

SEPARATION OF A TERNARY HOMOAZEOTROPIC MIXTURE BY PRESSURE SWING BATCH DISTILLATION

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The separation of a ternary mixture (n-pentane-acetone-cyclo-hexane) with two binary minimum azeotropes is studied by feasibility studies and rigorous simulation calculations. By the feasibility studies based on the analysis of the vessel paths in the residue curve maps at the two different pressures (P^I , P^{II}) the separation steps are determined for the two configurations studied (batch stripper (BS), double column batch stripper (DCBS)). The rigorous calculations are performed by the CCDColum professional dynamic flow-sheet simulator. For the DCBS two operational policies are compared.

Keywords: Batch Distillation, Separation of Azeotropes, Pressure Swing Distillation, Batch Column Configurations, Feasibility Study, Rigorous Process Simulation

Introduction

Distillation is the separation method most frequently applied in the chemical industry, which is based on the difference of volatility of the components of a liquid mixture. For the separation of the two components (A and B) forming an azeotrope a special distillation method must be applied such as the pressure swing distillation (PSD), extractive or heteroazeotropic distillation. The pressure swing distillation is the least studied from these three methods.

Batch distillation (BD) has always been an important part of seasonal, uncertain or low capacity and high-purity chemicals' production. It is a process of key importance in the pharmaceutical and several other industries and in the regeneration of waste solvent mixtures.

Many mixtures form an azeotrope, whose position can be shifted substantially by changing system pressure, that is, a pressure sensitive azeotrope. (At some pressure the azeotrope may even disappear.) This effect can be exploited to separate azeotropic mixtures without the application of a separating agent by the so-called pressure swing distillation.

LEWIS (1928) was the first, who suggested distilling the azeotropic mixtures by pressure swing distillation. This process has been suggested to separate azeotropic mixtures by e.g. BLACK (1980), ABU-EISHAH and LUYBEN (1985), CHANG and SHIS (1989). More details about the pressure swing continuous distillation can be found in books of VAN WINKLE (1967) and WANKAT (1988).

KNAPP et al. (1992) developed a new process, in which pressure swing continuous distillation was combined with entrainer addition. The possibility of the application of an entrainer for the separation of binary

azeotropic mixtures increases to a large extent the number of mixtures separable by this process. On the other hand the separation of the original components from the entrainer means an additional task.

PHIMISTER and SEIDER (2000) studied the separation of a minimum azeotrope (THF-water) by semi-continuous PSD and reverse-batch operation (batch stripping). In the semicontinuous column better performance was achieved than in the batch stripper. They also investigated the control and other practical aspects of these configurations, and their performance was compared with that of a continuous system, as well. WASYLKIEWICZ et al. (2003) developed an algorithm which allows the variation of compositions of azeotropes with pressure to be tracked, and all new azeotropes that appear within specified pressure range to be found.

To our knowledge REPKE et al. (2006) were the first, who investigated experimentally the application the pressure swing distillation in batch. They studied the separation of a minimum boiling, homoazeotropic mixture (acetonitrile-water) by pressure swing distillation in a batch rectifier and in a stripper with pilot-plant experiments and rigorous simulations. The aim of these authors was rather the experimental study of the pressure swing batch distillation than the exhausting theoretical study of the feasibility of the process. The above authors have not studied either the separation of ternary mixtures.

The aim of our work is to study the separation of a ternary mixture (n-pentane-acetone-cyclo-hexane) forming two binary minimum azeotropes by

- feasibility studies and
- rigorous simulation calculations.

By the feasibility studies based on the analysis of the vessel paths in the residue curve maps at the two

different pressures (P^I , P^{II}) the separation steps are determined for the two configurations studied (batch stripper (BS), double column batch stripper (DCBS)). The rigorous calculations are performed by the CCDColumn professional dynamic flow-sheet simulator.

Feasibility method

First the method applied for the assessment of feasibility is briefly presented, then the feasibility of different column configurations will be investigated.

