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Infinite/Infinite Analysis as a Tool for an Early Oriented Synthesis of a Reactive Pressure Swing Process

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Abstract

The study deals with the methyl acetate (MeAc) transesterification with ethanol (EtOH) to produce methanol (MeOH) and ethyl acetate (EtAc). A first screening has shown that a reactive pressure swing process would have the best performance regarding this reaction. This study provides insights on this process behaviour and control via the infinite/infinite analysis. The infinite/infinite analysis allows checking the interrelation of the system streams without any column design consideration. Unfeasible regions, low limit values, multiplicity regions, discontinuities, control difficulties, recommendable operation conditions and column profiles combination are predicted and discussed. All this information is useful to establish an early and suitable system design strategy.

Keywords: infinite/infinite analysis, reactive distillation, pressure swing

1. Introduction

The methyl acetate (MeAc) transesterification with ethanol (EtOH) would allow the recycling and revalorization of the residual methanol (MeOH)/methyl acetate (MeAc) azeotrope from the polyvinyl alcohol industry (España, 1996). A reactive distillation process has been selected to perform this reaction (Thery, 2002). The reactive residue curve map exhibit a boundary line and the reaction products are located in two different distillation regions (figure 1a). The boundary line composition is sensible to pressure changes and a pressure swing is presented as a good option to cross this boundary line (figure 1b). The high pressure reactive column produces pure EtAc (residue) and MeOH /MeAc azeotrope (distillate) while the MeOH is recovered in the second non reactive atmospheric column (residue). The second column distillate is recycled into the first one.

The sensitive variables of this process are selected according to a degrees of freedom analysis for the overall system. The selected sensitive variables are: the non reactive

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column residue flow rate (B2), the non reactive column distillate flow rate (D2) and the reactive column operating pressure (P1). The influence of each sensitive variable is determined individually while all other parameters are fixed to a common set point. The sensitivity analysis is generally performed using rigorous simulation. But, this approach requires to know the design of the column. The infinite/infinite analysis is another approach which can also give important insights on the process behaviour and controllability before any column design consideration (Petlyuk, F. and Avet'yan, V., 1971; Bekiaris, N. and M. Morari, 1996; Güttinger, T.E. and M. Morari, 1999; Ulrich, J., 2002).

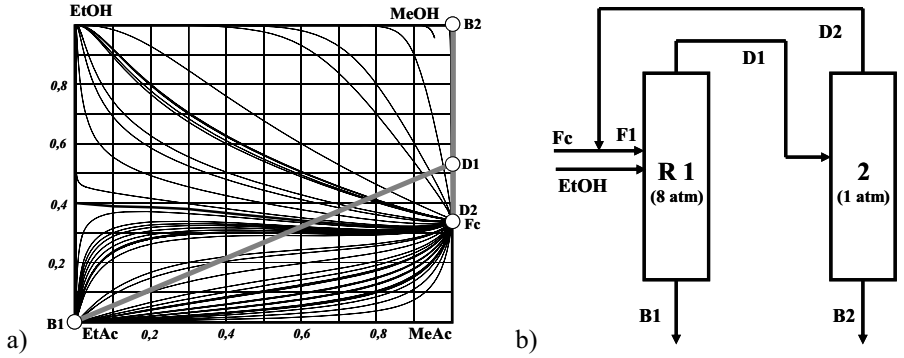


Figure 1. Studied transesterification system: (a) residue curve map and (b) system sketch.

The simplifying hypothesis of an infinite column reflux enables to consider the column profile as a section of a reactive residue curve. The simplifying hypothesis of an infinite column length implies that the column profile contains a singular point (pure component, azeotrope or reactive azeotrope). According to whether the singular point is an unstable node, a stable node or a saddle point, the column profile is said to be type I, II or III respectively.

