

CONCEPTUAL DESIGN OF REACTIVE DIVIDING WALL COLUMNS

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Economic and environmental reasons have led to process intensification in the process industries. Reactive distillation is the most prominent example. The integration of further separation steps with a reactive distillation column leads to a highly integrated process: a reactive dividing wall column. Within one apparatus, more than two products can be obtained and the capital cost can be reduced drastically. Furthermore, the well-known reduction in energy demand for dividing wall columns compared to a sequence of conventional distillation columns can lead to reduced operating costs. However, the simulation, design and operation of such complex columns is complicated. A novel approach for the conceptual design of reactive dividing wall columns is presented in this work. The methodology is based on the graphically-based boundary value method (BVM). Chemical equilibrium is assumed on every reactive stage of the column. Four component systems with one reaction are considered in this work.

KEYWORDS: reactive distillation, conceptual design, integrated processes, boundary value method

INTRODUCTION

The simulation, design and modelling of reactive dividing wall columns is still a comparatively new research area. Kaibel and Miller (2005) proposed the reactive dividing wall column as one of the new possible application areas for dividing wall columns. Mueller *et al.* (2004) presented a rate-based model for reactive dividing wall columns and showed corresponding simulation results. In contrast, considerable work has been carried out on the design of reactive distillation columns and non-reactive dividing wall columns. However, for the most complex reactive dividing wall column no such conceptual design methods exist.

REACTIVE DISTILLATION DESIGN

To exploit the potential of reactive distillation, methods have been developed for preliminary process design. Two major approaches exist for the generation of alternatives for a given reaction-separation problem: mathematical optimisation and graphically-based conceptual design methods. Mathematical optimisation methods are generally very powerful

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for generating and evaluating design alternatives (Ciric and Gu, 1994, Jackson and Grossmann, 2001, Sand *et al.*, 2005). However, they do not provide valuable and necessary insights into the process and are generally computationally intensive. Graphically-based methods overcome this problem (Ung and Doherty, 1995, Espinosa *et al.*, 1996, Hoffmaster and Hauan, 2004). Recently, Dragomir *et al.* (2004) presented a methodology for reactive distillation columns based on a boundary value method (BVM), which generates multiple designs without highly iterative procedures.

DESIGN OF THE NON-REACTIVE DIVIDING WALL COLUMNS (DWCs)

The initial design of thermally coupled columns is often based on shortcut methods (e.g. Halvorsen and Skogestad, 2004). The Fenske-Underwood-Gilliland shortcut design techniques are usually used to estimate the number of stages and minimum reflux ratios, in conjunction with the Kirkbride correlation to determine the location of the feed stage. Several authors have been used these techniques for process screening and to obtain reliable initialisation for the rigorous simulation (Cerdeja and Westerberg, 1981, Fidkowski and Krolikowski, 1987, Nikolaides and Malone, 1987, Triantafyllou and Smith, 1992). However, some common assumptions associated with shortcut methods, such as sharp separations, constant molar overflow and constant relative volatility limit their applicability. Some more rigorous approaches, such as that of Duennebieber and Pantelides (1999), in conjunction with mathematical programming, allow more accurate results to be obtained, at the expense of computing time.

Amminudin *et al.* (2001) introduced a new shortcut method for the design of thermally coupled distillation columns, using a semi-rigorous approach, which has been applied previously for azeotropic systems (Thong and Jobson, 2001). The method is based on a boundary value method and starts from given product compositions and works backwards to establish the design parameters. The proposed approach by Amminudin *et al.* (2001) is based on decomposing the dividing wall column into the prefractionator and the main column where the main column is further decomposed into two columns with a hypothetical reboiler for the top column and a hypothetical condenser for the bottom column. The design procedure uses the intersection of composition profiles to obtain an initial design for each column. The vapour flowrates of the hypothetical reboiler and condenser are then constrained to be equal. However, to insure a continuous profile in the main column the compositions of the streams at the bottom of the top column and at the top of the bottom column have to coincide. This is not ensured in the proposed approach. Moreover, in the case of non-ideal systems involving azeotropes, the decomposition of the main column into the two columns is not always possible.

In this work, a novel approach for the conceptual design of reactive dividing wall columns is presented. The methodology is based on the BVM where chemical equilibrium is assumed on every reactive stage of the reactive column. The methodology generates several designs for reactive dividing wall columns. A cost function is used to rank the feasible designs. The methodology will be illustrated for the hydrolysis of methyl acetate.