When making feasibility studies we suppose that maximal (perfect) separation can be produced. This involves the following assumptions:

- infinite number of stages,
- very high reflux/reboil ratio,
- negligible liquid plate hold-up,
- negligible vapour hold-up.

The method is based on the determination of the feasible compositions of products (continuously withdrawn) and those of residues (remaining in the vessel).

Since we consider ternary mixtures for the feasibility analysis, we study the residue curve maps.

Classification of residue curve maps

The concept of a residue curve map was first introduced by SCHREINEMAKERS (1901). A residue curve map is a triangular diagram (with the pure components at each vertex) which shows the locus of the liquid-phase composition as it varies with time during a simple distillation process. The trajectories of the various residue curves have a directional character which is represented by arrows (pointing toward increasing temperatures, and also increasing time during the simple distillation process).

A mathematical description is given by DOHERTY and PERKINS (1978), who developed a set of nonlinear ordinary differential equations, which model the liquid composition profiles as a function of time.

The most recently applied tools for the studying of the separation of ternary mixtures is the residue curve map analysis.

GURIKOV (1958) was actually the first to derive the rule of azeotropy and propose a thermodynamic topological classification of ternary mixtures.

Later, SERAFIMOV (1970) defined the topological classification of ternary mixtures into 26 diagrams.

An even more detailed classification is proposed by MATSUYAMA and NISHIMURA (1977), who also rank the components in the order of their boiling temperatures light(*L*), intermediate(*I*), and heavy(*H*). This classification includes 113 diagram classes of which 87 are graphically presented by DOHERTY and CALDAROLA (1985).

Nowadays these two methods are applied for the classification of ternary mixtures.

Neither of these two classification methods takes into consideration that with the variation of pressure:

- the azeotropic composition can considerably vary,
- the azeotrope may even disappear,
- the volatility order of components may change.

First MODLA et al. (2008) recognised the necessity of modifying these methods in the case of mixtures whose components form pressure sensitive azeotrope(s).

The classification of residue curve maps by MATSUYAMA and NISHIMURA is as follows:

The three digits signify the type of binary azeotropes on the *L-I*, *I-H*, and *H-L* edges of the triangle, respectively. The numbers are assigned by the following rules:

- 0: no azeotropes,
- 1: binary minimum-boiling azeotrope, node (must be unstable)
- 2: binary minimum-boiling azeotrope, saddle,
- 3: binary maximum-boiling azeotrope, node (must be stable)
- 4: binary maximum-boiling azeotrope, saddle

The single letter after the first three digits signifies the type of ternary azeotrope.

- m: minimum-boiling ternary azeotrope (must be an unstable node)
- M: maximum-boiling ternary azeotrope (must be a stable node)
- S: intermediate boiling ternary azeotrope (must be a saddle)

For the PSBD the classification of the RCM (eg by MATSUYAMA and NISHIMURA (1977, M&N) by SERAFIMOV (1970, S)) must be extended. The pressure sensitivity of an azeotrope must be always indicated even if there is no change in the type of RCM since it has influence on the separation method to be applied. (We write 'P' after the number of M&N if it is pressure sensitive). If the type of RCM varies it must be given for both pressures.

Feasibility region of the separation (FR) is defined as follows:

All feed compositions, from where all components can be purely recovered by maximal separation at the given pressure or by applying pressure swing.

The regions outside the FR can be

- conditionally feasible: from where FR can be reached by a preparatory step (distillation/stripping or addition of E)
- infeasible: from where a FR can not be reached.

Column configurations

The pressure swing batch distillation (PSBD) can be realised in configurations with either one or two column section(s). Because of the occurrence of the azeotrope the two pure components must be produced at two different pressures.

