



Modelling and Experiments for Application of Catalytic Distillation to TAME Synthesis

Alexandra E. Bonet-Ruiz^{a*}, Jordi Bonet^b, Grigore Bozga^a, Joan Llorens^b,
Valentin Pleșu^a, Alexandru Tuluc^a, Gheorghe Bumbac^a, Constantin Muscalu^a

^a University Politehnica of Bucharest, Centre for Technology Transfer in Process Industries (CTTPI), 1, Gh. Polizu Street, Bldg A, Room A056, RO-011061 Bucharest, Romania

^b University of Barcelona, Department of Chemical Engineering Martí i Franquès núm. 1, Planta 6, E-08028 Barcelona, Spain
pres2012@chim.upb.ro;

In the early stages of distillation process analysis, the residue curve maps are used to check its feasibility. The residue curve map represents the composition that follows the residue in the still of a Rayleigh distillation for several initial conditions. It is demonstrated in the literature by several authors that the compositions followed by a residue curve matches a column composition profile of a packed column operated at infinite reflux flow-rate. In the present work, it is demonstrated that the dimensionless time used to calculate the residue curves corresponds to the number of transfer units by applying mass balances in a section of a packed column operated at infinite reflux flow rate. However, when there is a reaction, the number of moles changes due to the reaction stoichiometry, a different expression is obtained by the residue curves than by the infinite reflux flow rate packed column. It is important to notice that when there is no reaction or the number of stages does not change by the reaction stoichiometry. This expression becomes equal to the Rayleigh distillation expression.

1. Introduction

The increasing processing power provided by computers nowadays allows performing calculations faster, more efficiently and with lower errors. Complex systems of equations can be managed sometimes with success and obtain solutions that fulfil the mass and energy balances. More rigorous is the model, more parameters are required to define exactly the system behaviour. Despite this fact, when the problem is approached, only the main components and the basic thermodynamic data are known. For a first approach several analysis are available to evaluate the feasibility of several process alternatives and obtain a first data of the compositions and flowrates between the units. Most of these analyses are based on the residue curve maps of the system and have been extended to systems that are more complex. Plesu et al. (2008) extended the use of the infinite/infinite analysis to kinetically controlled systems based on the reactive residue curve maps.

The residue curves are called in this way because each curve represents the evolution of a certain initial concentration of the residue in the still of a Rayleigh distillation where the vapour continuously removed is in equilibrium with the liquid. For non-reactive systems, several authors have demonstrated mathematically that the concentrations followed in the residue of the Rayleigh distillation match the concentrations of a distillation packed column operating at infinite reflux flowrate (e.g. Laroche et al., 1992). The advantage of the infinite reflux flowrate assumption is that it simplifies greatly the mathematical model, decreasing the number of equations and of degrees of freedom. If the separation

is feasible under infinite reflux, then with a high enough reflux it must be also feasible. Because working with too difficult separations is not advisable, Bonet-Ruiz et al. (2010) proposed an original way to take into account the difficulty of separation in the residue curve maps based on the number of transfer units.

In the present paper, a new mathematical approach based on the number of transfer unit equation is used to corroborate that the residue curves differential equations model corresponds to the same differential equations model obtained by applying mass balances in a section of a packed column operated at infinite reflux flow rate. It is important to notice that it corresponds to an infinite reflux flow rate and not to an infinite or total reflux ratio.

At total reflux ratio is assumed that no distillate flow rate is collected and all the vapour condensed in the head of the column is returned to the column at a finite flow rate. On the other hand, an infinite reflux flow rate means that the liquid and vapour flow rates descending and ascending respectively in the column have an infinite flow rate but the distillate flow rate is a finite value. The consequence of this assumption is that the feed position has no influence on the column. The feed flowrate, is a finite value and its effect is negligible in the column profile generated by the infinite flow rates inside the column. This allows a first plot of the residue curve map and in a second step to make an analysis taking into account the compositions of the input and output flows to and from the distillation column.

