DESIGNING COMPLEX REACTIVE COLUMNS WITH FEASIBLE REGIONS TO OPTIMIZE FEED DISTRIBUTION, CATALYST PLACEMENT, AND COLUMN PRESSURE

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Abstract

This paper develops a method for analyzing feasibility in complex reactive columns. Feasible regions are identified for non-reactive, reactive, side feed, and side draw column sections. These regions are then used to analyze feasibility for an ideal and non-ideal system. Design alternatives are generated and evaluated to optimize feed and reaction distribution as well as column pressure.

Keywords

Reactive distillation, Feasible regions, Difference points

Introduction

A complex chemical process is often designed by decomposing the entire system into sections such as unit operations. For each section, the type of equipment and set of design and operating conditions must be selected in order to satisfy a set of desired specifications (e.g. product purity). One design method based on decomposition captures the behavior of a section over the full range of design and operating parameters in what is termed a feasible region. The feasible region contains all design alternatives for a particular section of the overall process. By searching each feasible region and connecting sections, alternative designs are generated and evaluated to identify a suitable flow sheet for the entire process.

This approach has been successfully applied to the design of single feed distillation columns with two products (Westerberg and Wahnschafft, 1996; Hoffmaster and Hauan, 2002). A full column is divided into a rectifying and stripping section for which feasible regions can be constructed using simple geometric arguments. A feasible region encloses all possible feed compositions that can be distilled into the end-product for the specified column section. If the two feasible regions overlap in composition space, the full column is feasible which means that a set of feed and operating parameters must exist that allow the column to simultaneously produce both desired products (Castillo et al., 1998).

In our previous work, these feasible region techniques have been extended to design single feed reactive distillation columns with kinetically controlled reactions (Hoffmaster and Hauan, 2003). This paper will further extend the design method to account for complex reactive columns containing multiple side feeds and side draws. Two examples will be used to illustrate the approach: (1) an olefin metathesis reactive distillation column and (2) a TAME column and side reactor combination. Key design issues including optimal feed distribution, catalyst placement, and operating pressure will be addressed.

Feasible Region Identification

The theory of generalized difference points (Hauan et al., 2000) provides a consistent mathematical description of systems combining reaction and separation. One of the fundamental results of this theory is that any complex

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column can be represented by a combination of four basic building blocks as shown in Figure 1. Based on this decomposition, a general design method for complex columns can be developed by capturing all feasible profiles in each type of column section and connecting the sections to make a feasible full column. In this approach, each column section is assumed to operate with constant pressure, equilibrium VLE stages, negligible heat effects, and a known end-product composition.

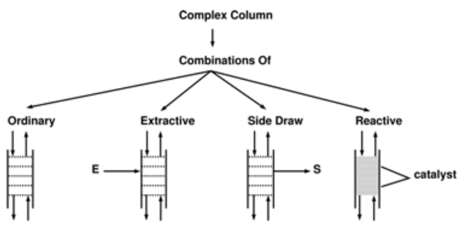

Figure 1. Building blocks for complex columns

The feasible region for a non-reactive section is parametric only in the reflux ratio. Minimum and total reflux curves passing through the specified end-product composition define the boundary of the feasible region except for highly non-ideal mixtures with S-shaped total reflux curves (Hoffmaster and Hauan, 2002). When reaction is added, two additional parameters appear and cause complications in the identification of the feasible region. The first parameter is reaction distribution which corresponds to the placement of catalyst or liquid holdup throughout the section. We assume reaction is monotonic in any reactive section meaning that only forward or reverse reaction can occur and not a combination of the two. The other parameter is reaction turnover which captures the total conversion in the section.

Two types of feasible regions are used for reactive column sections with a single kinetically controlled reaction. In the first type, the reaction turnover and reflux ratio are specified, while reaction distribution is variable. Under these conditions, the feasible region bounds are sectional profiles constructed with extreme reaction and separation policies. A schematic view of the identified bounds is shown in Figure 2. The bounds are formed by the liquid compositions along extreme profiles. One bound has all of the reaction in the condenser followed by non-reactive stages. This bound corresponds to maximum reaction followed by separation. Eventually, the bound terminates at a reactive pinch point (Hoffmaster and Hauan, 2003). Another bound has maximum separation followed by reaction. The separation is achieved by constructing the non-reactive profile until a pinch point is reached. As indicated, there are two possible policies for distributing reaction at the non-reactive pinch and connecting the two pinch points. A single flash calculation at the non-reactive pinch determines which reaction distribution policy gives the more extreme bound. This feasible region captures column section profiles with any number of stages and any reaction distribution policy. The second class of reactive feasible regions has variable reflux in addition to variable reaction distribution. The region under these conditions is constructed by combining the variable distribution regions for the full range of reflux ratios. The accuracy of the region depends on the range of reflux ratios used. The addition of variable reflux generalizes the feasible region to include sectional profiles for any number of stages, any reaction distribution, and any reflux ratio. In general, the second type of reactive section feasible regions is significantly larger than the first type.