The different pressures can be applied

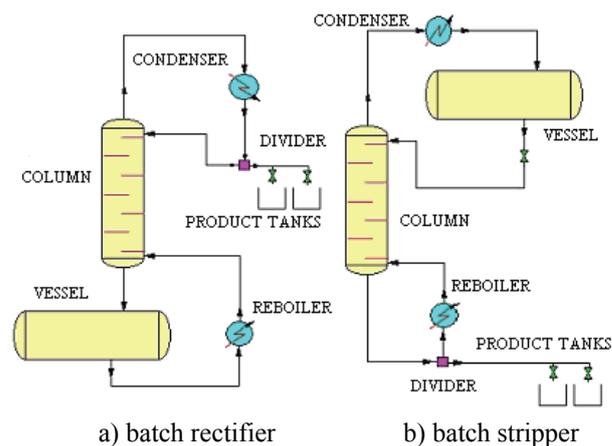
- at different times (in the same column section) or
- in different column sections (at the same time).

Configurations with one column section

In this case the pressure swing can be performed only in time. Hence there must be at least two sequential production steps at different pressures in one cycle.

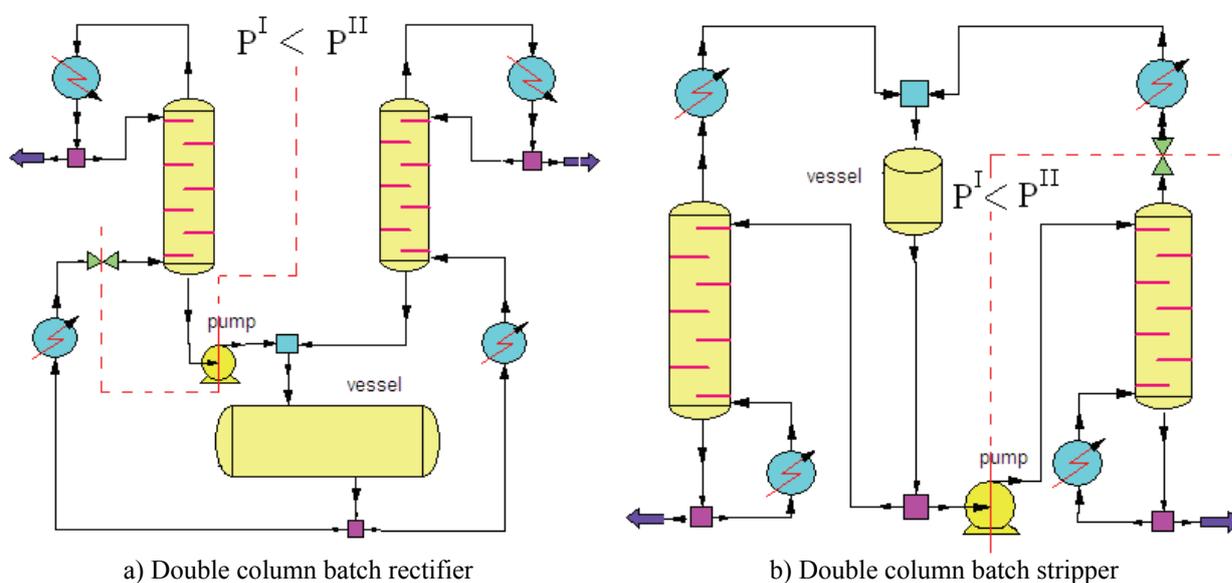
The pressure swing batch distillation (PSBD) can be realised in batch rectifier (BR) or batch stripper (BS).

The feed is charged into the bottom (rectifier, Fig. 1a), or top vessel (stripper, Fig. 1b). (In Fig. 1a for the sake of better comparability the two functions of the reboiler (storage(vessel) and evaporation(total reboiler)) are separated.) Continuous product withdrawal is performed from the top (rectifier) or the bottom (stripper). Depending on the feed composition and the type of the azeotrope In the case of a binary mixture A - B the first (and the following) product withdrawn can be pure A , pure B or the azeotropic mixture (MODLA and LANG, 2008).



a) batch rectifier b) batch stripper

Figure 1: Single column configurations



a) Double column batch rectifier

b) Double column batch stripper

Figure 2: Double column configurations

Double column configurations

The two different pressures are applied in different column sections. In the case of a ternary mixture it is theoretically possible to produce three pure components in a single production step. (Two components are withdrawn continuously and the third remains in the vessel.)

