Chemical Engineering and Processing 79 (2014) 56–68

Contents lists available at ScienceDirect

Chemical Engineering and Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep

A reactive distillation column with double reactive sections for the separations of two-stage consecutive reversible reactions

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ARTICLE INFO

Article history:
Received 30 October 2013
Received in revised form 11 February 2014
Accepted 10 March 2014
Available online 15 March 2014

Keywords:
Reactive distillation column
Double reactive sections
Internal mass integration
Internal energy integration
Process design

ABSTRACT

In this paper, a novel reactive distillation column with double reactive sections (RDC-DRS) is proposed for the separations of two-stage consecutive reversible reactions. The arrangement of two reactive sections not only allows the careful coordination of the two reaction operations involved, but also provides additional degrees of freedom for the reinforcement of internal mass integration and/or internal energy integration between the reaction operations and the separation operation involved, which could facilitate the RDC-DRS to be more advantageous than the conventional reactive distillation column with a single reactive section (RDC-SRS) in operating cost and capital investment. A representative hypothetical and real two-stage consecutive reversible reactions are chosen to evaluate the steady-state performance of the RDC-DRS. With the constraints of the same total number of stages and the same total number of reactive stages, the RDC-DRS is demonstrated to require less utility consumption than the RDC-SRS and this outcome indicates that the former could be a competitive alternative to the latter in the separations of the two-stage consecutive reversible reactions. The number of reactive sections should therefore be viewed as an important decision variable for the synthesis and design of reactive distillation columns especially in the separations of complicated reacting mixtures involving multiple reversible reactions.

1. Introduction

Generally speaking, reactive distillation columns can work effectively for the separations of three types of reactions, which include: (i) simple reversible reaction, (ii) parallel reversible reactions, and (iii) two-stage consecutive reversible reactions [1–3]. The first type of reactions involves most of the esterifications, etherifications, and hydrations and takes primarily the forms as $A+B \leftrightarrow C+D$, $A+B \leftrightarrow C$, or $A \leftrightarrow B+C$. The second type of reactions frequently occurs in etherifications and acetalizations and takes generally the forms as $A+B \leftrightarrow C$ and $2A \leftrightarrow D$ or $A+B \leftrightarrow D$ and $A+C \leftrightarrow E$. The third type of reactions is widely found in esterifications, acetalizations, trans-esterifications, aminations and takes generally the forms as $A+B \leftrightarrow C+D$ and $C+B \leftrightarrow E+D$ or $A+B \leftrightarrow C$ and $C+B \leftrightarrow D$. Regarding the separations of the first two types of reactions, there have already been a great number of patents and papers published on the application of reactive distillation columns, covering process synthesis and design [4,5], process modeling and analysis [6,7], and process dynamics and operation [8,9]. For the separations of the third type of reactions, however, only a few studies have been reported so far. With the aid of the residue curve maps, Ung and Doherty [10,11] indicated the feasibility of employing reactive distillation columns to the separations of reacting mixtures involving multiple reversible reactions. Thotla and Mahajani [12,13] demonstrated that through effective process design the selectivity of the two-stage consecutive reversible reactions could be substantially enhanced with the application of reactive distillation columns. They further pointed out that for the two-stage consecutive esterification of ethylene glycol with acetic acid it was even likely to approach 100% selectivity with 1,2-dichloro ethane chosen as entrainer. Hung et al. [2] derived a novel flowsheet involving both reactive and conventional distillation columns for the separations of two similar two-stage consecutive reversible reactions, i.e., the esterifications of adipic acid and glutaric acid,

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Abbreviations: DEC, diethyl carbonate; DMC, dimethyl carbonate; EMC, ethylmethyl carbonate; ETOH, ethanol; FL-A, feed location of A; FL-B1, feed location of B1; FL-B2, feed location of B2; FSR, feed splitting ratio of the common reactant to the first and second stage reactions involved; MEOH, methanol; N_m, number of stages between the upper and lower reactive sections; N_{rec}, number of stages in the rectifying section; N_{rs1}, number of stages in the upper reactive section; N_{rs2}, number of stages in the lower reactive section; N_s, number of stages in the stripping section; *NT*, total number of stages in a reactive distillation column; RDC-DRS, reactive distillation column with double reactive sections; RDC-SRS, reactive distillation column with a single reactive section; RDC-SRSFS, reactive distillation column with a single reactive section and a feed split of one of the two reactants; R_n, *n*th stage reaction.

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http://dx.doi.org/10.1016/j.cep.2014.03.003
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respectively, with methanol. Recently, Mueller and Kenig [14] proposed to use a reactive dividing-wall distillation column packed with potassium carbonate as heterogeneous catalyst for the separation of the two-stage consecutive trans-esterification of dimethyl carbonate with ethanol, however, Luo et al. [15] and Wei et al. [16] found, respectively, that a simple reactive distillation column could still do a good job. In terms of a homogeneous catalyst of sodium ethoxide, Keller et al. [17,18] conducted the separation of this reacting mixture with a pilot-scale reactive distillation column and developed further an evolutionary algorithm to maximize its product selectivity. It should be noted here that almost all of the studies performed so far had employed a reactive distillation column with a single reactive section (RDC-SRS) for the separations of the two-stage consecutive reversible reactions. Since a high conversion and a high selectivity are much more difficult to be reached simultaneously in this kind of reactions than in the first two types of reactions, the RDC-SRS might not always be a good design option. Therefore, a different configuration of reactive distillation columns is worth exploring for the separations of the two-stage consecutive reversible reactions and in this work a novel reactive distillation column with double reactive sections (RDC-DRS) is proposed and to be evaluated.