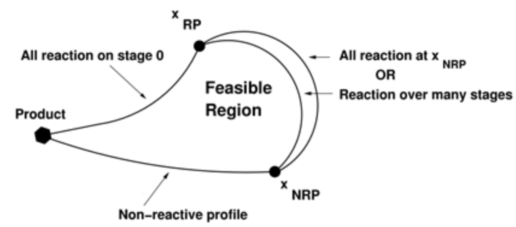

Figure 2. Reactive section feasible region

Side feed sections have similar feasible regions. To identify the side feed region, the feed is fully specified in terms of composition, flow, and quality. However, no restrictions are placed on how the feed is distributed in the column section. For a fixed reflux, the bounds on the side feed region are shown in Figure 3. In analogy to reactive feasible region bounds which represent maximum separation and reaction, the side feed bounds are constructed based on extreme policies for separation and feed addition. The bounds include: (1) all feed placed on the top stage followed by non-reactive stages to the side feed pinch and (2) non-reactive stages to the non-reactive pinch followed by either all feed on the pinch stage or feed distributed over many stages. This region includes sectional profiles for the specified feed distributed over any number and combination of stages. Like the reactive case, the side feed region can be generalized by combining the feasible regions for all reflux ratios.

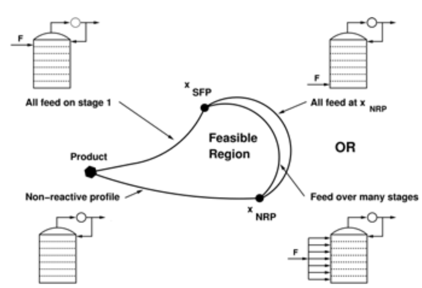

Figure 3. Side feed feasible region

For a side draw section, the side product is specified in terms of composition, quality, and total flow. Side draw feasible region bounds are identical to side feed regions except that flows are reversed. The feasibility bounds for the four section types can be constructed no matter if the column section is an end section or an internal section of a multi-section column. The importance of these feasible regions will be shown by developing a full column design algorithm and applying it to real systems.

Full Column Design with Feasible Regions

Feasible regions for column sections can be used to determine whether or not a set of design specifications will result in a feasible full column design. For feasibility in a two product column, a continuous profile must connect the specified distillate and bottoms compositions. Since the feasible regions contain all sectional profiles over the range of operating parameters that reach a specified end-product composition, full column feasibility can be checked based on whether or not the feasible regions overlap in composition space. If no overlap exists, the design is infeasible. It is important to note that an overlap does not guarantee a feasible full column design because every composition inside the feasible region does not necessarily satisfy the full column material balance.

To search feasible regions for good designs, a three part optimization strategy has been shown to be useful (Hoffmaster and Hauan, 2003). The three steps are: (1) infeasibility test, (2) initialization, and (3) optimization. The algorithm proceeds by specifying the necessary conditions to construct feasible regions for all column sections. If the feasible regions overlap, the sectional and overall material balance equations are solved as a nonlinear program using the same conditions defining the feasible regions. These equations are solved iteratively inside loops over the number of stages in each section. The objective is to find intersecting column section profiles by minimizing the composition difference on stages where sections join. Once an initially feasible design is found, any parameters that were held fixed can now be freed and the material balances are resolved to find a locally optimal design. The solution is stored and iterations continue through the number of stages in each section until all combinations have been checked. This algorithm generates many feasible solutions which can be evaluated and compared to determine a good design for a given set of design goals.

Examples

Feasible region techniques will be illustrated to generate and evaluate design alternatives using both an ideal (olefin metathesis) and non-ideal (TAME) system.

Olefin Metathesis

Reactive distillation column designs will be generated for the metathesis of 2-pentene to form 2-butene and 3-hexene. The mixture of olefins is assumed to behave as an ideal mixture, and simple mass-action kinetics are used to describe the reaction. The objective of the design is to convert a pure C_5H_{10} feed into 98 mol% of both C_4H_8 (distillate) and C_6H_{12} (bottoms).

The design algorithm described in this paper is executed using two column sections which include a reactive rectifying section with a specified reflux (r=2) and reaction turnover (50%) and a reactive stripping section with a specified reboil (s=3) and reaction turnover (50%). The initialization step in the algorithm finds feasible single feed designs under the conditions used to construct the feasible regions. These designs are then optimized in terms of feed and holdup distribution while keeping the external reflux and reboil ratios fixed. The pareto curves in terms of holdup versus number of stages are shown in Figure 4 for a range of feed qualities. Feed quality is defined as the moles of saturated liquid formed on the feed stage per mole of feed. The designs show improvement as the feed quality varies over a larger range. In addition, the number of feed stages increases as the range of feed qualities expands. The reflux and reboil constraints are then relaxed which results in a significant improvement as seen in Figure 5. Although the designs improve as the feed quality range expands outside the saturated regime, an economic study is necessary to determine whether this is cost effective.