Feasibility studies

The vapour-liquid equilibrium data of the ternary mixture (n-pentane-acetone-c-hexane) studied are given in Tables 1 and 2. The components of this mixture form two minimal boiling point binary azeotropes. One of them (acetone-n-pentane) is pressure sensitive, whilst the other one (c-hexane-acetone) is not.

The c-hexane (H) and acetone (I) vertices are stable nodes, while the n-pentane (L) vertex is a saddle. (Fig. 3a). The azeotrope I - H (Az_{IH}), which is not pressure sensitive, is a saddle. The azeotrope L - I (Az_{LI}), is the unstable

node, its location considerably depends on the pressure (Fig. 3b). The (extended) M&N class of the mixture: 1P-2-0.

Table 1: Boiling points of the pure components at the two different pressures

	$P^I=1.01$ bar	$P^{II}=10$ bar
n-pentane (L)	36.07 °C	124.74 °C
acetone (I)	56.25 °C	142.98 °C
c-hexane (H)	80.72 °C	182.31 °C

Table 2: Azeotropic data (temperature, composition) at the two different pressures

	1.01 bar	10 bar
n-pentane-acetone	32.75 °C	116.99 °C
	0.75-0.25	0.67-0.33
acetone-c-hexane	53.95 °C	140.27 °C
	0.77-0.23	0.79-0.21

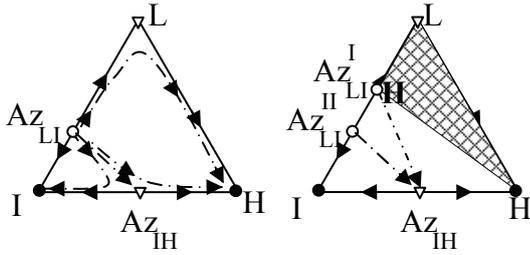


Figure 3: Sketch of the residue curve map (a) and PSBD regions (b)

Separation steps for the one column configuration

a. Charge composition in the region H:

1. Removal of component *H* from the mixture with a batch stripper (the residue is mixture *L-I*).
2. Separation *L/I* with pressure swing batch stripping.

b. Charge composition outside the region H:

In this case pressure swing must be applied already in the ternary area, as well:

0. Preparation step: the vessel composition is brought into the area of the triangle $Az_{LI}^I-Az_{LI}^{II}-Az_{IH}$.
1. In the first production series we get alternately pure components *H* and *I* as bottoms, until the vessel composition reaches the edge *L-I*.
2. In the second production series we get alternately pure components *I* and *L* as bottoms.

Separation steps for the double column configuration

a. Charge composition in the region H:

1. Removal of component *H* from the mixture by operating one of the two columns (the residue is mixture *L-I*).

b. Charge composition outside the region H:

0. Preparation step: the vessel composition is brought into the area of the triangle $Az_{LI}^I-Az_{LI}^{II}-Az_{IH}$ by operating only one of the columns.
1. Production of components *H* and *I* as bottom products of the two columns (the vessel residue is mixture *L-I*).
2. Production of components *L* and *I* as bottom products of the two columns.

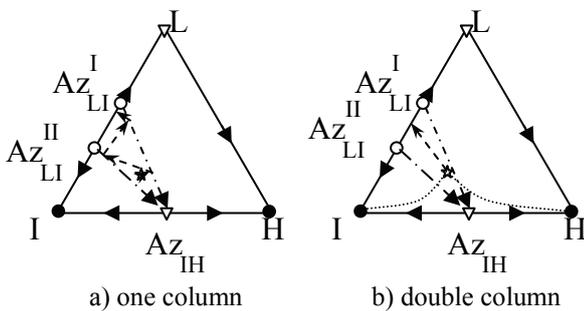


Figure 4: Vessel path (---) and x-profiles (...)

We investigate with rigorous simulation only the double column configuration since in the case of the one column configuration if the composition of the charge is located:

- in Region H, the ternary separation can be reduced to a binary one,

- outside Region H, sufficient recoveries can be only produced with a lot of separation steps beginning with pressure change.

