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A New Operation Mode for Reactive Batch Distillation in Middle Vessel Columns: Start-up and Operation

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Abstract

The most outstanding feature of batch distillation is its flexibility in design and operation. In particular, when chemical reactions and physical separations have some overlapping operating conditions the combination of these tasks can offer significant benefits. In this work, we propose a new operation mode for reactive batch distillation in middle vessel columns. The special feature of this novel operation mode lies on the fact that depending on the characteristics of the reaction mixture, the reaction will also take place either along the upper column or along the lower column. The performance of the novel operation mode is demonstrated through rigorous simulation of two industrial reactive batch distillation processes. Furthermore, since the performance of the start-up procedure has a large impact on the entire reactive batch distillation process, we also focus on the description of the dynamic behavior of the start-up operation starting from the cold and empty batch columns as the initial state. The proposed model includes both equation and variable discontinuity. Thus, we propose in this work a modeling approach to describe the state transitions during the start-up phase. To show its efficiency, the developed approach has been applied to the start-up operation simulation of different batch distillation column configurations with overlapping chemical reactions. Due to the reliable initial state, the developed models are employed for model based optimization and control.

Keywords: start-up modeling, reactive batch distillation, middle vessel column.

1. Introduction

Batch distillation is used in chemical, food, and pharmaceutical industries where flexibility is needed. This operational flexibility of batch distillation columns makes them particularly suitable for smaller amounts of products with high added value, multi-product or multi-purpose operations. Moreover, when chemical reactions and thermal separation have some overlapping operating conditions, the combination of these tasks can, in particular, offer considerable benefits. These benefits may involve: avoidance of reaction equilibrium restrictions, higher conversion, selectivity, yield, removal of side reactions and recycling streams, circumvention of non-reactive azeotropes. Although there is an intensive literature on batch distillation, relatively little has been published on reactive batch distillation. In the conventional reactive batch distillation column, the feed is charge into a large reboiler or reactor at the bottom of the rectifying column. The order of appearance of the components in the distillate is determined by the phase equilibrium characteristics of the mixture. At the end of the separation the content in the column will drain down into the still and a residual bottom fraction may be a remaining product. This is particularly appropriate when one of the reaction products has a lower boiling point than the other products and reactants. When all reaction products have

higher boiling temperatures, the inverted reactive batch distillation will be more suitable. There are, however, disadvantages associated with the use of a conventional reactive batch rectifier or batch stripper. A combination of these configurations is described as the middle-vessel batch reactive column. The feed mixture is loaded into the middle vessel, where the reaction take place, between the two separation sections, and the products are simultaneously obtained from the top and the bottom of the column reducing the way of separation and pushing the reaction further to the product side. Due to the two product streams, a middle-vessel batch reactive column shows superior performance to a typical or inverted batch distillation process, where distillate cuts of the light and intermediate products are taken sequentially. On the other hand, there are, in fact, some reaction systems (transesterifications or esterifications) where none of these batch column configurations are either suitable or can be used economically to improve the rate of conversion, yield and efficiency. Complications usually arise due to the existence of azeotropes or due to the risk of cracking occurrence (e.g. in esters). To overcome these difficulties, a new operation mode for reactive batch distillation in middle vessel columns is proposed with which the efficiency of reactive batch distillation can be improved, e.g., less batch time and energy consumption, less off-spec products, and more product amount.

2. A New Operation Mode for Reactive Batch Distillation

For equilibrium-limited reactions such as transesterifications, it has been demonstrated that conducting reaction and distillation simultaneously allows reaction to overcome the limitations of distillation and to bring reactions to complete conversion of the reactants because the products are continuously removed from the reaction zone. Furthermore, an excess of one educt can be used to shift the reaction towards the product side resulting in a semibatch operation mode. To illustrate the new operation mode, we firstly consider a generic reversible reaction of the form B+C<->A+D representing A and D the components with the lowest and highest boiling point, respectively. In the conventional reactive (or middle vessel) batch distillation column the relative volatilities of the reactants and the products should be such that the products can be removed from the reactor i.e. the reaction zone (middle vessel) easily while the reactants remain in the reactor or they will be shifted back to the middle vessel through thermal separation both in the upper column and the lower column such that they (B, C) meet again in the middle vessel (Fig. 1). In this way, the conversion and selectivity can be increased.