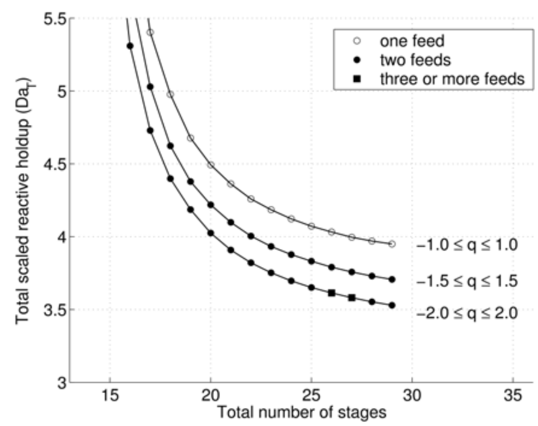

Figure 4. Feasible olefin metathesis designs with fixed reflux and reboil ratios

TAME

TAME is formed from isoamylenes reacting with methanol. The non-ideal behavior of the mixture is captured with the Wilson model, while the kinetics are described in terms of liquid activities by a Langmuir-Hinshelwood mechanism. A typical flowsheet for the process is shown in Figure 6. By specifying the conversion in both reactors as well as the feed and distillate streams, feasible regions are used to determine the remaining parameters. A non-reactive feasible region from the distillate product determines all possible side draw compositions and the side draw stage number. Then a side draw feasible region captures all possible flow rates for the side draw stream, and a flow rate is selected to achieve the desired conversion in the side reactor. Knowing the side draw conditions, the side reactor is designed and the side feed composition and flow rate are computed. Next, the side feed return stage(s) must be found. This is accomplished by constructing a side feed feasible region from the bottoms product. In order for the full column design to be feasible, the feasible region for the side draw section located above this section must overlap. A feasible design for a pressure of 2.5 bars is shown in Figure 7. The design achieves 90% isoamylene conversion with 11 stages and a reflux of r=15.

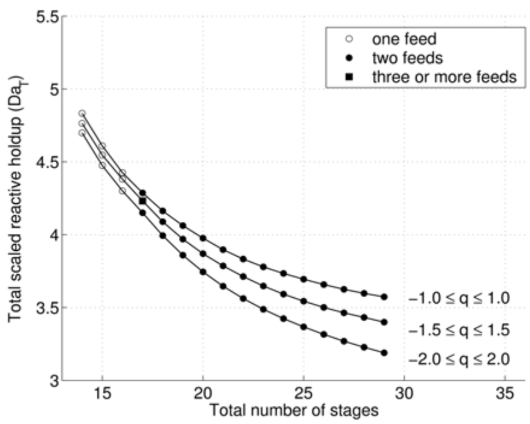

Figure 5. Feasible olefin metathesis designs with variable reflux and reboil ratios

Pressure has a significant effect on the TAME design. As pressure is increased, the methanol content of the azeotropes increases. Excess methanol is required in the feed to achieve the same conversion at a higher pressure. Increased pressure also shifts the reaction equilibrium curve toward the reactants due to the increased temperature and the fact that the TAME reactions are exothermic. This results in a substantial decrease in overall conversion; however, the reaction rates are higher with the increased temperature. The main disadvantage with operating at a lower pressure is the high catalyst requirements due to lower reaction rates. The process configuration shown in Figure 6 is feasible for a wide range of pressures, but the economics of the process are negatively impacted outside a small range of pressures.

Conclusions

We have shown how to construct feasible regions for non-reactive, reactive, side feed, and side draw column sections. Using these regions, design alternatives can be discovered for any complex column. We applied the method to the olefin metathesis reactive distillation column and generated multi-feed designs with optimal feed and holdup distribution. The designs show improvement as the feed quality, reflux, and reboil are varied. In addition, we found a TAME column design using feasible regions. Together, these feasibility analysis tools provide insight into how complex columns operate.

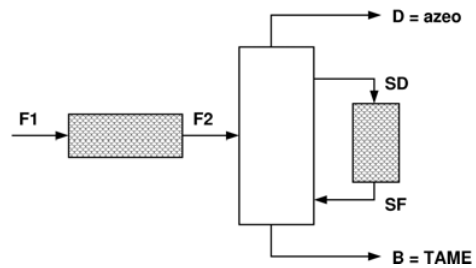

Figure 6. TAME flowsheet

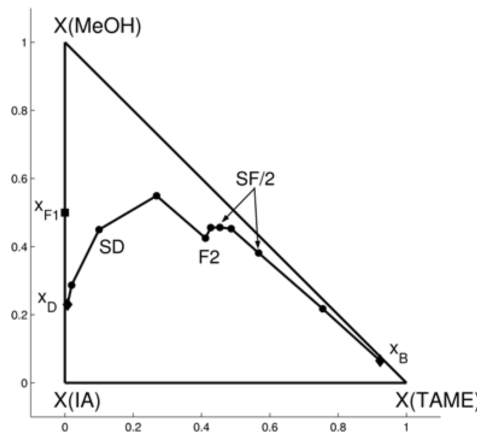

Figure 7. Feasible TAME design at 2.5 bars

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