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**STRUCTURAL ANALYSIS OF REACTIVE DISTILLATION
COLUMNS**

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Structural Analysis of Reactive Distillation Columns (Análisis estructural de columnas de destilación reactiva)

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Abstract

We present a model for a reactive distillation column, based on models by Taylor and Krishna (2000) and Almeida-Rivera (2005) consisting in pure separation stages combined with a reactive distillation sector, where both reaction and separation take place at the same time. An analysis is performed in order to show the impact on the global reactive separation system by adding or subtracting either non-reactive or reactive separation stages, keeping the number of total stages constant. For this study, we used a rigorous modeling of the column, with an equilibrium model for the reactive sector. An example on the study of the performance of a reactive distillation unit is presented. In particular, it is related to the production of methyl-tert-butyl ether.

Keywords: modeling, simulation, reactive distillation, equilibrium model, methyl-tert-butyl ether (MTBE), reboiler, condenser, fractions, azeotrope.

Resumen

En este trabajo se presenta el modelo de una columna de destilación reactiva, basado en modelos previamente desarrollados por Taylor y Krishna (2000) y Almeida-Rivera (2005), el cual consiste en etapas de separación pura combinadas con un sector de destilación reactiva, donde tanto la reacción como la separación se llevan a cabo al mismo tiempo. Se realizó un análisis con el objetivo de mostrar el impacto que tiene el agregado o remoción de etapas reactivas y no reactivas sobre el sistema global de separación, manteniendo el

número total de etapas constante. Para este estudio, se utilizó un modelo riguroso de la columna, con un modelo de equilibrio para el sector reactivo. Se incluye un ejemplo de análisis de rendimiento de una unidad de destilación reactiva para la producción de metil-terbutil-eter.

Palabras clave: modelado, simulación, destilación reactiva, modelo de equilibrio, metil-terbutil-eter (MTBE), rehervidor, condensador, fracciones, azeótropo.

1. Introduction

Reactive distillation columns constitute a clear example of process intensification. By process intensification it is meant the significant improvement achieved by a process. For example, the entire plant design is upgraded by reducing the number of units involved in a conventional process to obtain the same products.

However, reactive distillation is not suitable for every process where reaction and separation steps occur. Operating conditions, such as pressure and temperature of the reactive and separation processes and perhaps other requirements, must overlap in order to assure the feasibility of the combined process. This limitation can be overcome by fixing adequate operating conditions in the cases where this is possible.

Reactive distillation has been presented as a multifunctional reactor, where the reactive and separation tasks are combined into a single unit, thus reducing investment costs. The advantages of using this configuration have already been reported (Stankiewicz, 2003). 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 has not been presented previously.

The simplest case exhibits reactive and non-reactive sections with no interrelationship between them, except at the equipment level. Even when the interrelations between sections remain unchanged compared with traditional technology; significant savings (2.5 times as big as the equipment expenditure) can be obtained because of the smaller and cheaper plant needed to perform the same tasks. A clear example is the Urea2000plus™ technology, by Stamicarbon B.V., where a pool reactor is used to combine the urea reactor, the carbamate condenser and the inerts scrubber. However, further improvements can be obtained by really integrating the tasks, on the following items:

- On the reaction: because there is an equilibrium displacement, since the products are being withdrawn

- On the separation: because of the changes in the driving force for mass transfer due to the reaction.

This case is formally presented as a reactive separation, also called a separative reaction. Both tasks occur at the same level. Several disadvantages can be overcome by using these combined schemes, because the selectivity and the reaction yield increase. This makes it possible to avoid thermodynamic constraints, such as azeotropes, thus allowing a considerable reduction not only in the investment costs but also in the operating costs (energy, water and solvents, otherwise required as entrainers).

On the other hand, the mathematical model for this piece of equipment is more complex, and the requirements for simulating the combined process are higher. Non-linear coupling of reaction, phase equilibria, and mass and energy transport can give rise to many undesired effects, for example the appearance of reactive azeotropes (called arheotropes) and the multiplicity of steady states.

