SEPARATION OF WATER - ACETIC ACID MIXTURES BY CYCLIC DISTILLATION

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Acetic acid is a carboxylic acid, industrially produced for a large range of applications. All the processes include a water – acetic acid separation step which, due to the presence of a tangent pinch on the pure water end, is performed in practice through heterogeneous azeotropic distillation.

The current paper compares the separation of the water – acetic acid mixture through conventional distillation, cyclic distillation, and azeotropic distillation with i-butyl acetate as entrainer. Cyclic distillation is a better technique compared to the conventional distillation. However, for applications in which the contamination of acetic acid with i-butyl acetate is allowed, the azeotropic distillation is economically a better candidate.

Keywords: Water - Acetic Acid separation, Distillation, Heterogeneous azeotropic distillation, Cyclic distillation, Economic evaluation

1. List of notations

%wt	mass percent
A	Heat transfer area
B	Bottoms produc amomunt
$CAPEX$	Capital expenditures
d	Column diameter
D	Distillate amount
F	Feed amount
F_c	Corrosion factor
F_d	Correction factor
F_m	Material factor
F_p	Pressure factor
H	Column heigth
L	Molar reflux amount

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□	Heat of vaporisation
M	Molar liquid hold-up
M&S	Marshall and Swift index
OPEX	Operational expenditures
P	Pressure
T	Temperature
TAC	Total annual cost
t_{vap}	Vapour flow period duration
V	Vapour flow-rate
x	mole fraction in liquid phase
y	mole fraction in vapour phase
Φ	Mappings of the system state

2. Introduction

Acetic acid (CH_3-COOH) is a carboxylic acid found in very small concentrations in many plant and animal liquids. Some bacteria or fungi ferment fruit or vegetable juices to a solution containing 2-12% acetic acid, called vinegar. Acetic acid is a clear, colorless liquid, having the melting and boiling points at atmospheric pressure at 16.64^{o}C and 117.87^{o}C respectively. Both in vapor and liquid phase, acetic acid is found as a dimer, which leads to difficulties in modelling the vapor-liquid equilibrium of the mixtures containing this component [1].

Industrially, acetic acid is used as raw material in the production of vinyl acetate, terephtalic acid, acetate esters and acetic anhydride. Vinyl acetate is used in the production of latex emulsion resins for paints, adhesives, paper coatings and textile finishing agents. Terephtalic acid is the raw material for polyethylene terephthalate production, used as solid-state packaging resins, films and fibers. The main use of acetic anhydride is the production of cellulose flakes. The worldwide demand of acetic acid was 10 million tons in 2011, with an estimate demand for 2020 of 16 million tons [1].

The main routes for the commercial production of acetic acid are methanol carbonylation, acetaldehyde oxidation and the oxidation of butane and/or naphtha fractions. Relative small amounts are produced from synthesis gas, by liquid phase oxidation of butane and by direct oxidation of ethanol. Ethanol fermentation is used for vinegar production. All these processes contain a step for separating the acetic acid from water, leading to high purity acetic acid [1].

Although acetic acid and water do not form an azeotrope, the separation is difficult due to the tangent pinch present on the pure water end. A common industrial practice to overcome the tangent pinch is to add an entrainer and

therefore to use heterogeneous azeotropic distillation. Acetates of ethyl, n-butyl, vinyl or isobutyl, as well as para-xylene are common substances used as entrainer [2].

In the following sections a comparison between the separation of 10780 kg/h mixture of water (71%wt) and acetic acid (29%wt) [3] using distillation, heterogeneous azeotropic distillation using isobutyl acetate and cyclic distillation is presented. To our best knowledge, this is the first paper which investigates the economics of cyclic distillation. The paper is structured as following: first the equations used for the economic calculations are shown, after which each method is presented in a different section. The paper ends with conclusions.