2. Infinite/infinite analysis

For both columns, the set point used is the bottom product as pure component and the distillate at the azeotropic composition corresponding to the column pressure (figure 2). The pressure is set to 8 atm for the first column and to 1 atm for the second one. Figure 2 simplifies the reactive residue curve map for illustrative proposals by only representing the residue curves corresponding to the edges and the boundary line at 8 atm. The boundary line divides the reactive residue curve map in two distillation regions: A and B. When the pressure decrease the distillation region B becomes smaller. The diagonal represents the overall mass balance of the system: the first column bottom (EtAc), overall feed (OV) and the second column bottom (MeOH). The overall feed to the system (OV) is the intersection of the overall mass balance and the mixture of the reactive EtOH and crude MeAc/MeOH azeotrope. The mass balance for the first column is at the distillation region B between the bottom (EtAc) and the distillate (MeAc/MeOH azeotrope at 8 atm). The mass balance for the second column is at the MeAc/MeOH edge, between the bottom (MeOH) and the distillate (MeAc/MeOH azeotrope at 1 atm).

The pinch points fixed for the column profiles types of the first column are the next: (i) when type I, then the MeAc/MeOH azeotrope at 8 atm is collected by the distillate; (ii) when type II, then pure EtAc is collected at the bottom; (iii) when type III, then the column profile contains pure MeAc or EtOH/EtAc azeotrope. When the first column distillate is on the MeAc/MeOH edge, then the second column performs a binary distillation and the pinch points for the column profiles types are: (i) when type I, then the MeAc/MeOH azeotrope is collected by the distillate; (ii) when type II, then the MeOH is collected at the bottom. The combinations of column profiles types on the system are indicated together, for instance, type II-II means first column profile type II (pure EtAc at first column bottom) and second column profile type II (pure MeOH at second column bottom).

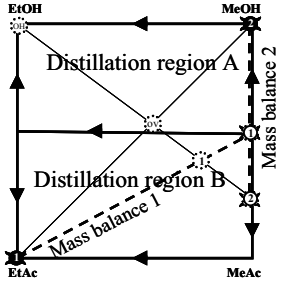


Figure 2. Mass balances representation at set point condition.

2.1 Influence of the column bottom flow rates at D2 flow rate constant.

The bottom flow rates of both columns are related by the system overall mass balance. An increase of the first column bottom flow rate (B1) is equivalent to the decrease of the second bottom flow rate (B2). The influence of the bottom flow rate on the bottom purities is the next: an increase of B1 flow rate impurifies the EtAc while the MeOH is collected pure at B2 (figure 3a). An increase of B2 is expected to produce the contrary: pure EtAc and non pure MeOH; but this is not possible due the first column distillate composition (figure 3b). The influence of the bottom flow rate on the distillates compositions is as follows: When B1 increase (or B2 decrease), then D2 must be enriched in MeOH to keep the D2 flow rate constant, accordingly to the lever rule on the mass balance of the second column (figure 3a). When B2 increase, then D1 must be enriched in MeOH to keep the D2 flow rate constant but it is not possible because the D1 composition should cross the boundary line to the distillation region A. The first column bottom (EtAc) is at region B and its distillate must be also on region B otherwise there would not be possible a residue curve from the distillate to the bottom and the operation is unfeasible (figure 3b).

The set point proposed lies at the limit and a B2 increase leads to an unfeasible situation. A security margin must be taken to keep the system controllable. A first option is to accept B1 to be non pure and to operate at B1 flow rates higher than the optimal. The first column distillate is fixed at the azeotropic composition (type I) and the second column bottom is fixed at pure MeOH (type II). A second option is to accept more MeOH on D1 and operate at D1 flow rates higher than the optimal (type II-I) to allow B2 to be non pure. The infinite/infinite analysis for the type I-II is drawn on figure 4a (lines). Simulations are performed at a distillate flow rate higher than the

minimal and at the optimal point presents a discontinuity due to the change from the first to the second option (from profile II-I to profile I-II). The discontinuity can be clearly identified at the distillate composition sensitivity analysis (figure 4b).

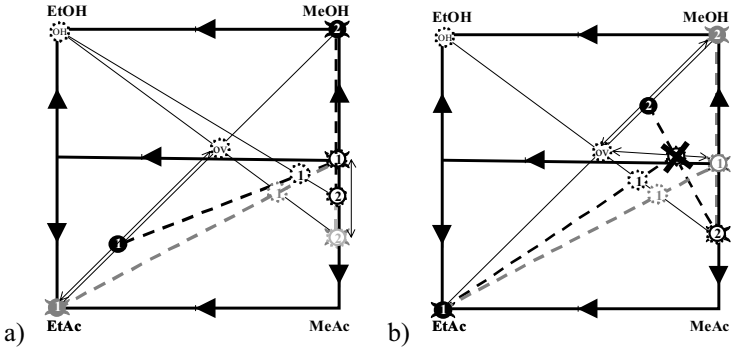


Figure 3. Mass balances: (a) B1 increase, (b)B2 increase.