The performance of reaction with separation in one piece of equipment offers distinct advantages over the conventional, sequential approach (Podrebarac *et al.*, 1998). As advantages of this integration, chemical equilibrium limitations can be overcome, higher selectivities can be achieved, the heat of reaction can be used for distillation, auxiliary solvents can be avoided, and azeotropic mixtures can be more easily separated than in conventional distillation. This may lead to an enormous reduction of capital and investment costs and may be important for sustainable development due to a lower consumption of resources (Al-Arfaj and Luyben, 2000).

Some industrial processes where reactive distillation is used are the esterification processes, such as the synthesis of methyl acetate (Agreda *et al.*, 1990); and the preparation of ethers, like MTBE (Jacobs and Krishna, 1993), TAME and ETBE, used as fuel additives. An explanation for the occurrence of steady-state multiplicity was provided by Huan *et al.* (1995).

A thorough review on the modeling aspects of reactive distillation can be found in Taylor and Krishna (2000), where special emphasis is put on the differences between equilibrium and non-equilibrium based models with their advantages and drawbacks. Doherty and Malone (2001) gave valuable commentaries on future trends and challenges,

and a thorough review on the design methods for reactive distillation can be found in Almeida-Rivera *et al.* (2004).

2. Reactive column model

The reactive distillation column is modeled as a plate column, using reactive and non reactive stages where appropriate. This is known as equilibrium model for reactive distillation, as the conventional MESH equations are used for the column adding one term taking account of the reaction in the mass and energy balances.

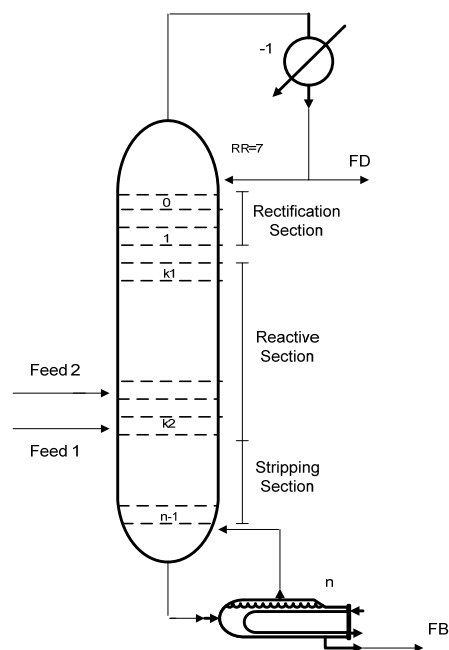
The base model as shown in Fig. 1 consists of n-theoretical stages, numbered from top to bottom from 0 to n-1, a total condenser numbered as (-1) and a partial reboiler numbered n. There are rectification stages above the reactive sector and stripping stages below the reactive sector. As steady state is analyzed, thus hydraulic equations are not needed in the model. Pressure change between stages is neglected, so as to simplify the model.

Equations required for the reactive column modeling are shown in the case study section, because some case-dependent parameters are required for fully developing the mathematical model. Thus, for the sake of clarity, we present the general equations together with the system-dependent equations.

3. Case study

The production of methyl tert-butyl ether (MTBE) is presented using a reactive distillation column in order to convert methanol and isobutene for obtaining MTBE, according to the global reaction:



Figure 1. Reactive distillation column scheme

Source: Of authors' own (2008)

In the feed mixture *n*-butane is present but it is inert for the reaction. For the conventional reactor-separator scheme, methanol is usually fed in excess in order to improve the conversion of $i\text{-C}_4^=$ into MTBE. This causes some problems for separating the product MTBE from the non reacted reactants, because MTBE forms azeotropes with methanol and $i\text{-C}_4^=$. The separation task is therefore difficult. Recently, a hybrid process to obtain pure MTBE from a reactor-separator scheme was presented (Daviou *et al.*, 2004) where the excess of methanol is recovered using a pervaporation membrane and recycled to the reactor, while MTBE is obtained as the bottom product of a single distillation unit with high purity and recovery (gasoline and laboratory grades).

