16th European Symposium on Computer Aided Process Engineering
and 9th International Symposium on Process Systems Engineering
W. Marquardt, C. Pantelides (Editors)

Conceptual design of reactive distillation flowsheets

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Abstract

Economic and environmental reasons have lead to process intensifications in the process industries. Reactive distillation is the most prominent example. However, often it is a challenge to satisfy the requirement for sufficient catalyst volume for the reaction while providing the interfacial area needed for mass transfer. The combination of a reactive distillation column with a pre-reactor is a valuable alternative. This paper presents an approach to identify promising designs for such flowsheets and the optimum distiribution of the reaction extent between the pre-reactor and the reactive distillation column. The methodology uses a boundary value method for the design of the column; Chemical equilibrium is assumed. The column usually consists of one reactive core, two rectifying sections and one stripping section. The methodology will be demonstrated for an ETBE case study.

Keywords: Reactive distillation, Conceptual design, Boundary value method

1. Introduction

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 methods have been developed [1-4]. However, they do not provide valuable and necessary insights into the process and are generally computationally intensive. Graphically-based methods overcome this problem [5-10]. Recently a methodology for reactive distillation columns based on a boundary value method (BVM) has been presented [11], which generates multiple designs without highly iterative procedures.

As powerful as the design methods presented are, they often fail to address the practicality of the proposed columns. In heterogeneously catalysed reactive distillation columns one often needs to maximize the catalyst volume inside the column [12], especially in slow reaction systems. A flowsheet configuration to overcome these practical problems for reactive distillation columns is the combination with a pre-reactor. In industry, often a substantial part of the conversion is carried out in reactors upstream of the reactive distillation column [13], thus reducing the catalyst volume in the column. This paper presents a methodology to identify near-optimal flowsheet configurations for reactive distillation flowsheets involving a ‘finishing’ reactive distillation column and a pre-reactor. The methodology uses a graphically-based boundary value method for identifying the promising column designs for a chosen pre-reactor configuration. A cost function will be used to rank the feasible designs. Chemical equilibrium is assumed and systems with two degrees of freedom, according to Gibbs phase rule, are considered. The methodology will be illustrated for ETBE production.

2. Flowsheet design

2.1. General considerations

The flowsheet considered includes heat exchangers upstream and downstream of the pre-reactor to preheat the feed to the reactor temperature and to adjust the feed condition for the column, respectively. The reactor is assumed to be isothermal. An expansion valve depressurises the feed from the reactor pressure (to be chosen such that the reactor effluent is in the liquid phase) to the pressure of the reactive distillation column. It is assumed that in the pre-reactor, as well as on every reactive stage of the column, chemical equilibrium is reached.

2.2. Methodology

The following assumptions enable us to use the boundary value method for the design of the reactive distillation column:

- Feed flow rate and composition are fixed and given
- The product purities are given
- A reasonable range for the pre-reactor temperature is given (might be constrained due to catalyst operating temperature, etc.)
- Pressure of the column and reactor are specified

The design parameters of the flowsheet are the inlet temperature of the pre-reactor T_R, the inlet temperature of the column T_F and the design details of the column itself, namely the operating conditions reboil and reflux ratio, the number of non-reactive and reactive stages inside the column and the feed stage location. The algorithm to solve this design problem is shown in Figure 1. For a set of operating conditions of the pre-reactor the designs for the reactive distillation column are calculated based on boundary value methods. The costs for the flowsheets are calculated and the flowsheets are ranked accordingly.

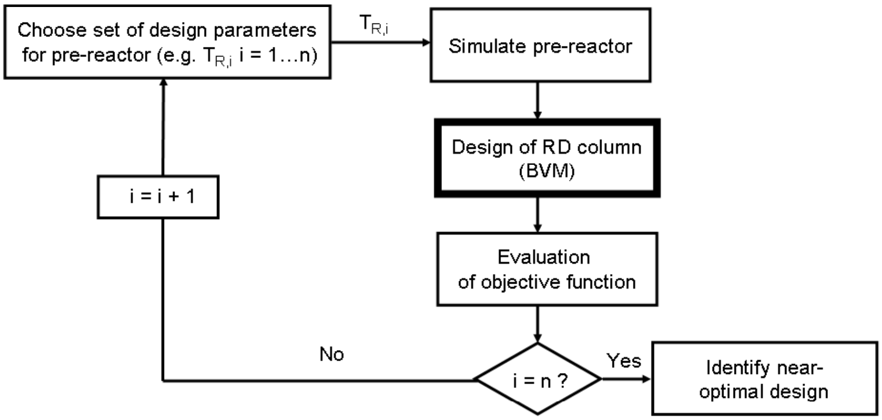

Figure 1 Algorithm for the identification of near-optimal pre-reactor – reactive distillation flowsheets

The cost function for the flowsheets involves the annualised capital cost of the equipment and operating costs for the utilities used.

