

Considering process requirements and hydraulic constraints for the design of reactive distillation columns

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Abstract

This work presents the design of reactive distillation columns taking account of process requirements and hydraulic constraints. Given a model for the distillation process together with the kinetics of the reactive system, a parametric study of the required distribution of stages and feeds is performed, solving a non linear optimization problem for different distributions of reactive and non reactive stages, where different objectives can be considered. The column structure that satisfies the minimum requirements on amount and purity of the product, together with the minimum amount of catalyst required in each reactive stage and the reflux ratio are the results of these optimizations. Once the feasible column structure is found, a hydraulic study is performed for the design of the column, where the required diameter, height and catalytic packing type are found. Thus, the diameter that can accommodate either the exact amount required or more catalyst than the minimum required amount is found.

The model of the reactive distillation column process plus hydraulics is implemented in GAMS for the case study of production of MTBE from methanol and isobutene, with n-butene as inert. For this case, only the bottoms of the column has the product of interest but it can be observed that the inert plays an important role on the column structure, as it has to be obtained as part of the top product in order to obtain high purity MTBE at the bottoms at a high conversion rate. Finally, a feasible and cost-effective design is found.

Keywords: Process Intensification, Reactive Distillation, NLP, Feasible Design.

1. Introduction

Reactive distillation constitutes a clear example of process intensification, discipline that has been receiving growing attention because of the savings on investment and operating costs, achieved by replacing the conventional reactor-separator scheme with a single unit. The advantages of using this configuration have already been reported (Stankiewicz, 2003). The potential of studying such systems via typical Process Systems Engineering methods together with the feedback of other fields of study has been recently pointed out (Klatt and Marquardt, 2009). Thus, modeling, simulation and optimization of reactive distillation units becomes an essential part of any study on such systems. Feasibility studies of reactive distillation systems are also important in order to define a pre-design of the column (Hoffmaster and Hauan, 2006). A thorough review on the design methods for reactive distillation can be found in Almeida-Rivera et al. (2004). However, a systematic analysis of the performance of reactive distillation columns changing structural variables and considering hydraulics has not been presented previously.

2. Model equations and assumptions

2.1. Reactive distillation column model

The complete model of the distillation column can be found in Domancich (2009). The first stage of this work was to find a feasible design, regarding the number of reactive and non reactive stages, minimum catalyst mass or equivalents, reflux ratio, product flow rates and feed locations. For such task the whole model was implemented in GAMS (2009), using a software package designed for developing equation oriented models MP4SO (Domancich et al, 2009). A parametric study was performed, changing the number of reactive and non reactive stages, and posing a non linear optimization problem where the objective was to maximize the purity of the bottom product of the column using these approaches:

- Different amounts of catalyst in each reactive stage,
- Different number of reactive stages keeping the total number of stages fixed,

This avoids posing a multiobjective optimization problem where the purity is maximized minimizing the catalyst mass and number of reactive stages.

The number of rectification stages is considered constant and equal to 3, because the top product of this column has no interest as a product. Thus, only the bottom product is analyzed. The total number of stages is fixed, being the condenser stage (1) and the reboiler stage (17). The total amount of catalyst required per stage is reported.

2.2. Hydraulic constraints

Once the number of stages for the stripping, rectification and reactive zones and the internal flows and feed locations are found, a comprehensive hydraulic study is performed for the design of the column, where the required diameter and height are calculated (Hoffmann et al., 2004). For this step, the reactive stages are replaced for equivalent height of catalyst packing, because using plates for the reactive section leads to a larger diameter of the column as the catalyst bags must be placed in the downcomer sector (Sundmacher and Kienle, 2003). Thus, the diameter that can accommodate either the exact amount required or more catalyst than the minimum required amount is found, leading to a feasible design. The equations representing hydraulics are included to size the column. They constitute a highly non linear set of equations that is included within the whole model. The minimum set of equations needed to find the column size is reproduced here. There are additional equations that can be added to the model to represent more precise hydraulic constraints but they are not dealt with in this paper.