In this work, it is proposed to feed equimolar quantities of methanol and $i\text{-C}_4^=$, in stoichiometric proportion, and a product with high purity of MTBE is obtained. Thus, the problem of splitting azeotropic mixtures is reduced because the reactive distillation scheme allows for “reacting away” the azeotropes (Taylor and Krishna, 2000). For this example,

$n=15$, and the reactive stages for the base case are stages from 2 (k1) to 9 (k2). The number of reactive stages will be changed keeping the total number of stages fixed, in order to show the effect on the composition of the products and the conversion of $i-C_4^=$.

In Table 1 all required data for the simulation of the base case is presented. The base case was taken from Seader and Henley (1998) and Almeida-Rivera (2005).

Table 1: Column data used for the base case

| OPERATING CONDITIONS | |
|-----------------------------|--------------------------------------|
| Number of trays | 15 |
| Number of reactive trays | 8 |
| Operating pressure | 11 bar |
| Reflux Ratio | 7 |
| Bottom Flow (FB) | 203 mol/s |
| Total mass of catalyst | 1632.8 kg (8000 eq _[H+]) |
| FEED DATA | |
| Feed 1 | |
| Temperature [K] | 350 |
| Pressure [bar] | 11 |
| Flowrate [mol/s] | 455 |
| Composition | |
| | n-C ₄ : 0.63 |
| | i-C ₄ : 0.37 |
| Location | On 9 th stage |
| Feed 2 | |
| Temperature [K] | 320 |
| Pressure [bar] | 11 |
| Flowrate [mol/s] | 168 |
| Composition | |
| | MeOH 1.0 |
| Location | On 8 th stage |
| PRODUCTS | |
| Distillate (FD): | |
| Temperature [K] | 353 |
| Composition | |
| | nC ₄ : 0.764 |
| | iC ₄ : 0.12 |
| | MeOH: 0.116 |
| | MTBE: 0.0 |
| Flowrate [mol/s] | 285 |
| Bottom (FB): | |
| Temperature [K] | 387 |
| Composition | |
| | nC ₄ : 0.341 |
| | iC ₄ : 0.011 |
| | MeOH: 0.0 |
| | MTBE 0.648 |
| HEAT DUTY [W] | |
| Condenser | 4.35.10 ⁷ |

Reboiler

3.13.10⁷*Source:* Of author's own (2008)

Reflux ratio is fixed at 7 because this value guarantees that there is no multiplicity of steady states (Singh *et al.*, 2005).

4. Model equations

The reactive distillation column was modeled and solved using the commercial software GAMS (Brooke *et al.*, 2004)

4.1. Non reactive trays

a) Component molar balance:

$$\begin{aligned} F_{Feed} z_i + F_{in,L} x_{i,in} + F_{in,V} y_{i,in} \\ - F_{out,L} x_i - F_{out,V} y_i = 0 \quad i = 1..nc \end{aligned} \quad (\text{Eq. 2})$$

b) Energy balance

$$\begin{aligned} F_{Feed} h_{Feed} + F_{in,L} h_{in,L} + F_{in,V} h_{in,V} \\ - F_{out,L} h_{out,L} - F_{out,V} h_{out,V} = 0 \end{aligned} \quad (\text{Eq. 3})$$

Note: The heat of reaction in the energy balance is omitted because the heat of formation is used as reference value for the enthalpy computations.

c) Phase equilibrium

$$\phi^L(T, P, x)_i x_i = \phi^V(T, P, y)_i y_i \quad i=1..nc \quad (\text{Eq. 4})$$

Note: Molar fractions are normalized for all the model sections.