3. Conceptual design of the reactive distillation column

3.1. Boundary Value Methods

Design methodologies using Boundary Value Methods are based on the ideas first developed for reactive distillation columns by Barbosa and Doherty [5-6]. For fully specified product compositions a feasible design is characterised by a continuous composition profile through the column, starting from the products. The profiles can be calculated via tray-by-tray calculations for a given reflux (or reboil) ratio. However, all approaches for design of columns achieving chemical equilibrium have in common that they assume the feed is located within the reactive section. This assumption may lead to backward reaction inside the column, depending on the operating conditions [8]. In general the reaction extent is concentrated around the feed stage and it may happen that on many reactive stages nearly no reaction takes place. In order to identify feasible and economical designs for a given design problem, reactive stages should only be used when necessary due to their high cost. Thus a design methodology should incorporate information on the reaction extent during the calculation procedure. The only approach incorporating this information is that of Espinosa *et al.* [8]. However, their approach concentrates on the feasibility for such columns; it aims for the identification of a single design at minimum reflux condition and involves no process economics.

3.2. Structure of the finishing reactive distillation column

This work presents a methodology to identify near-optimal designs for finishing reactive distillation columns. The main part of the reaction takes place in a pre-reactor upstream of the column. The task of the finishing column is to increase the overall reaction extent, while producing the desired products with the specified purity.

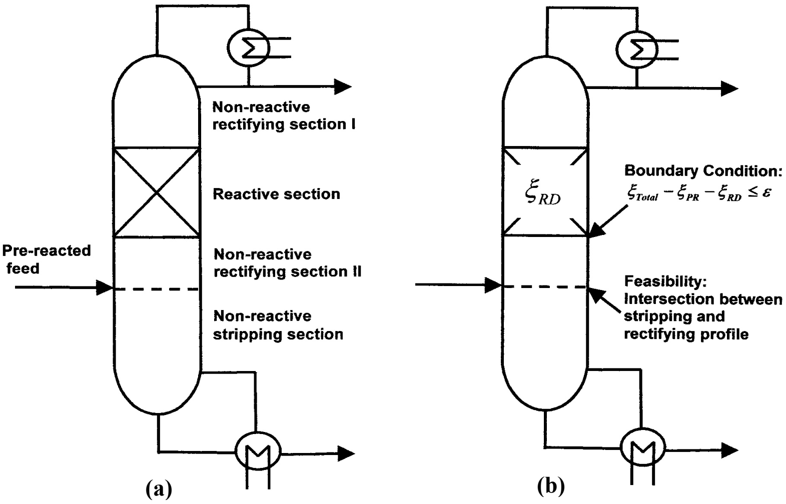

Figure 2: (a) Different zones for finishing reactive disitllation columns; (b) Boundary condition and feasibility criterion (ξ_{RD} , ξ_{PR} and ξ_{Total} represent the reaction extent in the column, reactor and overall process, respectively) .

Such flowsheets represent the typical implementation of reactive distillation in industry [14]. The columns are normally structured as shown in Figure 1 (a). The column consists of four different zones serving different functions. This structure is especially suited for etherification reactions, including ETBE, MTBE or TAME production. In the non-reactive stripping section, the main product (e.g. ETBE) is purified from the reactants. In the non-reactive rectifying section II the product, entering the column with the pre-reacted feed stream is separated from the reactants. This zone is necessary to avoid backward reactions in the lower part of the reactive section. In the reactive section the remaining part of the reaction takes place. In the non-reactive rectifying section I the low-boiling inert components and other reactants are separated from the remaining product.

3.3. Design procedure for finishing reactive distillation columns

The first step in the design procedure is to identify the product composition and the required reaction extent in the column. The input for the methodology is the composition and flow at the outlet of a pre-reactor. The definition of product purities for the bottom product and distillate enables the calculation of the overall mass balance of the column. Thus the reaction extent inside the column and the distillate and bottom product flow rates will be calculated. The overall reaction extent is the sum of the extent in the pre-reactor, ξ_{PR}, and that of the column ξ_{RD}. Once the purities for the bottom product and distillate are known, the column composition profiles can be calculated starting from the product compositions. To identify a range of feasible designs the profiles are calculated for several reflux and reboil ratios. Thermodynamic equilibrium is assumed on every stage. In the next step the starting point for the composition profile of the reactive core has to be determined. Here the distance to the reactive equilibrium surface is taken as a measure. If the distiance is below a given tolerance the point is accepted and the stage is tested for a minim reaction extent to be accomplished. The calculation of composition profiles proceed from the first stage of the reactive core for the corresponding reflux ratios. For the calculation of reactive profiles reactive and thermodynamic equilibrium is assumed. The calculation of the reactive core proceeds until the required reaction extent in the column is attained. This boundary condition (see Figure 1 (b)) can be formulated as:

$$\left\|\xi_{Total}-\xi_{PR}-\xi_{RD}\right\| \leq \varepsilon \tag{1}$$

At the stage where the boundary condition is satisfied, the non-reactive rectifying section II starts. The composition profiles can be calculated in the same manner as for the upper non-reactive rectifying section with the difference that the starting composition is that of the boundary condition and not that of the distillate. The non-reactive stripping profile is calculated starting from the bottom product for a range of reboil ratios. For a feasible design, a continuous profile throughout the column has to exist. The feasibility criterion is the intersection of the stripping section profiles and the profiles of the non-reactive rectifying section II (see also Figure 1 (b)). BVMs suffer from the high sensitivity of the composition profiles with respect to trace components in the products. To reduce this sensitivity a product region is defined for the bottom product and sets of composition profiles (manifolds) are used in the intersection search. This leads to a more robust design procedure.