CONCEPTUAL DESIGN OF REACTIVE DIVIDING WALL COLUMNS (RDWCs)

For a RDWC, where three or more products are to be obtained, similar considerations to non-reactive DWCs apply. However, the design of a RDWC is more complex, as a reactive section has to be considered. Therefore various configurations can be obtained depending on the location of the reactive section in the prefractionator. Various decisions have to be made for the design of the reactive section and non-reactive section of the column and the thermally coupled streams between them. Thus there are many degrees of freedom for the design of a reactive dividing wall column, as illustrated in Figure 1.

DESIGN PROCEDURE FOR REACTIVE DIVIDING WALL COLUMNS

For the design of the dividing wall column considered in this work, the column is decomposed as illustrated in Figure 3. The dividing wall column will be represented using a prefractionator and a thermally coupled main column. The main column is then further decomposed into the rectifying and stripping sections. The prefractionator can have one or more feeds. To design the reactive DWC, a combination of the boundary value method for non-reactive columns for the main column and for reactive columns as presented by Dragomir (2004) is proposed. The reactive section is considered to be confined to the prefractionator and the main column is used to separate the reaction products.

The following specifications have to be chosen. For the prefractionator arrangement, the compositions of net feeds to the main column, $x_{Pseudo1}$ and $x_{Pseudo2}$ are used as specified product compositions and correspond to the distillate and bottom product of the prefractionator (see Figures 2 and 3). The ratios D/F_{Pseudo} and B/F_{Pseudo} are specified. The pseudo feed flowrate F_{Pseudo} is defined as the sum of the prefractionator product

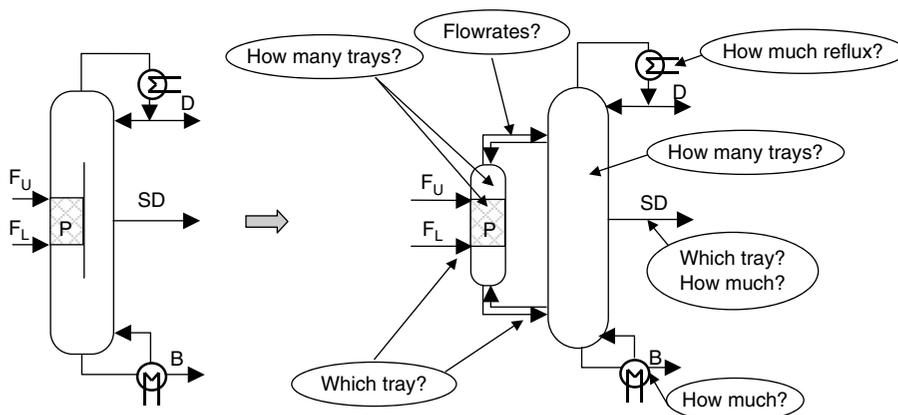


Figure 1. Decomposition and design specifications for a reactive dividing wall column with two feeds and one side-draw

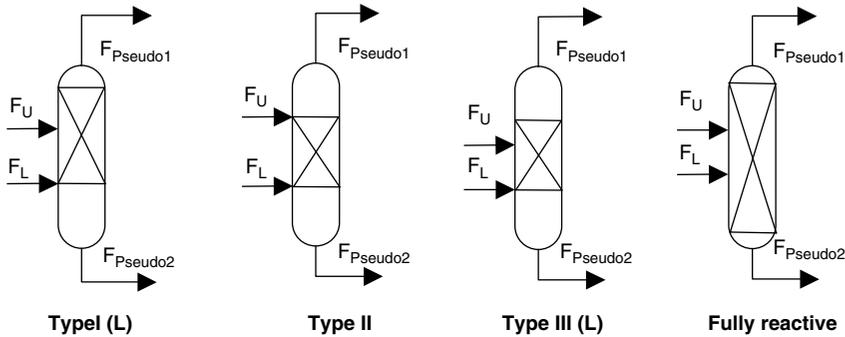


Figure 2. Alternative configurations for a double-feed reactive prefractionator (L – the lower feed is specified; configurations where the upper feed is specified are not shown)

flowrates ($F_{Pseudo} = F_{Pseudo1} + F_{Pseudo2}$). Finally a reaction extent and the split ratio f ($f = F_{Pseudo1}/(F_U + F_L)$) are specified.