4.2. Reactive trays

a) Component molar balance:

$$F_{Feed} z_i + F_{in,L} x_{i,in} + F_{in,V} y_{i,in} - F_{out,L} x_i - F_{out,V} y_i + r_{ij} = 0 \quad \dots i=1..nc, j=1..n_{Rx} \quad (\text{Eq. 5})$$

b) Energy balance

$$F_{Feed} h_{Feed} + F_{in,L} h_{in,L} + F_{in,V} h_{in,V} - F_{out,L} h_{out,L} - F_{out,V} h_{out,V} = 0 \quad (\text{Eq. 6})$$

c) Phase equilibrium

$$\phi^L(T, P, x)_i x_i = \phi^V(T, P, y)_i y_i \quad i=1..nc \quad (\text{Eq. 7})$$

d) Chemical reaction driving force (Sundmacher and Hoffmann, 1999)

$$g_j = \left(\frac{a_{i,C4}}{a_{i,MeOH}} - \frac{a_{i,MTBE}}{K_{eq} a_{i,MeOH}^2} \right) \quad i=1..nc \quad (\text{Eq. 8})$$

e) Activity

$$a_i = \gamma_i x_i \quad i=1..nc \quad (\text{Eq. 9})$$

f) Chemical reaction constant (Thiel *et al.*, 2002)

$$kf(T) = kf(T^\circ) e^{-\frac{Ea}{R} \left(\frac{1}{T} - \frac{1}{T^\circ} \right)} \quad (\text{Eq. 9})$$

where

$$kf(T^\circ) = 15.5 \cdot 10^{-3} \text{ mol} / (\text{s eq}[\text{H}^+])$$

$$Ea = 92400 \text{ J/mol}$$

$$T^\circ = 333.15 \text{ K}$$

g) Chemical equilibrium constant (Thiel *et al.*, 2002)

$$\ln K_{eq} = \ln K_{eq,0} + \alpha \left(\frac{1}{T} - \frac{1}{T^*} \right) + \beta \ln \left(\frac{T}{T^*} \right) + \sigma (T - T^*) + \delta (T^2 - T^{*2}) + \varepsilon (T^3 - T^{*3}) + \theta (T^4 - T^{*4}) \quad (\text{Eq. 10})$$

where

$$\alpha = -1.49277 \cdot 10^3$$

$$\beta = -7.74002 \cdot 10^1$$

$$\sigma = 5.07563 \cdot 10^{-1}$$

$$\delta = -9.12739 \cdot 10^{-4}$$

$$\varepsilon = 1.10649 \cdot 10^{-6}$$

$$\theta = -6.27996 \cdot 10^{-10}$$

$$T^* = 298.315 \text{ K}$$

$$K_{eq,o} = 284$$

h) Chemical reaction rate

$$r_{i,j} = v_{i,j} k_f^j g_j m_{cat}, i=1..nc, j=1..n_{Rx} \quad (\text{Eq. 11})$$

4.3. Condenser

a) Component molar balance:

$$F_{in,v} y_{i,in} - (FD + F_{ref}) x_i = 0, i=1..nc, j=1..n_{Rx} \quad (\text{Eq. 12})$$

b) Reflux ratio

$$RR = F_{ref} / FD \quad (\text{Eq. 13})$$

c) Energy balance

$$F_{in,v} h_{in,v} - (FD h_D + F_{ref} h_{ref}) - Q_{cond} = 0 \quad (\text{Eq. 14})$$

d) Phase equilibrium

$$\phi^L(T, P, x)_i x_i = \phi^V(T, P, y)_i y_i, i=1..nc, j=1..n_{Rx} \quad (\text{Eq. 15})$$

4.4. Reboiler

a) Component molar balance:

$$F_{in,L} x_{i,in} - (F_{out,L} x_i + F_{out,v} y_i) = 0, i=1..nc, j=1..n_{Rx}, \quad (\text{Eq. 16})$$

b) Energy balance

$$F_{in,L} h_{in,L} - (F_{out,L} h_{out,L} + F_{out,v} h_{out,v}) + Q_{reb} = 0 \quad (\text{Eq. 17})$$

c) Phase equilibrium

$$\phi^L(T, P, x)_i x_i = \phi^V(T, P, y)_i y_i, i=1..nc, j=1..n_{Rx} \quad (\text{Eq. 18})$$