4. Illustrative example

The proposed methodology has been used for design of a reactive disitllation flowsheet for the production of ETBE. The feed stream consists of a C4-stream containing the reactive component isobutene and an inert component n-butane as well as ethanol. The following reaction takes place over ion exchange resin catalysts as Amberlyst 15: *Isobutene + Ethanol ↔ ETBE*. The industrial flowsheet for ETBE and MTBE production are identical [15]. The reactants are fed to a pre-reactor (isothermal or adiabatic), where the feed nearly reaches chemical equilibrium. In the finishing reactive distillation column the remaining part of the reaction takes place and ETBE is produced at the desired purity. The range of reactor temperatures considered is 50-80 °C. The feed contains approximately 8 % excess ethanol, relative to to isobutene, to suppress side reactions and enhance the isobutene conversion.

Table 1. Product and feed compositions for ETBE system

Components	Stoichiometric coefficients	Boiling temp. at 8 bar	Distillate Compositon	Bottom product composition	Feed composition
	υ [-]	T_B [°C]	x_D mole fr.	x_B mole fr.	x_F mole fr.
Isobutene	-1	60.8	5.9E-6$^{\#}$	2.2E-4$^{\#}$	0.278$^{\#}$
n-Butane	0	69.4	0.952$^{\#}$	0.002	0.421$^{\#}$
Ethanol	-1	142.1	0.048	0.007$^{\#}$	0.301$^{\#}$
ETBE	1	156.7	4.1E-8$^{\#}$	0.991$^{\#}$	0.0$^{\#}$
Flow rate [kmol/h]			98.68	62.53	223.2$^{\#}$

$^{\#}$*Specified values*

The reactor is modelled using Aspen Plus^{TM} and the column feed stream is assumed to be in chemical equilibrium. The chemical equilibrium is described with an equation presented by Sundmacher *et al.* [16]. The column pressure is 8 bar. Table 1 shows the chosen purities for the system together with calculated values for distillate and bottom product. The chosen purities lead to an overall conversion of 99.97 % for isobutene; nearly pure ETBE is collected in the bottom product stream. At the top of the column a near-azeotropic mixture of n-butane and ethanol is produced. For this system the structure shown in Figure 1 (a) is needed to produce nearly pure ETBE since ETBE is not located on the reactive surface [9]. For the calculation of all thermodynamic properties an interface to Aspen Plus™ is used. The chosen range for the reflux and reboil ratio is 0.2 to 15. Energy balances are included during the calculation of composition profiles.

Multiple column designs of various configurations are obtained for these specifications for each temperature of the reactor. Table 2 shows the best designs for a temperature grid of 10 °C based on total annualised cost. In Table 2 NRI denotes the number of non-reactive stages in rectifying section I, NRC the number of reactive stages in the reactive core, NRII the number of non-reactive stages in rectifying section II, NS the number of non-reactive stripping stages, R the reflux ratio and S the reboil ratio. It can be seen that the optimal temperature of the pre-reactor is around 60 °C.

The results obtained can be used to initialise simulations with Aspen Plus™. Excellent agreement between the designs generated and the simulation results reveals the potential of the approach to generate and evaluate designs for a given reaction system systematically.

Table 2. Best flowsheet designs based on total annualised cost

TR [°C]	NRI [-]	NRC [-]	NRII [-]	NS [-]	N_{TOT} [-]	R [-]	S [-]	Cond. Duty [kW]	Reb. Duty [kW]	Total Cost [€/yr]
50	1	7	6	9	23	1.63	1	1317	415	359000
60	1	7	7	7	22	1.88	1	1440	415	348000
70	4	7	7	9	27	1.99	1	1498	415	357000
80	4	7	4	5	20	2.34	2.84	1670	1180	400000

5. Conclusions

This paper presents a methodology for the conceptual design of pre-reactor – reactive distillation flowsheets. These are advantageous in cases where practical issues favour the use of a pre-reactor. The approach avoids designs that give rise to reverse reaction in the column. The methodology identifies the optimal distribution of the reaction extent between column and pre-reactor. The approach has been illustrated for the production of ETBE.

Acknowledgements

We acknowledge the financial support provided by the European Commision within the 6th Framework Programme, Project "INSERT – Integrating Separation and Reaction Technologies"; Contract-No: NMP2-CT-2003-505862.

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