Gas superficial velocity and volumetric flow rate, with $F=$ factor for gas load, ($\text{Pa}^{0.5}$)

$$u_G \left[\frac{\text{m}}{\text{s}} \right] = \frac{F}{\sqrt{\rho_G}} \quad \dot{V}_G \left[\frac{\text{m}^3}{\text{s}} \right] = \frac{\dot{G} \left[\frac{\text{kmol}}{\text{s}} \right] M_G}{\rho_G} \quad (1)$$

Area and diameter of the transversal column section

$$A_C = \frac{\dot{V}_G}{u_G} \quad d_C = \sqrt{\frac{4A_C}{\pi}} \quad (2)$$

Specific surface area a , volume fraction of catalyst ψ and void fraction ε of the packing are obtained from Hoffmann et al. (2004), obtaining a correlation via a regression model. For example, for MULTIPAK-II packing with different particle sizes, the height of two layers Δz is 0.25m, which is also the height of an equivalent stage:

$$a \left[\frac{\text{m}^2}{\text{m}^3} \right] = 0.1454 \left(\frac{1}{d_c} \right)^2 - 7.1658 \left(\frac{1}{d_c} \right) + 325.5312 \quad (3)$$

$$\psi \left[\frac{\text{m}^3}{\text{m}^3} \right] = 0.000265 \left(\frac{1}{d_c} \right)^2 - 0.018827 \left(\frac{1}{d_c} \right) + 0.559770 \quad (4)$$

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$$\varepsilon \left[\frac{m^3}{m^3} \right] = -0.000373 \left(\frac{1}{d_c} \right)^2 + 0.023378 \left(\frac{1}{d_c} \right) + 0.341186 \quad (5)$$

Liquid volumetric flow rate

$$\dot{V}_L \left[\frac{m^3}{s} \right] = \frac{\dot{l} \left[\frac{kmol}{s} \right] M_L}{\rho_L} \quad (6)$$

Liquid superficial velocity and maximum liquid load (estimated)

$$u_L = \frac{\dot{V}_L}{A_C}, \quad u_{L,MAX} = 29 \frac{m^3}{m^2 h} \quad (7)$$

Catalyst mass per stage, if the particle density ρ_P is known (Void fraction of the bed $\varepsilon_{CB}=0.3$ for MULTIPAK-II):

$$\text{CatMass} \left[\frac{kg}{stage} \right] = \frac{1}{4} \pi d_c^2 \Delta z \psi (1 - \varepsilon_{CB}) \rho_P \quad (8)$$

If the catalytic bed apparent density ρ_{CB} is known:

$$\text{CatMass} \left[\frac{kg}{stage} \right] = \frac{1}{4} \pi d_c^2 \Delta z \psi \rho_{CB} \quad (9)$$

Equations (1), (2), (4), (6), (7) and (8) or (9) define a minimum set of equations that are added to the column model in order to find the diameter and thus the maximum amount of catalyst allowed in each stage. Catalyst bags must be placed occupying a height Δz per reactive stage. The catalyst mass found using this set of equations has to be equal or larger to the amount of catalyst calculated using the equations of the previous section.

3. Results

3.1. Feasibility study

In Table 1 the base case is shown. Both feeds are located at the end of the reactive section. The objective was to find a feasible column design that complies with the specifications for fuel grade MTBE at the bottom of the column.

Figure 1: Schematic of the column

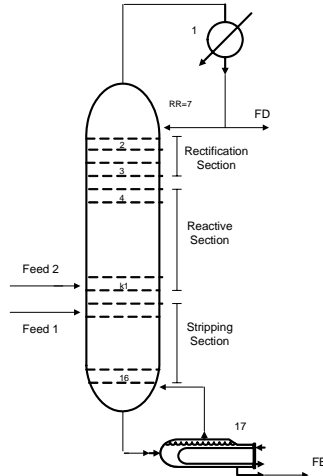


Table 1: Column data for base case

Feed 1		Feed 2	
Temperature [K]	350	Temperature [K]	350
Pressure [bar]	11	Pressure [bar]	11
Flowrate [mol/s]	455	Flowrate [mol/s]	168
Composition		Composition	
n-C4	0.63	Methanol	1.0
i-C4:	0.37		

From Figures 2 (a) and (b) it can be seen that there is an incremental improvement in the conversion and purity changing from $k_1=8$ to $k_1=9$, for different mass of catalyst used. However, if there is an increase of more than 750 kg catalyst, the improvements do not justify adding more reactive stages or more catalyst to the stages (94.4% conversion, 97.1% MTBE purity mass base) because the column reaches chemical equilibrium. Thus, as a base case design, a column with 6 reactive stages ($k_1=9$) and 750 kg catalyst in each of the 6 stages is used. The hydraulic feasibility of such design is object of study in next section,

because this study guarantees that a column with such characteristics can yield the desired product, but do not guarantee that the size of the column is feasible.