2. Mathematical model

2.1 Rayleigh distillation model

The result from the mass balances for a Rayleigh distillation with several reactions has the following expression:

$$\frac{H}{V} \cdot \frac{d(x_i)}{dt} = (x_i - y_i^*) + \frac{H}{V} \cdot \sum_{j=1}^M (v_{i,j} - x_i \cdot v_{T,j}) \cdot r_j \quad (1)$$

where H is the liquid hold up in the still, V is the vapour flow rate, x_i and y_i^* are the compositions of component i in the liquid and vapour phase in equilibrium with the liquid, t is the time, $v_{i,j}$ is the stoichiometric coefficient of component i in the reaction j, $v_{T,j}$ is the net generation of moles from the reaction j, r_j is the reaction rate of the reaction j out of M reactions taking place simultaneously. There are so many differential equations as components i. The H/V ratio is expressed in units of time. A change of variable for t is applied providing a dimensionless time. In the residue curve map is represented the evolution in the liquid composition, but the time does not appear in the diagram. Therefore this change of variable is "changing the scale of time" but not the liquid composition evolution of each residue curve.

$$d\xi = \left(\frac{V}{H}\right) dt \quad (2)$$

becoming

$$\frac{d(x_i)}{d\xi} = (x_i - y_i^*) + \frac{H}{V} \cdot \sum_{j=1}^M (v_{i,j} - x_i \cdot v_{T,j}) \cdot r_j \quad (3)$$

Some authors (Bonet-Ruiz et al., 2009), instead of using the H/V ratio directly as a time variable, they transform it to obtain it related to a Damköhler number divided by a kinetic constant defined at a certain temperature. But independently of how it is defined this term, for the same overall value of this time variable, the same residue curve is obtained.

2.2 Infinite reflux flow rate model

The mass balance for the rectifying section of a distillation column is the next:

$$V \cdot y_i = D \cdot x_i^D + L \cdot x_i + \sum_{j=1}^M v_{i,j} \cdot r_j \cdot H \quad (4)$$

where D is the distillate flowrate, L is the liquid flowrate inside the column entering the section to which mass balance is applied, x_i^D is the composition of component i in the distillate stream. The overall mass balance is the next:

$$V = D + L + \sum_{j=1}^M v_{T,j} \cdot r_j \cdot H \quad \text{where} \quad v_{T,j} = \sum_{i=1}^N v_{i,j} \quad (5)$$

$$\left(D + L + \sum_{j=1}^M v_{T,j} \cdot r_j \cdot H \right) \cdot y_i = D \cdot x_i^D + L \cdot x_i + \sum_{j=1}^M v_{i,j} \cdot r_j \cdot H \quad (6)$$

$$y_i = \frac{D \cdot x_i^D + L \cdot x_i + \sum_{j=1}^M v_{i,j} \cdot r_j \cdot H}{D + L + \sum_{j=1}^M v_{T,j} \cdot r_j \cdot H} \quad (7)$$

$$y_i = \frac{\frac{D}{L} \cdot x_i^D + \frac{L}{L} \cdot x_i + \sum_{j=1}^M v_{i,j} \cdot r_j \cdot \frac{H}{L}}{\frac{D}{L} + \frac{L}{L} + \sum_{j=1}^M v_{T,j} \cdot r_j \cdot \frac{H}{L}} \quad (8)$$

As L is infinite and D is a finite number, then $D/L=0$, $L/L=1$ and H/L correspond to the residence time on the column section:

$$y_i = \frac{x_i + \tau \cdot \sum_{j=1}^M v_{i,j} \cdot r_j}{1 + \tau \cdot \sum_{j=1}^M v_{T,j} \cdot r_j} \quad (9)$$

Notice that when there is no reaction or the residence time is zero, then

$$y_i = x_i \quad (10)$$

which matches with the well known fact that at infinite reflux, the mass balances correspond to the vapour compositions. The operation line in the McCabe-Thiele diagrams for binary systems becomes the diagonal.