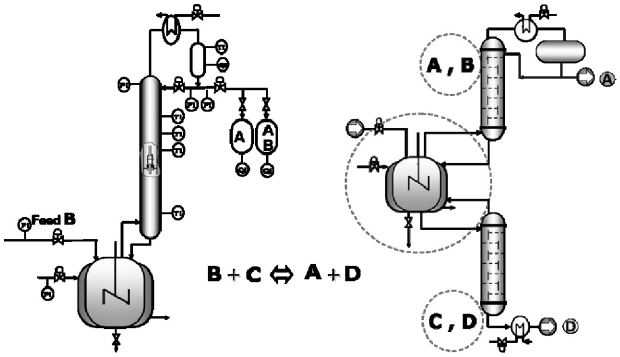

Figure 1. Reactive batch distillation in a batch rectifier and a middle vessel column.

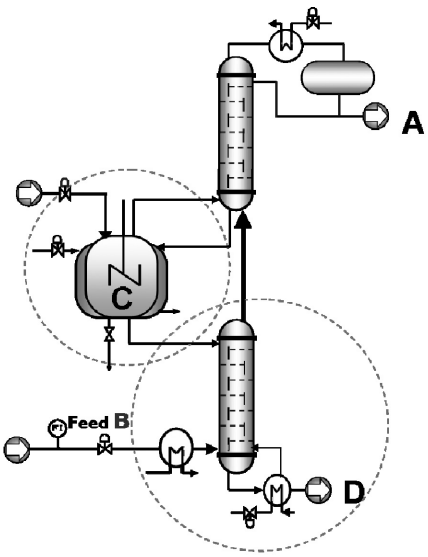

Figure 2. The new operation mode for reactive batch distillation in middle vessel columns.

However, for the industrially relevant and for this work exemplary selected transesterification reaction, which can be described as follows:
educt alcohol (B) + *educt ester* (C) <-> *product alcohol* (A) + *product ester* (D)
isopropanol + methyl myristate <-> methanol + isopropyl myristate, the middle vessel configuration depicted in Fig. 1 can not be used so easily. Both alcohols could, indeed, be separated thermally in the upper column, but in the lower column is not possible to separate the esters due to the risk of cracking. For other reaction systems could be the problem that azeotropes appear. To overcome these problems, the reaction will be displaced to the entire lower column such that the increase of the column temperature will be limited by the chemical equilibrium. For this purpose, the complete middle vessel configuration will be operated in semibatch mode where the excess of educt alcohol (heated steam) will be supplied to the reboiler of the lower column, and the most volatile components (both alcohols) will be evaporated out of the lower column towards the upper column through a vapor bypass configuration during the batch (Fig. 2). Generally speaking, the special feature of the novel operation model lies on the fact that depending on the characteristics of the reaction mixture, the reaction could take place not only in the middle vessel (or reactor) but also along the upper column or along the lower column. In the former case, the reaction will be enhanced by adding one of the educts into the top of the upper column, and a liquid by-pass configuration connecting both columns. In the latter, as stated before, the educt will be supplied to the reboiler of the lower column (Fig. 2).
Another interesting feature of the new operation mode is the possibility of performing those reaction/distillation systems with a low tonnage, which are not suitable to be operated continuously, but at the same time too large charge for a batch process. For this purpose, the flow rates of the educt streams in the new configuration (for instance: C into the middle vessel and B to reboiler, see Fig. 2) will change periodically from continuous to discontinuos mode. Concerning this point, the production of dimethyl ether will be presented as a further case study. To simulate the new operation mode in both case studies, a dynamic rigorous detailed model is used. Comparisons with their conventional operation clearly indicate the improvement by the new operation mode.

3. A Modelling Approach for the Start-up of Reactive Batch Columns

An inherent characteristic of batch distillation is that a batch column will frequently be started up from a cold and empty state. Moreover, the amount, composition as well as nature of the components in the initial charge may be variable from batch to batch. Furthermore, due to the overlapping reaction the states variables will constantly change from the very beginning i.e. the use of conventional modeling strategies like a pseudo-warm state or total reflux will not provide a reliable initial state (but may be a model consistent initial state). Therefore, modelling and simulation of the reactive batch distillation start-up operation from the cold and empty batch columns as the initial state plays an important role in the optimal design and operation of such processes.