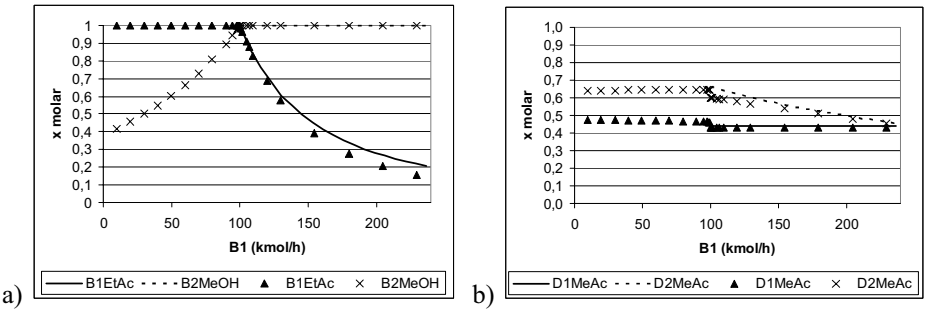


Figure 4. Bottom flow rate sensitivity analysis: (a) products purities, (b) influence on MeAc of distillates. (Infinite/infinite analysis: lines; simulation: points).

2.2 Influence of the column distillate flow rate at bottom flow rate constant.

To study the influence of the distillate flow rate one of the bottom flow rates must be fixed (B1 or B2) and consequently all the product purities and flow rates (B1 and B2) become fixed by the overall mass balance of the system. This means that the distillate flow rate has no influence on the bottom purities and its value must be fixed from an operational and performance point of view. As the bottoms are fixed, a decrease of D2 must results in a D1 richer in MeOH or D2 richer in MeAc. If the operational point of both distillates is at the azeotrope compositions, the decrease of D2 is unfeasible because the distillate compositions lie in a different distillation region than their corresponding bottom compositions (figure 5a). To avoid this problem, one of the distillate compositions must be out the azeotropic composition to allow the possible fluctuations and the distillate flow rate must be higher than the minimal value.

On the other hand, an increase of D2 can be compensated by a D1 richer in MeAc, by a D2 richer in MeOH or also by multiple combinations of variation of both distillate purities (figure 5b). This means that a column profile type II-II produces multiplicities (figure 6a-b). Both distillate compositions can change freely without changing any

degree of freedom leading to an uncontrollable system. From a control point of view, one of the column profiles must be of type I to fix one of the distillate compositions at its azeotropic composition and avoid the multiplicities.

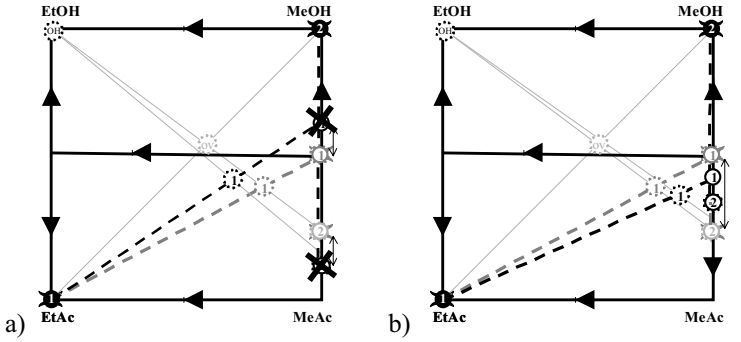


Figure 5. Mass balances: (a) D2 decrease, (b) D2 increase.