It is traditional for chemical engineers to model packed columns through the concept of transfer units (NTU) according to a dimensionless expression (Taylor and Krishna, 1993). The NTU depends only on the composition column profile and it does not depend on the characteristics and performance of the packing:

$$\frac{dy_i}{d\zeta} = NTU_T \cdot (y_i^* - y_i) \quad (11)$$

where y^* is the vapor composition in equilibrium with the bulk liquid (x) and y is the vapor composition in contact with the bulk liquid (x). The difference between y and y^* is the driving force for the components transfer from the liquid phase (x) to the vapor phase (y), $\zeta=z/L_c$ is a dimensionless height ratio where z is height and L_c represents the overall height of packing. This expression is used when the total number of transfer units along the overall height of the column is fixed. The number of transfer units that are at each value of ζ are:

$$NTU = NTU_T \cdot \zeta \quad (12)$$

In this way, the dependence of the composition with NTU is as following:

$$\frac{dy_i}{dNTU} = (y_i^* - y_i) \quad (13)$$

For a non reactive column, substituting equation 10 in equation 13:

$$\frac{dx_i}{dNTU} = (y_i^* - x_i) \quad (14)$$

The similitude of this equation with the residue curve expression without reaction is obvious. The dimensionless time of the residue curve can be directly related to the number of transfer units (NTU) for non reactive systems.

$$d\xi = -dNTU \quad (15)$$

For a reactive column, substituting equation 9 in equation 14, the general expression is obtained:

$$\frac{dy_i}{dNTU} = \frac{dy_i}{dx_i} \cdot \frac{dx_i}{dNTU} = \left(y_i^* - \frac{x_i + \tau \cdot \sum_{j=1}^M v_{i,j} \cdot r_j}{1 + \tau \cdot \sum_{j=1}^M v_{T,j} \cdot r_j} \right) \quad (16)$$

As the reflux flow rate inside the column is infinite and the mass balance must be fulfilled, the same variation of the composition in the liquid entering in the mass balance limits must be equal to the vapour going out. As it can be assumed that the reaction takes place only in the liquid phase then

$$\frac{dy_i}{dx_i} = 1 \quad (17)$$

For non reactive distillation columns, expression 16 is equivalent to the Rayleigh equation, as stated previously:

$$\tau = 0 \text{ then } \frac{dx_i}{dNTU} = (y_i^* - x_i) \quad (18)$$

For reactive columns where there is no change in the total number of moles due to the reactions, $v_{T,j} = 0$, expression 16 becomes mathematically equal to the Rayleigh expression with the same simplification, where the constant H/V corresponds to τ :

$$\frac{d(x_i)}{d\xi} = (x_i - y_i^*) + \frac{H}{V} \cdot \sum_{j=1}^M v_{i,j} \cdot r_j \quad (19)$$

$$\frac{dx_i}{dNTU} = \left(y_i^* - x_i - \tau \cdot \sum_{j=1}^M v_{i,j} \cdot r_j \right) \quad (20)$$

However, both expressions become different, when the total number of moles changes due to the reactions:

$$\frac{d(x_i)}{d\xi} = (x_i - y_i^*) + \frac{H}{V} \cdot \sum_{j=1}^M (v_{i,j} - x_i \cdot v_{T,j}) \cdot r_j \quad (3)$$

$$\frac{dx_i}{dNTU} = \left(y_i^* - \frac{x_i + \tau \cdot \sum_{j=1}^M v_{i,j} \cdot r_j}{1 + \tau \cdot \sum_{j=1}^M v_{T,j} \cdot r_j} \right) \quad (21)$$

The difference between them can be written as:

$$\left(\frac{\tau^2 \cdot \sum_{j=1}^M v_{T,j} \cdot r_j \cdot \left(\sum_{j=1}^M v_{i,j} \cdot r_j - \sum_{j=1}^M v_{T,j} \cdot r_j \cdot x_i \right)}{\left(1 + \tau \cdot \sum_{j=1}^M v_{T,j} \cdot r_j \right)} \right) \quad (22)$$