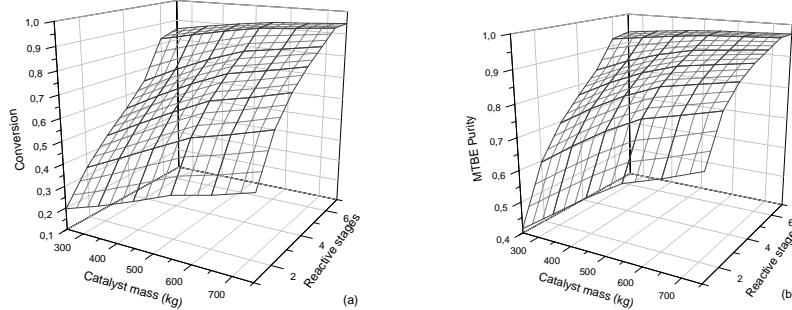


Figure 2 (a) and (b): Conversion and purity parametric study for different number of reactive stages and different amount of catalyst in each plate

3.2. Hydraulic design

The column height, diameter and catalyst amount corresponding to the design with 6 reactive stages and different cases are found. The objective is to maximize MTBE purity. For the selected feasible design results are reported in table 2. The column diameter obtained agrees with values reported in literature (Almeida et al., 2004). Costs are included for the optimized cases (Domancich, 2009).

Table 2: Results for the hydraulic design using MULTIPAK-II - (*) Hoffman et al, 2004

VARIABLES	Fix.	Calc.	Maximiz.	Minimizing
	$u_{L,MAX}$	$u_{L,MAX}$	Purity	Cost
Conversion	0.944	0.944	0.987	0.967
Purity (mass fraction)	0.971	0.971	0.976	0.956
u_G (m ³ /m ² h)	849.6	731.00	709.2	856.8
$u_{L,MAX}$ (m ³ /m ² h)	29(*)	25.72	29(*)	29(*)
u_L (m ³ /m ² h)	29	24.95	24.3	29
Ψ – catalyst volume fraction	0.557	0.557	0.557	0.556
F-factor for gas load (Pa ^{0.5})	1.148	0.851	0.8	1.173
Column area (m ²)	27.74	32.23	32.66	25.488
Diameter (m)	5.94	6.40	6.451	5.698
Cost (\$/y 10 ⁻³)			3200	3058

3.3. Low and high conversion designs for the minimum required purity

It is clear that from purities over 92% mass basis the amount of catalyst (and also the costs) are increasingly higher for obtaining only slight changes in purity. After performing a parametric analysis and hydraulic analysis of the reactive distillation column, posing an optimization problem where the MTBE purity is fixed in 92% mass basis and minimizing the catalyst mass, it was found that 200 kg/stage are required for 6 reactive stages, this can be seen in Figure 2(b). There are two situations that can be clearly identified, with low and high conversions respectively. The results are presented to provide with some more insight on the column behavior.

3.3.1. Low conversion design – 5 reactive stages

The main characteristic of the low conversion design is the behavior of the inert (n-C4). From figure 3 it can be seen that the composition of n-C4 remains almost constant (around 0.75) and suddenly decreases in the stripping stages.

The stripping zone has a size just enough to split (but not completely) the inert and the limiting reactant from the pseudo-component “ethanol-MTBE” due to the high concentration of the inert in the reactive section core.

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3.3.2. High conversion design – 6 reactive stages

Figure 4 shows the characteristics of a profile for high purity and conversion. The steep change in the inert composition in the reactive core is the main difference between this design and that presented in the previous section (Figure 4).

As a result, the first three stages of the stripping section are enough to separate the pseudo-component “ethanol-MTBE” from the inert, and the last stages are enough to separate the alcohol from the ether, having this design one stripping stage less than the previous one. For this high conversion design it can be foreseen that adding more stripping stages to the column the MTBE purity can be increased.