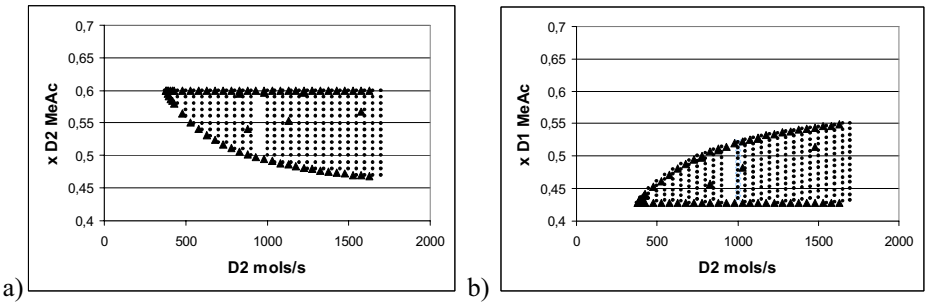


Figure 6. Distillate flow rate sensitivity analysis: (a) multiplicities on D2, (b) multiplicities on D1.

2.3 Influence of the reactive column operating pressure

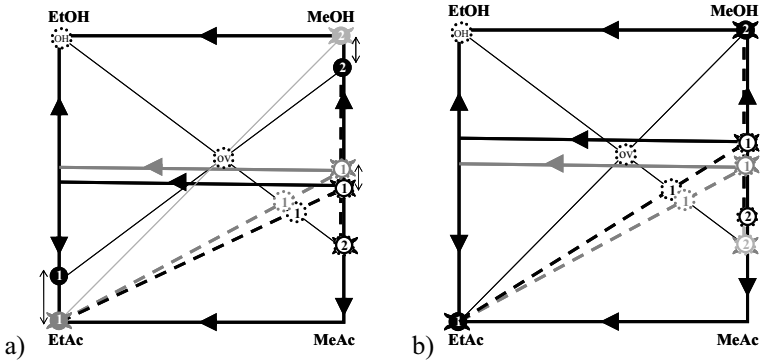
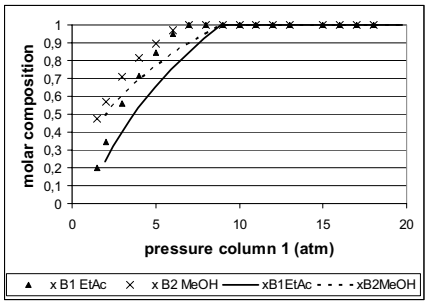


Figure 7. Mass balances: (a) decrease of P1, (b) increase of P1.

To manage to decrease the pressure in the first column, the system profiles must be of type I-I or III-I and non pure bottom must be accepted (figure 7a). A pressure increase with profiles II-II produces a multiplicity region: there are several distillate composition combinations that fulfil the D2 flow rate constant (figure 7b). To avoid these

multiplicities, one of the column profiles must be of type I. The pressure sensitivity analysis on the bottom and the distillate compositions is represented on figures 8a and 8b.

a)



b)

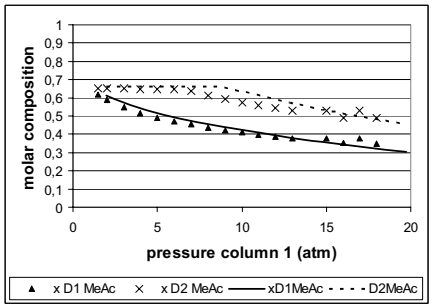


Figure 8. First column pressure sensitivity analysis: (a) bottom compositions, (b) distillate compositions.

3. Conclusions

From the infinite/infinite analysis has been observed that (a) B1 must be non pure to avoid operate at the limit of an unfeasible region, (b) one of the distillate compositions must be fixed to avoid multiplicities and (c) the product purity depends on bottom flow rates and is independent of the distillate flow rates. On figure 9, a feasible operation condition is shown respecting the last points and using an overall feed poorer in EtOH than the reaction stoichiometry. An increase of B1 flow rate produces column profiles type I-II and a decrease of B1 produces type III-I.

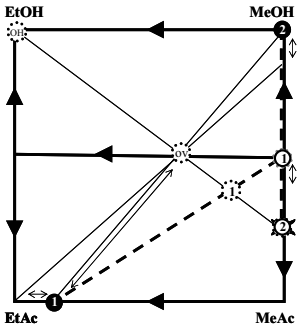


Figure 9. A feasible operation condition.

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