3. Verification for the TAME synthesis

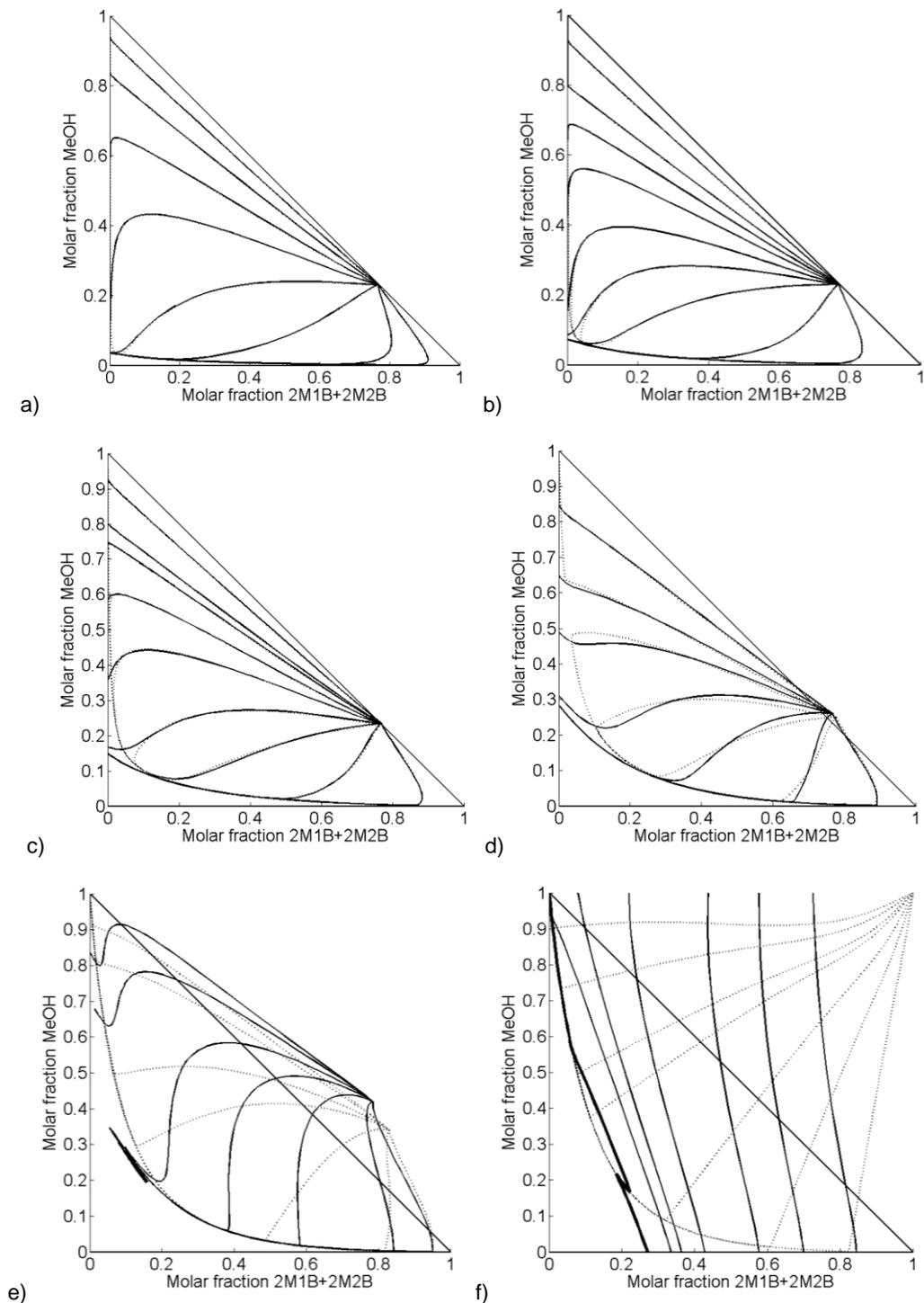


Figure 1: Reactive residue curve map (discontinue line) and infinite reflux column profiles (continuous line) for the TAME reactive distillation at 1 bar and a value of H/V of a) 0.0001, b) 0.001, c) 0.01, d) 0.1, e) 1 and f) 100.