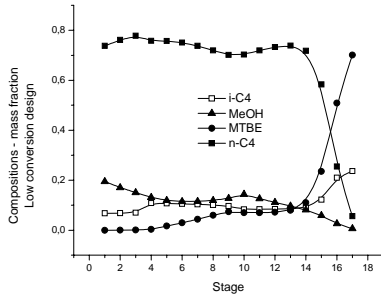


Figure 3: Composition profiles

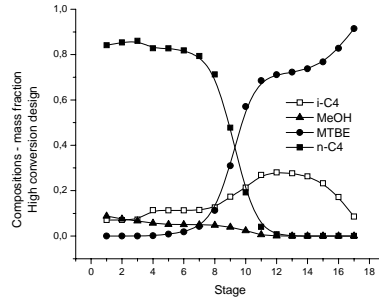


Figure 4: Composition profiles

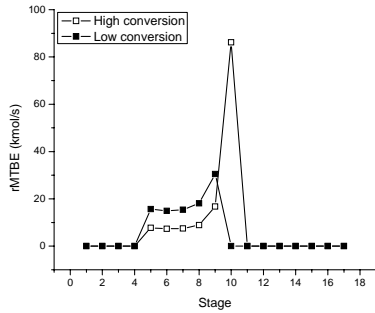


Figure 5: Rate of MTBE production

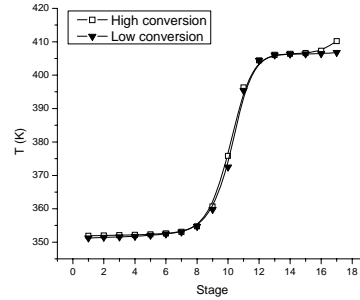


Figure 6: Temperature profile

The profiles change because of the presence of the inert component. The key to this is the separation task that has to be performed in the stripping section of the column. On the other side, the rate of MTBE production for the high conversion case confirms that the column is operating near to chemical equilibrium, because it can be seen that the reaction takes place mainly in one of the 6 reactive stages (Figure 5). Temperature profile, however, does not show differences except in the reboiler (Figure 6). A function of the activities of the components of the mixture and the equilibrium constant K_{eq} to evaluate the departure from chemical equilibrium is posed as

$$g_j = \left(\frac{a_{i,C4}}{a_{i,MeOH}} - \frac{a_{i,MTBE}}{K_{eq} a_{i,MeOH}^2} \right) \quad (10)$$

K_{eq} is calculated as shown in Almeida et al. (2004). The kinetic constant for every reactive stage is shown in figure 7 for both cases. Figure 8 shows that the design with 6 reactive stages and 200 kg catalyst/stage operates nearer to equilibrium than the design with 5 reactive stages and 200 kg catalyst/stage.

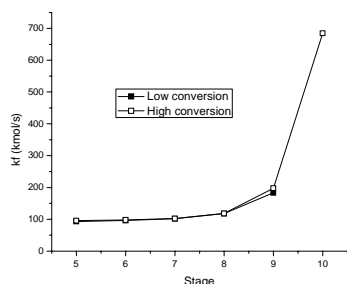


Figure 7: Chemical reaction constant

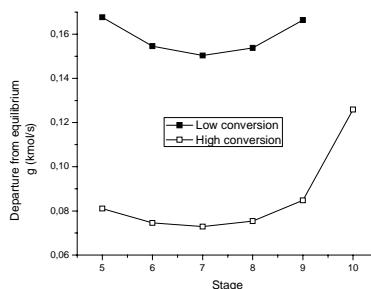


Figure 8: Departure from equilibrium

4. Conclusions and future work

A methodology to design reactive distillation columns following a two stage approach was presented. The first stage deals with the design feasibility, the second stage with the feasibility of the column hydraulics and sizing of the column taking account of such hydraulic constraints. The optimization posing as an objective function the total cost of the reactive distillation column leads to a design both feasible from the process and hydraulic point of view. Costs are reduced by posing an optimization problem where the total cost is minimized, varying the catalyst amount and using the hydraulic constraints for keeping its value below the maximum allowed for the column diameter used. A feasible design for the minimum required purity requires a substantially lower amount of catalyst, thus the cost decreases. This is subject to further study.

5. Acknowledgements

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