4.5. Thermodynamic model

$$y_i \phi P = x_i \gamma_i p_i^V \quad (\text{Eq. 19})$$

The vapor phase is assumed to behave ideally ($\phi = 1$), and the liquid-phase is modeled using Wilson activity coefficient equation. This method is accurate for multicomponent mixtures that do not form two liquid phases (Kooijman and Taylor, 2000), and the set of equations is:

$$\ln(\Lambda_{ij}) = a_{ij} + \frac{b_{ij}}{T} \quad (\text{Eq. 20})$$

$$S_{w_i} = \sum_{j=1}^{j=nc} x_j \Lambda_{ij} \quad (\text{Eq. 21})$$

$$\ln(\gamma_i) = 1 - \ln(S_{w_i}) - \sum_{k=1}^{k=nc} \frac{x_k \Lambda_{ki}}{S_{w_k}} \quad (\text{Eq. 22})$$

The values for the model parameters a_{ij} and b_{ij} , at 11 bar were taken from Ung and Doherty (1995) and Guttinger (1998), shown in Tables 2a and 2b.

5. Discussion of results

The base case was defined as shown in Table 1. MTBE is required as the bottom product of the column. As methanol and isobutylene are fed in stoichiometric proportion and they are required in 1-1 proportion, the conversion is presented as a function of the number of reactive stages in Fig. 2. It is shown that for the maximum proposed number of reactive stages the conversion reaches 80%. However, for this high conversion it is not possible to obtain high purity MTBE as a bottom product for the base case, as shown in figure 3. The reason is the amount of n-butane fed to the column that - according to the thermodynamic prediction- distributes itself and contaminates the MTBE in the bottom product. The molar composition shown corresponds to an MTBE mass composition of 0.73, which is lower than the required gasoline grade of MTBE (0.95). However, 100% of the produced MTBE is recovered when using any reactive distillation scheme.

Table 2a: Values for parameters a_{ij}

| a_{ij} | iC ₄ | MeOH | MTBE | nC ₄ |
|-----------------|-----------------|----------|--------|-----------------|
| iC ₄ | 0 | -0.742 | 0.2413 | 0 |
| MeOH | 0.742 | 0 | 0.9833 | 0.81492 |
| MTBE | -0.2413 | -0.9833 | 0 | 0 |
| nC ₄ | 0 | -0.81492 | 0 | 0 |

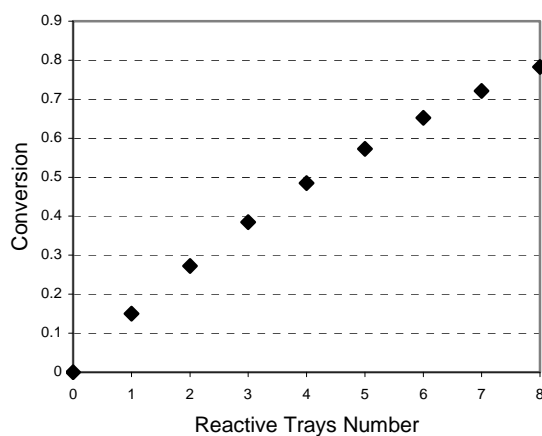
Source: Ung and Doherty (1995); Guttinger (1998)

Table 2b: Values for parameters b_{ij}

| b_{ij} | iC ₄ | MeOH | MTBE | nC ₄ |
|-----------------|-----------------|--------|---------|-----------------|
| iC ₄ | 0 | -85.54 | 15.22 | 0 |
| MeOH | -1296.7 | 0 | -746.39 | -1149.28 |
| MTBE | -136.6 | 204.5 | 0 | 0 |
| nC ₄ | 0 | -192.4 | 0 | 0 |