Figure 1 shows the reactive residue curve maps and the column profiles for an infinite reflux packed column. Comparing the residues curves with the column profiles, it is observed that the behaviour is quite similar at low H/V values. The reason is that the reaction term is small compared to the separation term. The main difference is that for the residue curves the TAME singular point moves towards the middle of the graph due to the reaction and for the column profiles becomes outside the graph. The main implication of this fact is that the reactive column bottoms can be composed of a TAME/methanol mixture free of the volatile isoamylenes. Both models show that as the retention time H/V increase, then the maximum purity of TAME that can be collected at the bottoms decreases due to TAME decomposition.

For middle values of H/V, the differences between both models become more obvious (figure 1e). The unstable node becomes out of the graph in both models but its position is different. The profiles rich in isoamylenes tend for both models to the same boundary. But for the column profiles rich in methanol it is observed a maximum concentration of TAME in the middle of the column which decreases and reaches a bottom composition with less volatile isoamylenes. The point of enrichment in TAME of the profiles coincides with the boundary line of the residue curves at this value of H/V.

The most interesting results are for very high retention times H/V (figure 1f). The reactive residue curves show that the simple Rayleigh distillation tends to behave just like a simple reactor when the reaction term is predominant over the separation term. A section of the residue curve follows the chemical equilibrium. But the reactive distillation column profiles at infinite reflux behave quite different than a simple reactor although a part of the column profile can be at chemical equilibrium. For mixtures rich in isoamylenes, the column profile contains an almost constant quantity of isoamylenes and the TAME is collected at the bottoms and the methanol at the top, both of them mixed with a great quantity of isoamylenes. For mixtures with less isoamylenes, the bottoms collected are a mixture of isoamylenes and TAME free of methanol but part of the column profile is in chemical equilibrium. In a limit situation, when the column profile follows the chemical equilibrium curve, methanol is collected at the top of the column, while towards the lower part of the column, the profile moves away from chemical equilibrium and a mixture of isoamylenes and TAME is collected at the bottom. TAME concentration is lower than the maximum to be obtained when the reaction reaches the chemical equilibrium (thicker line in Figure 1f).

4. Conclusions

The residue curve maps are useful at the early stages of feasibility analysis because they match the column profile of a distillation column operated at infinite reflux. Unfortunately, this match is not true for reactive distillation columns taking into account a kinetic where the number of moles is not constant. For low retention times in the column, the deviations of the residue curves from the column profiles are not very important. But as the retention time increases, the residue curves calculated as a Rayleigh distillation tend to behave like the profile of a simple reactor.

References

- Bonet-Ruiz A.E., Bonet J., Bozga G., Llorens L.J., Plesu V., 2010, Number of transfer units information on residue curve maps., *Chemical Engineering Transactions*, 21, 1417-1422.
- Bonet-Ruiz A.E., Bonet-Ruiz J., Plesu V., Bozga G., Llorens L.J., Costa L.J., 2009, New Contributions to Modelling and Simulation of TAME Synthesis by Catalytic Distillation, *Chemical Engineering Transactions*, 18, 959-964.
- Laroche L., Bekiaris N., Andersen H.W, Morari M., 1992, Homogeneous Azeotropic Distillation: Separability and Flowsheet Synthesis, *Ind. Eng. Chem. Res.*, 31, 2190-2209.
- Plesu A.E, Bonet J., Plesu V., Bozga G., Galan M.I., 2008, Residue curves map analysis for tert-amyl methyl ether synthesis by reactive distillation in kinetically controlled conditions with energy-saving evaluation, *Energy*, 33, 1572-1589.
- Taylor R., Krishna R., 1993, *Multicomponent Mass Transfer*, John Wiley & Sons Inc., New York.