

## Multi-Objective Design of Reactive Distillation

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### Abstract

This work addresses the multi-objective design of complex reactive distillation columns. The concept of feasible regions is employed to investigate the use of internal reaction distribution, as well as superheated and subcooled feeds. We generate the Pareto surfaces relating the amount of reactive holdup, the number of stages and a cost indicator reflecting energy usage and column size. The most promising designs are identified and investigated further using rigorous simulations in Aspen Plus.

**Keywords:** Reactive distillation, feasible regions, multi-objective optimization.

### 1. Introduction

The design and multi-objective optimization of complex reactive distillation columns can be addressed through a framework that combines the use of feasible regions and optimization techniques. The concept of feasible regions [1] was extended to the design of distillation columns with kinetically controlled reactions and multiple feed streams by Hoffmaster and Hauan [2]. Once the specifications for every section of the full column are fixed, the feasible regions, which enclose all possible sectional profiles over the full range of operating parameters, can be built. The overlap of the regions in the composition space indicates the existence of potentially feasible designs. Hoffmaster and Hauan [3] optimized the design of reactive distillation columns with multiple feeds. Specifically, they generated trade-off curves relating the

minimum number of stages (NS) and the minimum amount of reactive holdup (RH) to compare different design alternatives. In considering columns with distributed feeds, it was discovered that several solutions on the Pareto front involved combining superheated and subcooled feeds. As pointed out by the authors, the economics of these solutions should be investigated further. The combination of different feed qualities provides a source or a sink of heat at specified stages of the columns, which, while favorable to the reaction, tend to increase the internal flows in some sections of the column, demanding larger column diameters. Also, the cost of the production of superheated vapor and subcooled liquid is not negligible and should therefore be incorporated into the design and optimization procedure.

In this work, we extend the previous approach to simultaneously consider capital cost, energy consumption as well as the cost of catalyst and develop the Pareto surface describing the optimal trade-off between all these different factors. To this effect, the capacity variables concept introduced by Jobson et al. [4] for vapor-liquid equilibrium separation processes are adopted and used as a basis for a cost indicator for a reactive distillation column. The modified variables [6] handles a three components system, with no preset policy for distributing the pure reactant feed. The multi-objective optimization problem presented involves the minimization of two objective functions: the amount of RH and a linear function of the capacity variables and is solved using the  $\epsilon$ -constraint method [5]. In previous work [6] this approach was used with fixed reflux (R) and reboil (S) ratios and performance trends identified. We now further develop the analysis to include variable R and S for a set of three ideal systems with different ratios of relative volatilities for reactants and products. In addition, we verify a selected number of optimal designs using Aspen Plus simulations. With this last step we aim at checking for agreement between these two approaches while verifying the extent of small adjustments in some of the design variables with a view to improve their practical implementation.

## 2. Methodology

The approach used is based on several steps with details as described in previous work [6]. In brief, it starts by generating the initial profiles for the rectifying and stripping sections for a given NS in each section. This initialization is made while minimizing the holdup. Intersection of both sectional profiles in the composition space is then checked, verifying potential feasibility of the overall design. If the solution is not infeasible, the design is then optimized for minimum RH and minimum cost indicator, using the  $\epsilon$ -constraint method. The procedure is repeated for different NS in each section after which we construct the Pareto surface relating NS, RH and cost indicator. It is important to note that the  $\epsilon$ -constraint method does not guarantee global convergence. We alleviate this issue by using a series of different initialization techniques to expand the number of different local minima.

Feasibility analysis considers column decomposition into smaller sections operating under steady state conditions. Constant pressure and vapor-liquid equilibrium are assumed at every stage and a kinetically controlled reaction is considered in the liquid phase. For the first stage of this work, all heat effects are considered to be negligible, allowing the decoupling of the material and energy balances. The sectional profiles can then be constructed using only material balances [2]. Subsequent Aspen simulation evaluate the heat effects in more detail.

The large number of alternatives to be evaluated justifies the adoption of a cost indicator instead of a detailed costing methodology. Jobson et al. [4] defined and used capacity variables to systematically estimate and compare costs for different vapor-liquid equilibrium separation processes. These variables incorporate both the energy and capital cost of the column by considering the size of internal flows as well as NS providing a quick method for the estimation of the column costs. The sum of the boiling and condensing capacities is used as the objective function; from now on referred to simply as “capacity”. The use of this approach is also justified since the focus of this work is on the identification and evaluation of feasible designs, not on the complete definition of column specifications. In an advanced stage of the design process, the best solutions identified should be compared using more rigorous costing methods.