Despite the fact that the RDC-DRS might not be a completely new idea, it has rarely been studied up to now. To the best of our knowledge, Tung and Yu [19] were known to firstly recommend using a RDC-DRS for the separations of quaternary reacting mixtures with the most unfavorable relative volatilities (i.e., the two reactants are the lightest and heaviest components and the two products are the light and heavy ones). Their RDC-DRS was characterized by a special configuration, in which the two reactive sections were arranged, respectively, in the top and bottom (including the top condenser and bottom reboiler as well) in order to cater to the thermodynamic behaviors of the reacting mixtures separated. Sundmacher et al. [20,21] once mentioned that a reactive distillation column with multiple reactive sections might be favorable for the indirect hydration of cyclohexene to cyclohexanol with formic acid as reactive entrainer. They, however, presented no further outcomes on process synthesis, design and operation. Since the RDC-DRS involves more degrees of freedom (e.g., the number of reactive stages in either reactive section and the number of stages between the two reactive sections) for process synthesis and design than the RDC-SRS, it is quite likely that it holds relatively high potential for the reinforcement of internal mass integration and/or internal energy integration between the reaction operations and the separation operation involved [22]. As a result, a substantial improvement is likely to be secured in steady-state performance.

In this work, a novel reactive distillation column with double reactive sections, i.e., the RDC-DRS, is proposed for the separations of the two-stage consecutive reversible reactions. In contrast to the RDC-SRS, the RDC-DRS features two separate reactive sections, which could provide additional degrees of freedom for the coordination of the two reaction operations involved as well as the reinforcement of internal mass integration and/or internal energy integration between the reaction operations and the separation operation involved. Two examples, including the separations of the representative hypothetical ideal two-stage consecutive reversible reactions, $A+B \leftrightarrow C+D$ and $C+B \leftrightarrow E+D$, and the two-stage consecutive trans-esterification of dimethyl carbonate with ethanol, are chosen as illustrative examples to evaluate the steady-state performance of the RDC-DRS. In terms of thorough comparison between the RDC-SRS and the RDC-DRS, the potential advantages of arranging two reactive sections in reactive distillation columns are highlighted. Possible extension to the arrangement of multiple reactive sections in reactive distillation columns is also discussed and some concluding remarks are summarized in the last section of the article.

2. Principle, configuration, and design of the RDC-DRS

For the two-stage consecutive reversible reactions: $A+B \leftrightarrow C+D$ and $C+B \leftrightarrow E+D$, the intermediate product C acts, respectively, as a product in the first stage reaction and a reactant in the second stage reaction. Based on the Le Chatelier's principle, one can readily understand that while a low concentration of the intermediate product C favors the first stage reaction, a high concentration of the intermediate product C favors the second stage reaction. Thus, an intricate coordination problem exists between the first and second stage reactions and must be carefully tackled during process synthesis and design. It should be stressed here that if the coordination problem has not been well resolved either a low conversion rate or a low selectivity can be aroused for this kind of two-stage consecutive reversible reactions. The unbalance may further affect adversely internal mass integration and/or internal energy integration between the reaction operations and the separation operation involved. These represent essentially the unique characteristics of the separations of the two-stage consecutive reversible reactions with reactive distillation columns. For the RDC-SRS as shown in Fig. 1a, owing to the availability of only one reactive section, it is likely that a satisfactory coordination cannot be fully achieved between the first and second stage reactions and this will inevitably deteriorate internal mass integration between the reaction operations and the separation operation involved. Furthermore, if the first and/or second stage reactions involved accompany thermal heat, then internal energy integration should be carefully considered between the reaction operations and the separation operation involved. In this aspect, the availability of only one reactive section in the RDC-SRS might still be a hindrance for the improvement of system performance.

In the case of the RDC-DRS as shown in Fig. 1b, the situation could be quite different from that of the RDC-SRS. The arrangement of two reactive sections renders the RDC-DRS with more degrees of freedom than the RDC-SRS and these include the number of stages in the upper or lower reactive section, the number of stages between the upper and lower reactive sections, the feed splitting ratio of the common reactant to the first and second stage reactions involved, and the feed location of B1 or B2. These additional degrees of freedom allow not only a careful coordination between the first and second stage reactions but also the reinforcement of internal mass integration and/or internal energy integration between the reaction operations and the separation operation involved. As a result, a substantial enhancement could be expected in steady-state performance from the RDC-SRS to the RDC-DRS. For example, while the first stage reaction occurs dominantly in the upper reactive section, the second stage reaction proceeds primarily in the lower reactive section (indicated here with the shadowed areas). Thus, a deliberate compromise between the two reaction operations involved could be permitted with the adjustment of the number of reactive stages in the upper and lower reactive sections and the number of stages between the two reactive sections.

During the synthesis and design of the RDC-DRS, the variables to be determined can generally be classified into two broad categories: structural design variables and operating design variables. While the structural design variables include the number of stages in the rectifying section (N_{rec}), the number of stages in the stripping section (N_s), the number of stages in the upper reactive section (N_{rs1}), the number of stages in the lower reactive section (N_{rs2}), the number of stages between the upper and lower reactive sections (N_m), the feed location of B1 (FL-B1), the feed location of B2 (FL-B2), and the feed location of A (FL-A), the operating design variables include the total amount of catalyst, the feed splitting ratio of the common reactant to the first and second stage reactions involved (FSR), the reflux flow rate, and the reboiler heat duty. Since the structural design variables are in nature discontinuous, the