Rigorous simulation results

The amount of charge: 1 m³ (13.42 kmol). Its composition is shown in Table 3.

Table 3: The composition of the charge

	<i>n</i> -pentane (<i>L</i>)	acetone (<i>I</i>)	<i>c</i> -hexane (<i>H</i>)
mol%	19.3	64.5	16.2
vol%	25.6	54.3	20.1

The prescribed purity for both products: 98 mol%.

Both columns of the DCBS contains 40 theoretical plates ($N^I = N^{II} = 40$). The pressures: $P^I = 1$ bar, $P^{II} = 10$ bar, the liquid hold-up: 2 dm³/plate.

The liquid flow rate leaving the common top vessel, which is divided between the two columns: $L_{total} = 10$ m³/h (cca. 11.6 kmol/h). (The reboil ratios are not fixed.)

At different liquid division ratios ($\eta = L_I/L_{total}$) the optimal operation conditions (where the energy consumption is minimal) are determined. Two different operational policies are studied and compared:

1. The production is begun in each column immediately when the bottoms reaches its prescribed purity (Policy 1).
2. The production is begun in both columns at the same time when both bottoms have already reached the prescribed purity (Policy 2).

In both cases two production steps can be performed:

1. Production of *H* and *I*
2. Production of *L* and *I*

In our case (at the given charge composition) at the end of Step 1 the amount of residue is so small, that this residue can not be separated in the given (industrial size) installation therefore only Step 1 is performed.

The evolution of the composition of vessel and two product tanks in Step 1 is shown for Policy 1 ($\eta = 0.6$) in Figs. 5 and 6a-b, respectively. Depending on the value of the bottoms composition the values of reboil ratios were varied with a PID controller whose parameters ($A_P^I = 0.1$, $T_I^I = 0.9$ s, $T_D^I = 13$ s, $A_P^{II} = 0.1$, $T_I^{II} = 0.9$ s, $T_D^{II} = 13$ s) were selected by trials.

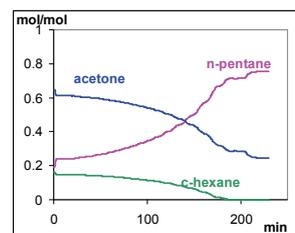


Figure 5: The evolution of the vessel liquid composition

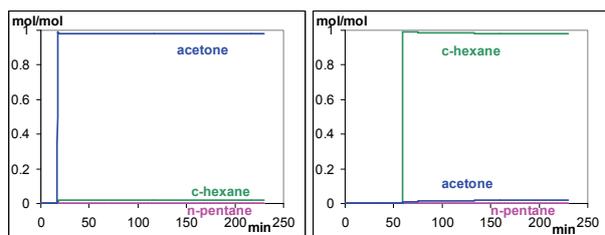


Figure 6: The evolution of the two product compositions

At the end of Step 1 the whole amount of c-hexane is recovered. The vessel liquid of low quantity contains a binary mixture of n-pentane-acetone.

The production is begun earlier in Column I (Fig. 6a) than in Column II (Fig. 6b). The purity of acetone in product tank I remained at the prescribed value (0.98). The purity of the c-hexane slightly decreased in time but at the end it was near to its prescribed value (0.981).

Policy 1

Step 1: Production of *H* and *I*

On the increase of the liquid division ratio the recovery of product *H* increases and that of product *I* decreases (Fig. 7a). The average recovery slightly increases. The average energy consumption has a minimum at $\eta = 0.55$ (Fig. 7b).