Prefractionator design

The methodology to design the reactive column is similar to the methodology developed for double-feed reactive columns (Dragomir, 2004). Feasible designs are obtained by the

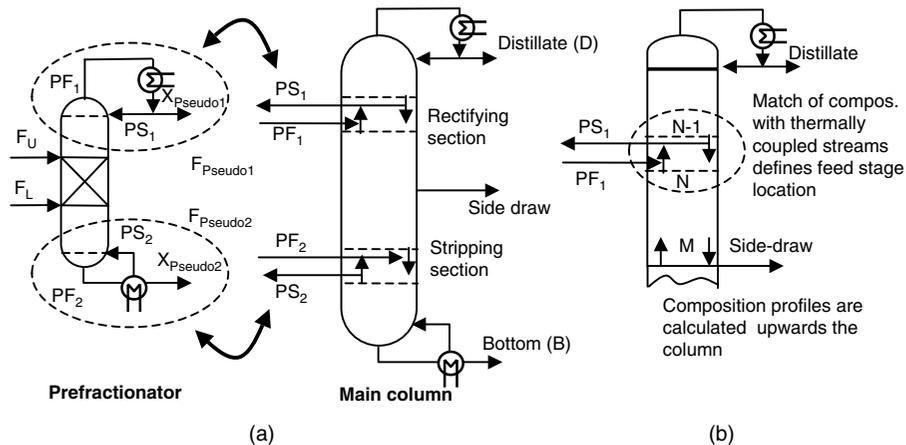


Figure 3. Design of the main column: (a) use of streams from the prefractionator column as thermally coupled streams (b) calculation of feed stage location and composition profiles of the main column

use of the BVM. Thus the intersection between composition profiles calculated from the specified prefractionator products are used to identify the design details. Multiple designs can be obtained, of various configurations: fully reactive columns or hybrid columns with the reactive section located at different positions in the column as shown in Figure 2.

Main column design

To identify designs for the main column a continuous profile throughout the column has to be identified. An intersection search between the stripping and rectifying profiles has to be performed. Since for BVMs the profiles inside the column are highly sensitive to the trace component composition in the products the chances of identifying an intersection between two lines in 3-dimensional space are very slim.

To handle this problem for the main column design two of the distillate, bottom product and side draw product are completely specified. For the other one a product region is defined. The product region is constructed from a set of product compositions with constant mole fraction for the dominating component (Thong and Jobson, 2001). This concept can only be used for nearly pure product streams. This highly increases the probability to find designs for the main column and leads to a much more robust design procedure. In the remainder of the paper we assume that for the side draw product a product region can be defined.

The streams from the prefractionator column are used as thermally coupled streams to the main column. The overhead vapour is used as the upper feed to the main column and the liquid stream leaving the first stage of the prefractionator is used as a side-draw (Figure 3). Similarly, the streams entering and leaving the reboiler of the prefractionator are used as thermally coupled streams in the stripping section of the main column as shown in Figure 3.

For the stripping section of the main column, composition profiles are calculated for a range of boil-up ratios starting from the specified bottom product. Thermally coupled columns, such as dividing wall columns, are thermodynamically efficient as re-mixing effects are eliminated when the composition of the liquid feed to the main column is nearly equal to the composition of the stream on the feed stage (Petlyuk *et al.*, 1965, Schultz *et al.*, 2002).

In order to capture this behaviour, the composition profiles are checked against the thermally coupled streams. The stages where the compositions of the stripping profile and the thermally coupled streams from the prefractionator design match are identified as feed and side-draw stage locations.

The stripping profiles are further calculated from the identified feed stage location until the side draw composition region for the main column is reached. Now composition profiles are calculated from all corner points of the defined product region for the side draw product upwards the column. An energy balance around the complete column is used to calculate the reflux ratio corresponding to the identified reboil ratio. For this reflux ratio the composition profile is calculated downwards the column. A check against the thermally coupled stream composition is also here used to identify promising feed stages. Starting from the feed stages identified the profiles are calculated downwards the

column. Finally an intersection search between the rectifying profiles and the stripping profiles is carried out. An intersection guarantees a continuous profile throughout the column. A cost function including capital and operating costs is used to rank the designs found.

Overall design procedure

The overall procedure to obtain feasible designs for a reactive dividing wall column is as follows:

1. Specify product compositions for distillate and bottom products and product region for the side draw.
2. Specify a range of reflux or reboil ratios for the main column as well as for the prefractionator.
3. Set a value for the split ratio in prefractionator (f), specify an initial value for the reaction extent and specify ratios D/F_{pseudo} and B/F_{pseudo} .
4. Specify the composition for one of the pseudo product streams ($X_{\text{Pseudo}1}$ or $X_{\text{Pseudo}2}$). The other stream can be obtained with mass balances around the prefractionator.

Prefractionator design

5. Generate designs for the prefractionator starting from the pseudo product streams.
6. Calculate the compositions and flowrates of the thermally coupled streams for these designs.