3. Equations used for the economic calculations

The total annual cost has been calculated according to equation (1), where TAC, OPEX and CAPEX represent the total annual cost, operational expenditures and capital expenditures respectively.

$$TAC = OPEX + \frac{CAPEX}{payback\_period} \tag{1}$$

It has been assumed that the operating time is 8000 h/year and that the payback period is 3 years. 6 bar steam (160 ^{o}C, 7.78 \$/GJ) and cooling water (0.72 \$/GJ) have been used as utilities. The cost of the column has been calculated according to equation (2) [5].

$$C_{Column} = \left(\frac{M\,\&\,S}{280}\right)\cdot\left(957.9\cdot d^{1.066}\cdot H^{0.802}\right)\cdot\left(2.18\cdot F_C\right) \tag{2}$$

where M&S represents the Marshall and Swift index (1536.2), d is the column diameter, H is the column height and F_c is the corrosion factor, calculated according to equation (3):

$$F_C = F_p + F_m \tag{3}$$

The pressure factor F_p depends on the pressure *(P)* according to equation (4) [6], and the value of the material factor F_m for carbon steel is 1.

$$F_p = 1 + 0.0074\cdot\left(P - 3.48\right) + 0.00023\cdot\left(P - 3.48\right)^2 \tag{4}$$

The cost of the trays has been calculated using equation (5) [6]:

$$C_{Trays} = \left(\frac{M\ \&\ S}{280}\right) \cdot 97.2 \cdot d^{1.55} \cdot NT \cdot F_c \tag{5}$$

The costs of the condenser and reboiler have been calculated according to equation (6), where A represents the heat transfer area [6]:

$$C_{Heat\_exchanger} = \left(\frac{M\ \&\ S}{280}\right) \cdot \left(474.7 \cdot A^{0.65}\right) \cdot \left(2.29 + F_c\right) \tag{6}$$

Where F_c is calculated using equation (7):

$$F_C = F_m \cdot \left(F_d + F_p\right) \tag{7}$$

The value of F_m for carbon steel is 1 and the value of F_p for pressures lower than 10 bar is 0. The value of the correction factor F_d has been considered 1.35 for the reboiler and 0.8 for the condenser.

In the calculation of the heat exchange area, a heat transfer coefficient of 500 W/m^2/K has been assumed.

4. Water acetic acid separation by conventional distillation

The water acetic acid equilibrium is characterized by a tangent pinch on the pure water end, as illustrated in Fig. 1, for an arbitrary chosen mixture. A tangent pinch means that, on the McCabe-Thiele diagram, the operating line is tangent to the equilibrium curve at the minimum reflux. The presence of a tangent pinch, together with the relatively close boiling points of water and acid acetic, make the separation of this mixture difficult, as shown in Fig. 2.

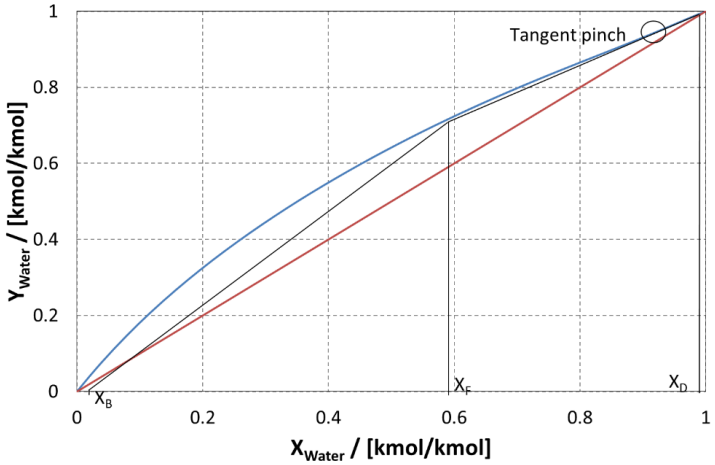

Fig. 1. X-Y diagram for the water-acetic acid system

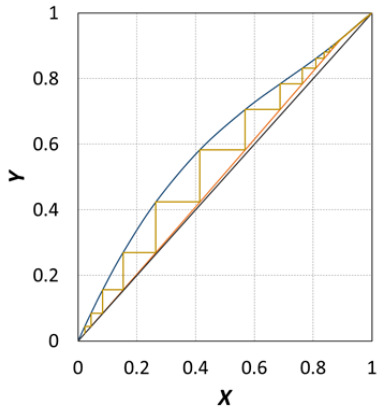

Fig. 2. McCabe-Thiele diagram of the water acetic acid separation column

A column having 70 theoretical trays is required to separate a water acetic acid mixture containing 79%wt water. The number of trays has been determined based on the minimum total annual cost, as presented in Fig. 3. The mass balance of the column is presented in Table 1.