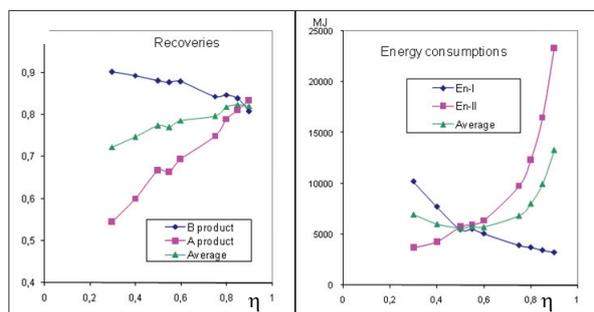


Figure 7: The effect of the liquid division ratio η on the a) recoveries b) energy consumptions (Policy 1)

Policy 2

Step 1: Production of *H* and *I*

On the increase of the liquid division ratio the recovery of product *H* increases and that of product *I* decreases (Fig. 8a). The average recovery slightly increases. The average energy consumption has a minimum at $\eta = 0.65$ (Fig. 8b). It must be still noted that for liquid division ratios smaller than 0.6 the prescribed product purity was not reached at all.

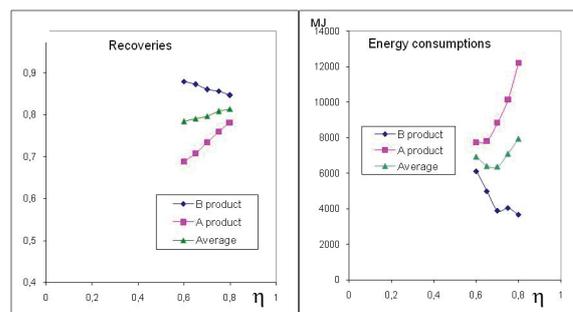


Figure 8: The effect of the liquid division ratio, η on the a) recoveries b) energy consumptions (Policy 2)

Comparison of the different operational policies

By the two operational policies similar recoveries were produced but the energy consumption was lower by the operational Policy 1 (Fig. 9).

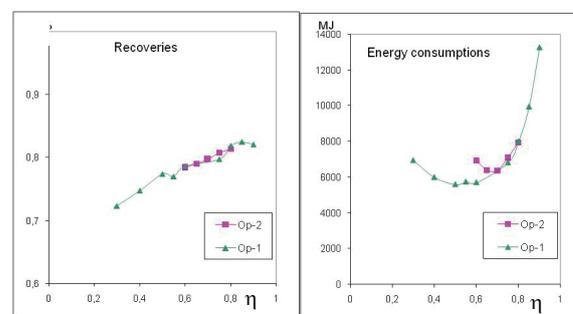


Figure 9: Comparison of the two operational policies

A further advantage of this operational policy is that it can be applied in a wider liquid division ratio which is favourable from the point of view of the control of the process. The location of the minimum of the average energy consumption is different at the two operational policies.

Conclusion

The separation of a ternary mixture (n-pentane-acetone-cyclo-hexane) with pressure swing batch distillation was investigated by feasibility studies and rigorous simulation calculations.

By the feasibility studies based on the analysis of the vessel paths in the residue curve maps at the two different pressures (P^I , P^{II}) the separation steps are determined for the two configurations studied (batch stripper (BS), double column batch stripper (DCBS)). We stated that it depends on the charge composition that the application of the one or the double column configuration is more favourable.

The rigorous simulation calculations were performed with the CCDColumn program of the CCDColumn professional dynamic flow-sheet simulator package for a given separation problem. For the double column batch stripper two different operational policies were compared. By the two policies similar recoveries were reached. However the operational policy by which in the column whose bottoms has already reached the prescribed purity we begin the production immediately (before reaching the prescribed purity in the other column) provided more favourable results from the point of view of energy consumption. A further advantage of this operational policy is that it can be applied in a wider liquid division ratio.

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APPENDIX

a. Antoine constants :

$$\ln(p) = A - \frac{B}{T + C}$$

where

p vapour pressure [torr],
T temperature [K]

component	A	B	C
n-pentane (L)	15.993	2554.6	-36.25
acetone (I)	16.732	2975.9	-34.52
c-hexane (H)	15.802	2797.6	-49.10

b. UNIQUAC parameters

i,j	$u_{ij}-u_{ji}$, cal/mol	$u_{ji}-u_{ij}$, cal/mol
L,I	571.98	-95.033
L,H	-48.806	71.682
I,H	-77.536	543.590

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