The optimization framework sets no minimum limit on the reactive holdup or on the distribution of the feeds. Furthermore, the negligible heat assumption introduces small deviations into the results. These arguments suggest that there should be some room to investigate small modifications to the reported column designs specifications. A selected number of design cases located at the Pareto front are then used to initialize simulations in Aspen Plus and their performance evaluated for small changes on the RH distribution and the feed quality.

### 3. Case studies

A real system and two variants are investigated. The base case for this study is the olefin metathesis wherein 2-pentene ( $C_5$ ) reacts in the presence of a catalyst to form 2-butene ( $C_4$ ) and 3-hexene ( $C_6$ ) in an attempt to rebalance the light olefins obtained from cracking. The physical properties and reaction kinetics are taken from the literature [7]. The reaction is considered only to occur in the liquid phase with a negligible heat of reaction and ideal vapor-liquid equilibrium behavior at atmospheric pressure. The reactant has an intermediate boiling point, allowing for a wide range of feasible column designs.

The conditions for the olefin metathesis are taken from Hoffmaster and Hauan [3]. The goal is to convert a pure pentene feed into products streams of butene and hexene; each with a purity of no less than 98 mole percent. The distribution of fresh feed as well as the reflux and reboil ratios are allowed to vary freely while the feed quality is limited to the range of -2 to +2 which correspond to superheated and subcooled states. After the original case (A) where the relative

volatilities are  $\alpha_{C4/C6} = 9$  and  $\alpha_{C5/C6} = 2.9$ , two artificial parameter sets were defined to explore the impact of reactant volatility:  $\alpha_{C5/C6} = 2.0$  for case B and  $\alpha_{C5/C6} = 4.0$  for case C.

## 4. Results & discussion

### 4.1. Optimization of identified feasible designs

The Pareto front was built from the optimization results by selecting the lowest capacity for each value of RH and NS. When compared to the cases where fixed R and S were used, the minimum RH was further reduced (Fig.1). The difference is more noticeable for smaller columns, where the R and S can now have higher values to decrease the total RH. Also, the vapor and liquid feeds (near the top and bottom, respectively) used to satisfy R and S values, are found not to be required. The minimum RH value increases as the relative volatility for the reactant increases (Fig. 2) which is related to the lower availability of the reactant in the liquid phase, where reaction takes place. Nevertheless, the separation is not favored and case A reports the smallest feasible column and also the smallest value for capacity. Capacity versus NS is no longer a growing function but clearly shows a minimum (Fig. 3) that is 10% lower than the previously reported minimum with fixed R and S. The reactant volatility has a significant effect on the feed location and, as the volatility increases, the feed moves towards the bottom of the column, increasing reactant availability.

The distribution of the reaction through the column is optimized with our approach and we noticed that the reactive trays are mainly located near the feeds, either near or below the liquid feeds or above the vapor ones. The availability of fresh reactant in the liquid phase explains why this occurs. For smaller columns only one vapor feed is usually assigned for low holdup values. For larger columns two or more feeds, typically a combination of vapor in the