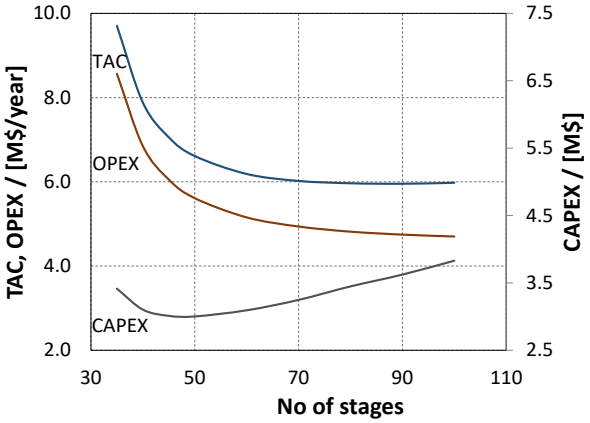

Fig. 3. Total annual cost for the water - acetic acid distillation column

The optimal feed tray, leading to minimum reboiler duty, has been identified through sensitivity analysis in Aspen Plus as tray 53. It is observed that the separation in the stripping section is not very difficult. However, due to the tangent pinch present in the rectifying section, a very high number of trays is required for obtaining high purity water, as emphasized in Fig. 4. The characteristics of the column are shown in Table 2.

Table 1

Mass balance of the water acetic acid separation column

Stream	Feed	Distillate	Bottoms
Flow-rate / [kmol/h]	476.9	424.4	52.5
Water mole fraction	0.8919	0.9982	0.0230
Acetic acid mole fraction	0.1081	0.0018	0.9770
Water mass fraction	0.7100	0.9940	0.0070
Acetic acid mass fraction	0.2900	0.0060	0.9930

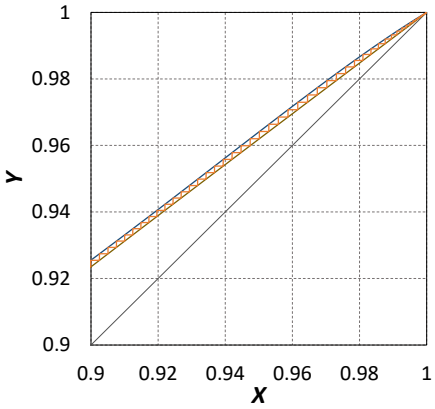

Fig. 4. Trays in the distillation zone of the water-acetic acid separation column

Table 2

Water acetic acid distillation column characteristics

Number of trays	70
Feed tray	53
Molar reflux ratio	2.9
Diameter / [m]	3.7
Height / [m]	42
Reboiler duty / [kW]	19230
Condenser duty / [kW]	18892

A total annual cost of 6.2 M$/year is required, assuming a 3 year pay-back time. The calculations are summarized in Table 3.

Table 3

Cost calculation of water acetic acid distillation column

Column / [10^3 $]	1317
Trays / [10^3 $]	1597
Reboiler / [10^3 $]	1129
Condenser / [10^3 $]	521
CAPEX / [10^3 $]	4564
Cooling water / [10^3 $/year]	391
Steam / [10^3 $/year]	4308
OPEX / [10^3 $/year]	4700
Total annual cost / [10^3 $/year]	6221

5. Water acetic acid separation through azeotropic distillation with i-butyl acetate

As an alternative for the water - acetic acid separation through distillation, azeotropic distillation has been proposed in literature. Isobutyl acetate was shown to be a better component in terms of energy requirement compared to the conventional ethylene dichloride, n-propyl acetate, n-butyl acetate and vinyl acetate [4] [3]. The ternary diagram with residual curves of the water - acetic acid – isobutyl acetate has been calculated in Aspen Plus using NRTL – Hayden O'Connel (HOC) as thermodynamic model and it is presented in Fig. 5.