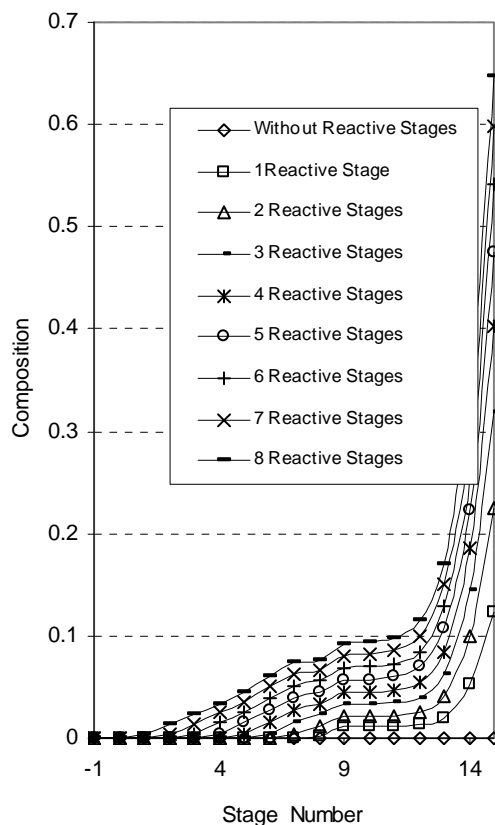
Source: Ung and Doherty (1995); Guttinger (1998)

Using more than 8 reactive stages does not improve the conversion significantly. Although not explicitly shown for more than 8 reactive stages, it can be seen from Fig. 2 that the conversion does not increase linearly with the number of reactive stages, and the rate becomes lower as that number increases. The effect of adding reactive stages is evident for the first reactive points included. From 8 stages onwards, the difference decreases significantly and there is no relevant improvement in the conversion when adding more reactive trays.

Figure 2. Conversion as a function of the number of reactive stages – base case

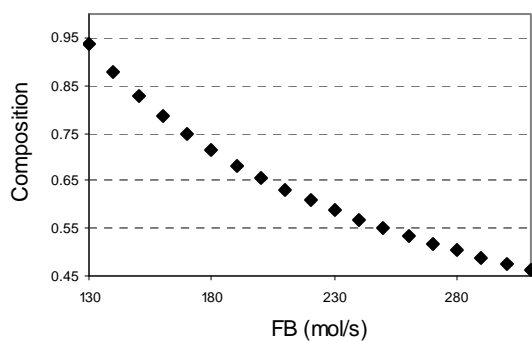
Source: Of authors' own (2008)

Figure 3. MTBE molar composition profiles for different number of reactive trays (liquid phase)



Source: Of authors' own (2008)

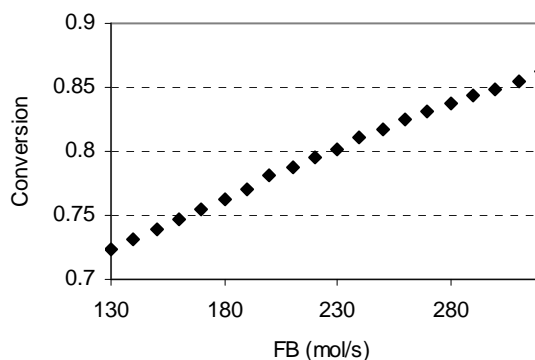
Figure 4. MTBE molar composition as a function of the bottom molar flow rate FB



Source: Of authors' own (2008)

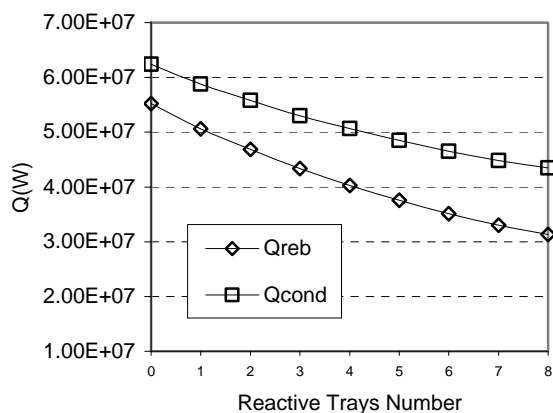
The alternative for further improvement of the MTBE composition in the bottom product is to decrease the bottoms flow rate (Fig 4). This action will have an adverse effect on the reaction itself, as it will displace the equilibrium of the reaction towards the reactants and lower the conversion. This can be seen in Fig. 5. The impact on the energy requirement, however, is that the heat load required in the reboiler and condenser decreases (Fig 6), due to the favorable heat integration scheme of the reactive distillation column. MTBE never appears in the top product because the reaction is just displaced towards the reactants and the conversion decreases.