Owing to the dynamic nature, initialization of such a system is a challenging problem. Thus, we propose in this work a hybrid modeling approach to describe the state transitions during the start-up phase. The proposed model includes both equation and variable discontinuity. To show its efficiency, the developed approach has been applied to the start-up operation simulation of different batch distillation column configurations with overlapping chemical reactions (conventional, inverted, middle vessel batch configurations). A detailed tray-by-tray model for each operation mode has been developed. The total equation system consists of mass balance, energy balance, vapour-liquid equilibrium relations and tray hydraulics. The tray hydraulics is related to the geometry of the trays and essential for computing the pressure drop and hold-up of each tray. The reaction kinetics is added to the model to depict the reaction both in the middle-vessel and the corresponding batch column. During the start-up phase each tray will be described from a non-equilibrium phase, in which only mass and energy transfer are taking place, to an equilibrium phase in which the vapour-liquid equilibrium is held (Wang et al., 2003). The switching point between these two phases is decided by the relationship of bubble point temperature at the operating pressure. The equilibrium state is attained tray by tray either from bottom to top of the column or vice versa, whereas the liquid hold-up of each tray is mainly filled due to the reflux flow. Figure 3 shows the state transition of the trays in the upper and lower batch columns during start-up. Accordingly, at certain time point, a tray may be at the state of empty (EM), liquid accumulation (LA1 or LA2) or vapour-liquid equilibrium (VLE). The new operation mode involves both start-up approaches: upwards and downwards (Fig. 3). However, the outcomes evidently show the efficiency of the start-up approach to describe the dynamic behaviour during the start-up from the cold and empty state. From this issue, some useful start-up heuristics/strategies could be derived and compared.

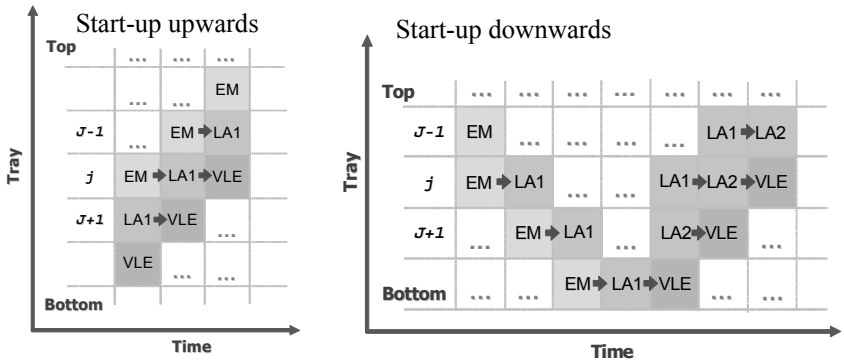

Figure 3. State transition of the trays during the start-up.

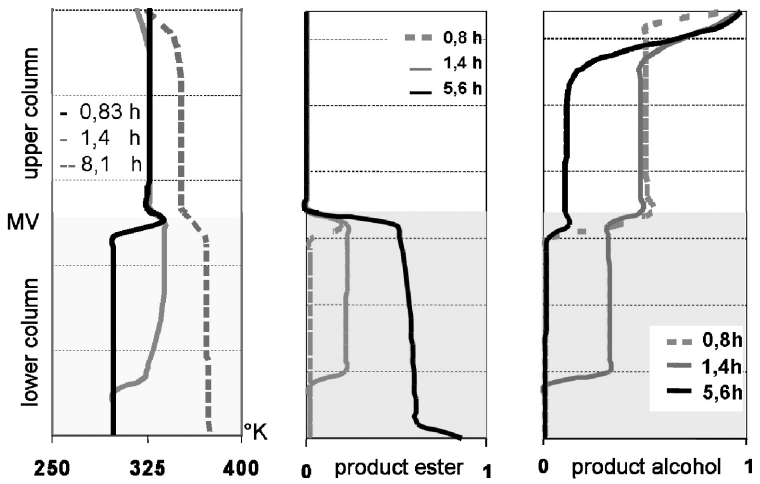

Figure 4. Temperature and product concentration profiles during the batch.