It is observed that water forms a heterogeneous azeotrope with isobutyl acetate and a 2-phase region is present in the diagram. The water - isobutyl acetate azeotrope is an unstable node, while the acetic acid is a stable node [4]. Based on the diagram, a separation method using two distillation columns and a decanter is proposed. The initial mixture is represented by the point F1. This is mixed with isobutyl acetate, leading to the mixture F, which is fed to the first distillation column. High-purity acetic acid is obtained as bottoms product, while the water – isobutyl acetate azeotrope is obtained in the distillate (L1). The 2-phase azeotrope mixture is separated in a decanter. The organic phase is returned into the first column as reflux. The aqueous phase is fed into the second column, where water is produced as bottoms product and azeotrope is produced as distillate (L2) [3]. The process scheme is shown in Fig. 6.

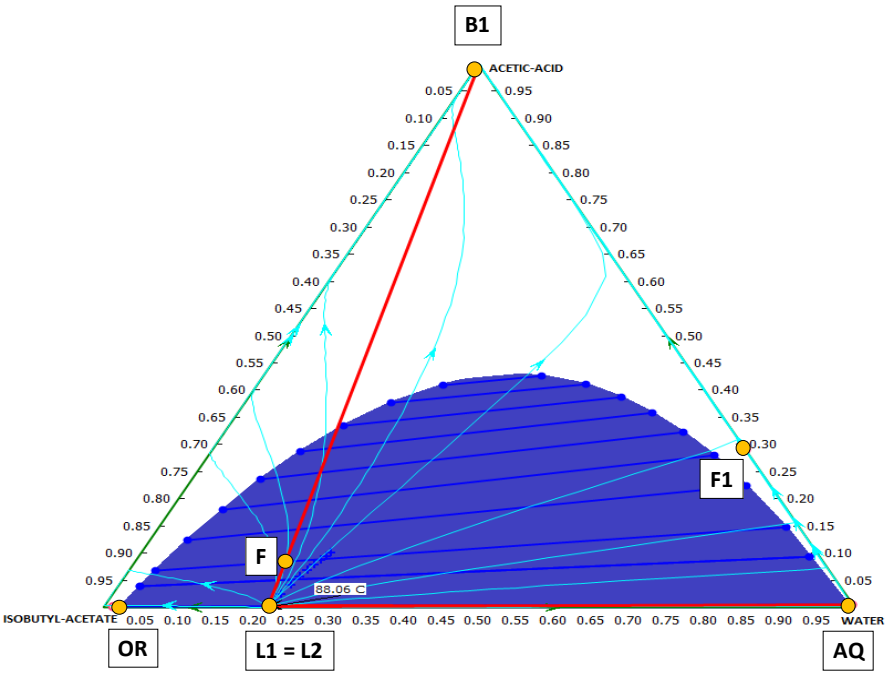

Fig. 5. Water - acetic acid - isobutyl acetate ternary diagram

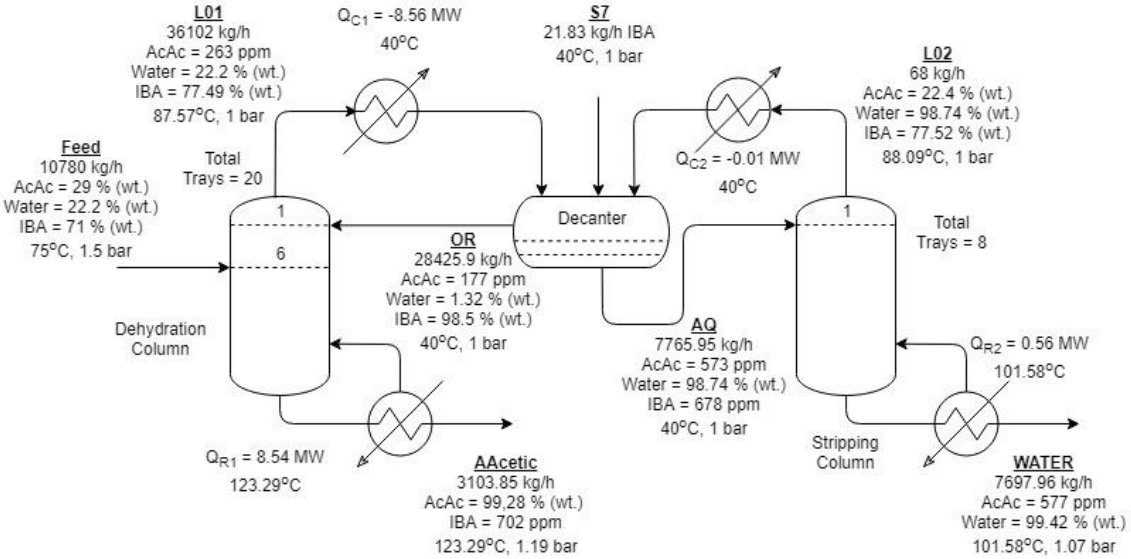

Fig. 6. Process scheme of the water acetic acid separation using iso-butyl acetate as entrainer

The characteristics of the two columns are presented in Table 4. The mass balances of the two columns are shown in Table 5.

Table 4

Characteristics of the distillation columns

Column	Acetic acid column	Water column
Number of trays	20	8
Feed tray	6	1
Molar reflux ratio	0.38	-
Diameter / [m]	2.3	0.45
Height / [m]	11	3.6
Reboiler duty / [kW]	8542	561
Condenser duty / [kW]	8567	16.2

Table 5

Mass balance of the acetic acid column

Column	Acetic acid column				Water column		
Stream	Feed	Entrainer	Distillate	Bottoms	Feed	Distillate	Bottoms
Flow-rate / [kmol/h]	476.91	262.72	688.11	51.52	426.87	1.30	425.57
Mole fractions							
Water	0.8908	0.0793	0.6477	0.0004	0.9972	0.6505	0.9982
Acetic acid	0.1092	0.0032	0.0023	0.9960	0.0018	0.0004	0.0018