Figure 5. MTBE conversion as a function of the bottom molar flow rate FB

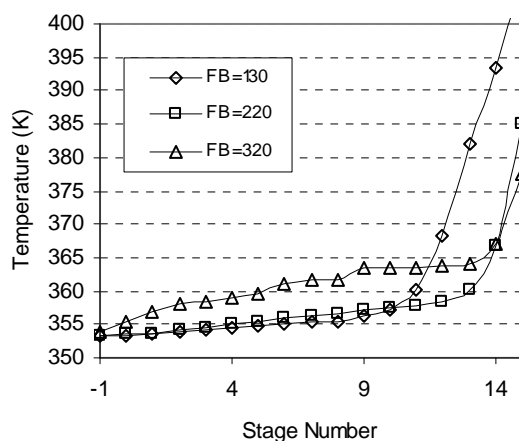


Source: Of authors' own (2008)

Figure 6. Heat duty for different reactive trays number



Source: Of authors' own (2008)

Figure 7. Temperature profiles for different bottom flow rates – base case

Source: Of authors' own (2008)

Observing the temperature profiles for the case with 8 reactive stages (Fig. 7) the temperature in the reactive sector increases with increasing bottom flow rate, but inverts the behavior in the stripping sector. This is due to the higher MTBE composition in the bottom product and the displacement of the reaction equilibrium towards MTBE when the flow rate decreases. In the reactive stages the temperature is higher when the bottom flow rate is higher because the reaction is endothermic and a higher temperature is required to produce more MTBE. The reaction equilibrium is forced towards the product in this case.

6. Conclusions and future work

There is a trade-off between the conversion and the purity of the bottom product, which deserves better analysis. The results can be improved by increasing the amount of catalyst used in each stage, but it would also increase the cost of the process. There is also a strong influence of the thermodynamic model parameters chosen, and it is of crucial importance to use the best set of parameters available. Experimental data should be used, when available,

to validate the model, because there is a high amount of uncertainty regarding the accuracy of the thermodynamic model.

For the conventional production process, an excess of methanol is required in order to increase the conversion of *i*-C₄. For a reactive distillation system, it is unnecessary to feed methanol in excess, but it will also increase the conversion. The problem of separating unreacted methanol from the bottom product appears when using this scheme, and work is being carried out regarding this issue.

The cost for the various options analyzed is not reported in this paper, but it will be addressed in future communications. It is interesting to note that the optimization of reactive distillation systems is different from the optimization of conventional distillation columns because the flow rate of the products is no longer an optimization variable. Then, the structure becomes an important variable when carrying out the optimal design of such processes.

7. Notation

a: Activity

F: Molar flow [mol/s]

g: Driving force

h: Enthalpy [J/mol]

K_{eq}: Temperature-dependent chemical equilibrium constant

k_f: Forward reaction rate constant [mol/(s·eq_[H⁺])]

n_c: Number of components

n_{RX}: Number of reactions

P: Pressure [Pa]

p^v: Vapor pressure [Pa]

Q: Heat duty [W]

r: Reaction rate [mol/s]

RR: Reflux ratio

- x : Mole fraction in the liquid phase
- y : Mole fraction in the vapor phase
- z : Mole fraction in either vapor or liquid phase
- γ : Activity coefficient

8. Subscripts

- Feed*: Feed stream
- L*: Liquid
- V*: Vapor
- D*: Distillate
- ref*: Reflux
- i*: Component index
- j*: Reaction index
- reb*: Reboiler
- cond*: Condenser

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