. An excess of FA is needed to properly extract MT from the vapor stream. The extractive section profiles reach the MF-FA edge before entering the rectifying section, and the rectifying profile proceeds towards the MF vertex. With the removal of MF and the addition of FA, the methanol is consumed and the still pot trajectory proceeds towards the FA-W edge. Pure MF can also be produced in a continuous double-feed column since both products are saddles.

Conclusions

A batch reactive rectifier is feasible if the light product is an unstable node that is reachable from the reaction equilibrium curve by simple distillation. A batch reactive stripper is feasible if the heavy product is a stable node that is reachable from the reaction equilibrium curve by simple distillation. Batch reactive middle vessel columns and single-feed continuous reactive columns are both feasible if the light and heavy products are an unstable node and stable node, respectively, and lie in the same distillation region as a part of the reaction equilibrium curve. If the light and heavy products are both saddles and one of the products forms an unstable node azeotrope, then a BRED column or a double-feed continuous reactive distillation column is needed to break the azeotrope and produce pure products. In future work, we will extend these feasibility criteria to the case of multiple reaction systems.

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