Main column design

7. For the stripping section, calculate composition profiles for a range of boil-up ratios starting from the specified bottom product composition. Check for the profiles for which the composition of the stream on a particular stage matches closely with the thermally coupled streams from the prefractionator design. This defines the stage locations for the thermally coupled streams.
8. Calculate the profiles starting from the identified stage locations until middle product composition region is reached.
9. Calculate the composition profiles starting from the corner points of the product region for the side draw product.
10. For the rectifying section, calculate composition profiles for the corresponding reflux ratios starting from the specified top product composition. Identify which profiles match the thermally coupled streams from the prefractionator and continue profile calculation down the column.
11. Search for intersections between the rectifying and stripping profiles.
12. Calculate total cost for the designs and sort them.

CASE STUDY: HYDROLYSIS OF METHYLACETATE

The case study to illustrate the synthesis and design procedure is the hydrolysis reaction of methyl acetate (MeAc) with water (H_2O) to methanol (MeOH) and acetic acid (AcAc).

Table 1. Specifications for the design procedure

Specification	Value
f	0.0305
D/F _{pseudo}	0.0733
B/F _{pseudo}	0.6128
Initial reaction extent [kmol/kmol feed]	0.0204

This system has been studied during the European Union project INSERT.



Since the chemical equilibrium for this reaction is far on the side of the reactants, an excess of water is fed to the column; complete conversion cannot be achieved. The hydrolysis of methyl acetate takes place in the prefractionator to give the methyl acetate-methanol azeotrope with traces of other components as a top product and a mixture of methanol, water and acetic acid as a bottom product. Further separation of the products take place in the main column, where the methyl acetate-methanol azeotrope is obtained as a top product, a high purity methanol stream is obtained as a side product and the remaining water and acetic acid are obtained as a bottom product. The bottom product stream is then further separated into acetic acid and water products.

The chemical equilibrium for the system is described with an equation presented by Poepken *et al.* (2000). The column is operated at 1 bar. For the calculation of all thermodynamic properties, an interface to Aspen PlusTM is used. The specifications for the design procedure are listed in Table 1. Table 2 lists the compositions and product regions for the three products of the reactive dividing wall column.

Multiple column designs of various configurations are obtained for these specifications. Table 3 shows the best 3 designs based on total annualised cost. In Table 3 NRM_p denotes the number of reactive middle stages in the prefractionator, NR_p denotes the number of non-reactive stages in the rectifying section of the prefractionator, NS_p

Table 2. Product specifications for the three products of the RDWC (mole fractions)

Component	Distillate	Middle product	Bottom product
Methanol	0.3347	0.96*	0.0050
Methyl acetate	0.6652	–	6.2e-08
Water	3.1e-06	–	0.7508
Acetic acid	5.3e-15	–	0.2442

*Product region

Table 3. Best 3 designs: details for the reactive prefractionator

No.	NR _p	NRM _p	NS _p	NT _p	QF _p
1	9	21	4	34	1
2	10	21	4	35	1
3	8	22	5	35	1

Table 4. Best 3 designs: details for the main column

No.	NR _{M1}	NS _{M1}	NR _{M2}	NS _{M2}	NT _M	R _M	S _M	Condenser duty [kW]	Reboiler duty [kW]	Total cost [10 ⁶ €/yr]
1	9	13	16	4	40	14.95	1.42	4507	4730	1.81
2	9	9	18	4	40	13.5	1.5	4604	4855	1.92
3	9	14	14	3	40	16	1.75	5409	5664	1.99

denotes the number of non-reactive stages in the stripping section of the prefractionator, NT_p denotes the total number of stages in the prefractionator, QF_p denotes the quality of the feed to the prefractionator.

In Table 4, NR_{M1} denotes the number of stages above the top feed in the main column (i.e. in the rectifying section), NR_{M2} denotes the number of stages below the top feed and above the side stream in the main column, NS_{M1} denotes the number of stages below the bottom feed in the main column (i.e. in the stripping section), NS_{M2} denotes the number of stages above the bottom feed and below the side stream in the main column, NT_M denotes the total number of stages in the main column, R_M denotes the reflux ratio in the main column, S_M denotes the boil-up ratio in the main column.

Excellent agreement between the designs generated and Aspen Plus simulation results reveals the potential of the approach to generate and evaluate designs for a given reaction system systematically.

CONCLUSIONS

This work presents a methodology for the conceptual design of reactive dividing wall columns. The procedure generates several designs and a cost function is used to rank the designs. The results of this approach can be used for initialising further, more rigorous, simulation studies. The approach has been illustrated for the hydrolysis of methyl acetate.

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