Isobutyl acetate	-	0.9175	0.3500	0.0035	0.0010	0.3491	-
Mass fractions							
Water	0.7099	0.0132	0.2225	0.0001	0.9877	0.2242	0.9940
Acetic acid	0.2901	0.0018	0.0026	0.9931	0.0059	0.0005	0.0060
Isobutyl acetate	-	0.9850	0.7749	0.0067	0.0064	0.7754	-

The cost of the two colums has been calculated using the same procedure as for the conventioal distillation column. The results are presented in Table 6.

Table 6

Cost summary for the distillation columns

Column	Acetic acid column	Water column
CAPEX / [10^3 $]	**1470**	**95.6**
Column / [10^3 $]	305	19.6
Trays / [10^3 $]	45	1.2
Reboiler / [10^3 $]	515	64.7
Condenser / [10^3 $]	605	10.1
OPEX / [10^3 $/year]	**2092**	**125.9**
Cooling water / [10^3 $/year]	178	0.3
Steam / [10^3 $/year]	1914	125.6
Total annual cost / [10^3 $/year]	**2582**	**158**

6. Separation through cyclic distillation

Cyclic operation of distillation columns consists in a vapour flow period and a liquid flow period. During the vapor flow period, the liquid remains stationary on the tray while the vapour is flowing upwards through the column. During the liquid flow period vapor flow is stopped, reflux and feed are supplied to the column, and the liquid holdup is dropped from each tray to the tray below. The principle is schematically illustrated in Fig. 7. Schematics illustrating the working principle of cyclic distillation: (a) vapor-flow period; (b) liquid flow-period; (c) beginning of a new vapor-flow period.

7. This mode of operation can be achieved by using perforated trays, without downcomers, combined with sluice chambers located under each tray. If the vapor velocity exceeds the weeping limit, the liquid does not overflow from tray to tray during vapor-flow period (Fig. 7. Schematics illustrating the working principle of cyclic distillation: (a) vapor-flow period; (b) liquid flow-period; (c) beginning of a new vapor-flow period.