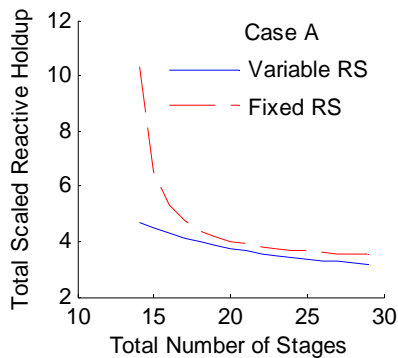


Figure 1 – Pareto solutions: RH vs. NS. Comparison with variable RS case

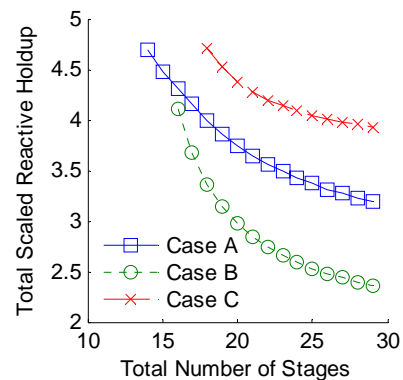


Figure 2 – Pareto solutions: RH vs. NS

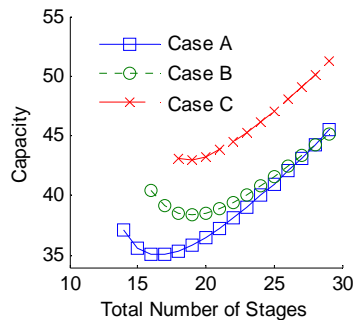


Figure 3 – Pareto solutions: Capacity vs. NS

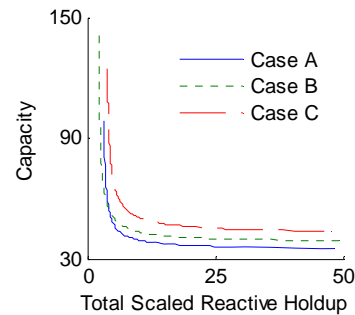


Figure 4 – Pareto solutions: Capacity vs. RH

bottom and liquid in the top, are favored. As RH increases and capacity decreases, the feed quality moves away from the specified boundaries ( $\pm 2$ ). That is, typically, solutions with low holdup (high capacity) have superheated and subcooled feeds while high holdup (low capacity) solutions have moderately heated feed.

#### 4.2. Detailed simulations using Aspen Plus

A selected number of obtained cases located at the Pareto front were used to initialize simulations in Aspen Plus employing the RadFrac model and an Ideal property method. The values for NS, S, distillate to feed ratio, location and quality of the feeds and reactive holdup distribution specifications, were taken from the optimization results. The feed quality specification was modeled using a design specification to look for the feed temperature that resulted in the adequate change in the internal liquid flow. Using the optimization results to initialize Aspen Plus models resulted in readily converging solution indicating that the approach is capable of identifying feasible design alternatives for more detailed cost studies. The resulting composition profiles were close to the ones reported in the optimization method, and product purity specifications were typically met or exceeded.

To investigate simplifications on the reaction and feed distributions and also to analyze the sensitivity of the solution, further refinements were attempted. For a selected number of optimal designs, the holdup values at each tray were thus adjusted in an attempt for further improvement in capacity and/or purity. As said before, most of the reaction occurs near the liquid feed stage, so the trays in its vicinity were chosen to place the catalyst using different and more manageable distribution strategies. Equal amounts were placed over a reduced NS surrounding the feed stage while holding constant the total RH. For a single feed case with  $q = -0.4$  only slight changes in the capacity and product purity were noticed. Moving the reactive zone up in the column by 1 or 2 trays had no significant effect while moving it down decreased product purity. The reactant is fed as vapor so it moves up in the column. Similarly, for a case with two

combined feeds, the product purity decreases when the reactive zone is moved up in the liquid feed vicinity.

The location of the energy supply was also checked for this single feed configuration. Feed quality was changed from -0.4 to 0 (saturated vapor) and the remaining required energy was supplied through the reboiler. Two alternatives for catalyst placement were tested: the configuration reported in the optimization step and a new one where the catalyst was equally distributed between the feed tray and the 4 surrounding trays. For both cases, a reduction of approximately 11% in total energy requirements was noticed while capacity suffered a reduction of 9%. As mentioned before, the use of superheated and subcooled feeds reduces the requirements for RH and this can also be seen in these results. There is a decrease in the purity when  $q$  changes to zero, suggesting that a higher RH would be required to achieve the same conversion. The effect of increasing RH was investigated and we concluded that an increase of 25% is required to maintain product purity when  $q$  changes from -0.4 to 0, i.e. to the point where the feed is no longer superheated.

## 5. Conclusions

The interactions between feed quality, total NS and RH were analyzed in this work. The effectiveness of manipulating the feed quality to override limitations in the RH was demonstrated. This feature can be advantageous when more reaction turnover is required and RH cannot be increased or when catalyst activity has decreased, preventing its earlier replacement.

The data from the optimization approach was successfully used to initialize Aspen Plus models. Based on our previous experience, the importance of the availability of these results as a starting point for Aspen Plus simulations should be emphasized as they greatly facilitate the initialization of the simulations, providing near optimal solutions for further investigation.

Based on the insights gained from the designs reported, more functional arrangements for catalyst were successfully tested and guidelines for catalyst distribution established for this system.

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