In Fig. 4 the simulated temperature and product concentration profiles along both column sections are presented. It shows the changes of the state variables at different time points during the batch including the start-up phase. In this work, different start-up strategies have been investigated for the transesterification process operated with the new operation mode. The strategies differ in the time point when to start up both batch columns. They are summarized as follows: a) after the VLE is achieved in the middle vessel, the upper column will get started and the downstream valve to the lower column will not be opened until the whole upper column has been stabilized; b) both the reflux ratio valve of the upper column and the downstream valve will be opened simultaneously; c) shortly after the vapor from the middle vessel (or reactor) arrive at the bottom of the upper column, the downstream valve to the lower column will then be opened. However, with the proposed simulation approach from the cold and empty state, all strategies were squarely evaluated. It could be proven that depending on the reaction system and the purity requirements, one start-up strategy can perform better than the other. For the slightly endothermic tranesterification is the strategie a) according to the results to be presented the most appropriate. Figure 4 shows also that the product alcohol is enhanced by the reaction taking place along the lower column. The conversion of product ester increases towards the reboiler of the lower column.

4. Operational Aspects of the New Operation Mode

In this work, rigourous simulation comprising the start-up phase is applied to conduct a dynamic analysis and to develope rough optimal policies for both batch process case studies complying with the equality constraints of the detailed model equations and the production constraints, which include product purity specifications and the physical restrictions considering all operational decision variables. For the new operation mode, a wide variety of degrees of freedom such as reflux ratio (upper column), downstream flow rate from middle vessel to the lower column, feed rate into the lower column, heat supply both in the middle vessel (or reactor) and in the lower column reboiler, and/or the boil up rate were considered. Computation results of applying this operation mode to two industrial reactive batch processes show significant improvements of operation efficiency in comparison to the conventional operation modes on industrial site.

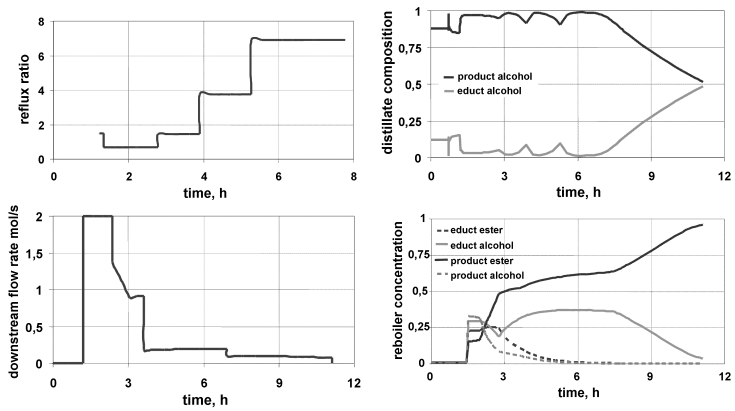

Figure 5 shows the developed operating policies for the transesterification process as well as the corresponding composition profiles. A slow increase of the reflux ratio in the first 4 hours is allowed, since a large amount of product alcohol results from the increase of the downstream flow rate. However, the increase of the reflux ratio in the upper column is required in order to fulfill the distillate purity requirements. The drastic decrease of the downstream flow rate can be explained by the time delay between the fill up of the lower column during the start-up and the feed supply of educt alcohol. Further on, the educt alcohol is also restricted to a certain amount. Figure 5 also shows the instantaneous values of the distillate composition as well as the time-dependent changes of the lower column reboiler concentration. However, high purity specifications of both product alcohol and product ester can be achieved.

5. Concluding Remarks

A new operation mode for reactive batch distillation in middle vessel columns is proposed. Its performance is studied through simulation of two industrial reactive batch distillation processes. Comparisons between the operation modes with respect to the total batch time, the total amount of required energy and the profit of a batch run provide evidence of the advantage using the new operation mode. However, with the proposed operation mode, the benefits of reactive distillation (driving reactions to the product side, azeotrope breaking, and the potential reduction of costs, etc) can be added to those of the batch operation and its flexibility. Furthermore, an efficient modelling approach for the start-up of reactive batch columns starting from the cold and empty state is also proposed. Based on the reaction system, different start-up strategies are derived. Moreover, due to the reliable initial state, the developed models are currently employed for model based optimization and control. Conceptual designs concerning the application of the new operation mode to other relevant complex reaction systems will be introduced.

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