7a). When the vapor supply is interrupted, the liquid drops down by gravitation to the sluice chamber (Fig 7b). When the vapor supply is started again, the sluice chambers open and the liquid is transferred by gravity to the tray below (Fig 7c). The operation is presented in detail in [7].

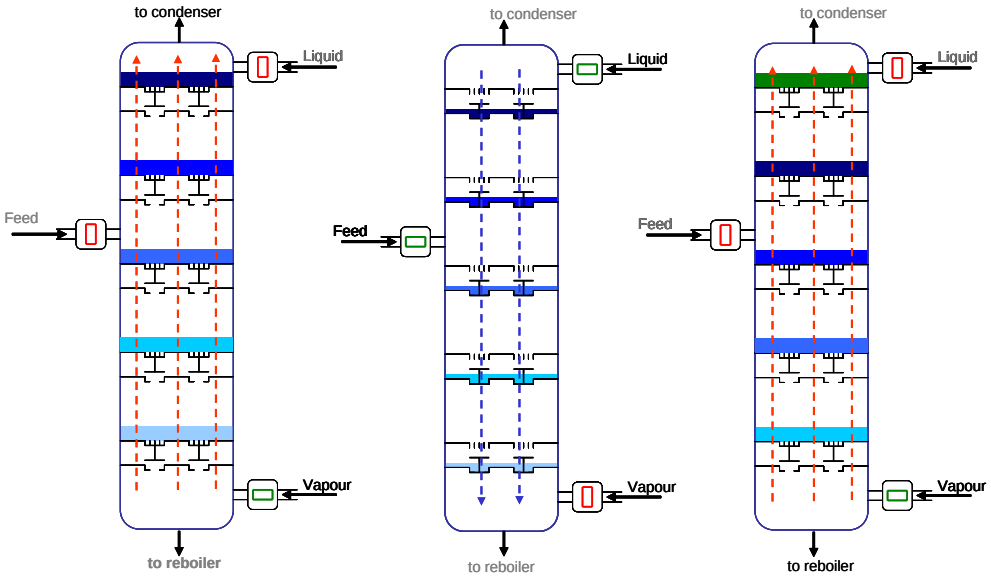

Fig. 7. Schematics illustrating the working principle of cyclic distillation: (a) vapor-flow period; (b) liquid flow-period; (c) beginning of a new vapor-flow period.

In order to study the separation of water and acetic acid via cyclic distillation, the mathematical model presented in [7] [8] [9] has been considered. The model was derived under the following assumptions:

1. Vapor-liquid equilibrium is reached on every tray
2. On each tray the liquid is perfectly mixed
3. The vapor holdup on each tray is neglected
4. The column is fed with saturated liquid

The input variables are the molar feed flow-rate F and composition x_F, the duration of the vapour period t_{vap}, the molar reflux amount L, the bottoms vapor flowrate $V_{NT,}$ and the total molar hold-ups in the reflux and bottoms tanks at the end of the vapor-flow period. The mass balance equations of the mathematical model for the vapor-flow period describe the evolution of tray-holdup M for each component $j = 1, NC$. V_k represents the vapor flow-rate which leaves the tray k. The following equations are written:

Condenser:

$$\frac{dM_{1,j}}{dt} = V_2 \cdot y_{2,j} \tag{8}$$

Trays:

$$\frac{dM_{k,j}}{dt} = V_{k+1} \cdot y_{k+1,j} - V_k \cdot y_{k,j}, \qquad k = 2, NT-1 \tag{9}$$

Reboiler:

$$\frac{dM_{NT,j}}{dt} = -V_{NT} \cdot y_{NT,j} \tag{10}$$

The vapour-liquid equilibrium is described by equations (11) - (13):

$$x_{k,j} = \frac{M_{k,j}}{\sum_j M_{k,j}} \qquad j = 1, NC \tag{11}$$

$$P_k \cdot y_{k,j} \cdot \varphi_{k,j}\left(y_1 ... y_{NC}, T_k, P_k\right) - P_j^{vap} \cdot x_{k,j} \cdot \gamma_{k,j}\left(x_1 ... x_{NC}, T_k\right) = 0 \quad j = 1, NC \tag{12}$$

$$\sum_j y_{k,j} - 1 = 0 \tag{13}$$

The fugacity and activity coefficients have been calculated using the NRTL activity model [10] for the vapor-liquid phase and Hayden O'Connell [11]

(HOC) fugacity coefficient model for the vapor phase. The parameters for the NRTL and HOC models have been regressed from the NIST TDE database using Aspen Plus. The equilibrium curve together with some experimental data taken from the same database are given in Fig. 8.

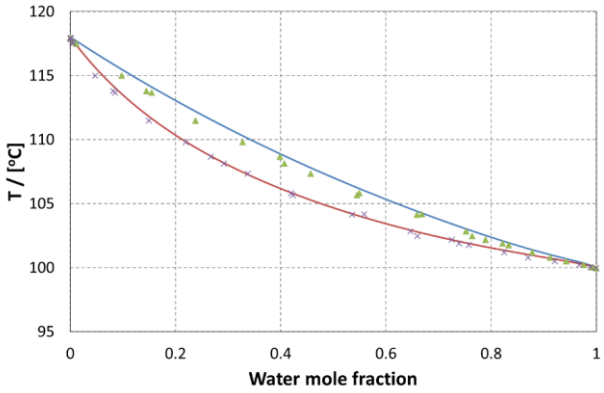

Fig. 8. Water acetic acid vapor-liquid equilibrium. Markers – experimental data. Lines – values calculated using the NRTL-HOC model.

The pressure drop on each tray has been calculated as the hydrostatic pressure of the liquid present on the tray. The pressure on each tray can be calculated using equations (14) and (15):

$$P_2 = P_{cond} \tag{14}$$

$$P_k = P_{k-1} + \Delta P\left(M_{k-1}\right) \tag{15}$$

The variation of the vapor flow-rate between the trays results from the energy balance written on each tray, as shown in equation (16). A constant heat of vaporization λ has been considered for the water and acetic acid.

$$V_{NT-k} \cdot \sum_j \lambda_j \cdot y_{NT-k,j} = V_{NT-k+1} \cdot \sum_j \lambda_j \cdot y_{NT-k+1,j} \qquad k = 1, NT-1 \qquad j = 1, NC \tag{16}$$

The mass balance equations of the mathematical model for the liquid-flow period describe the movement of the liquid from one tray to the tray below, product removal and the mixing that occurs at the feed and inside the reboiler. *D*, *B*, *F* and *L* represent the distillate, bottoms, feed and reflux amounts respectively. The equations written for condenser, trays and reboiler are the following:

Condenser:

$$M_{1,j}^{(L)} = M_{1,j}^{(V)} - \left(D + L\right) \cdot x_{1,j}^{(V)} \tag{17}$$

Trays, rectifying section:

$$M_{2,j}^{(L)} = L \cdot x_{1,j}^{(V)} \tag{18}$$

$$M_{k,j}^{(L)} = M_{k-1,j}^{(V)} \qquad k = 2, NF \tag{19}$$

Feed tray:

$$M_{NF+1,j}^{(L)} = M_{NF,j}^{(V)} + F \cdot x_{F,j} \tag{20}$$

Trays, stripping section:

$$M_{k,j}^{(L)} = M_{k-1,j}^{(V)} \qquad k = NF+2, NT-1 \tag{21}$$

Reboiler:

$$M_{NT,j}^{(L)} = M_{NT,j}^{(V)} - B \cdot x_{NT,j} + M_{NT-1,j}^{(V)} \tag{22}$$

The solution method is described in [7] and is based on the observation that the state of the system at the beginning of the vapor-flow period is the same as the state at the end of the liquid-flow period. If $\Phi^{(V)}$ and $\Phi^{(L)}$ are the mappings relating the system state at the start and the end of the vapor-flow and liquid-flow periods, the system of equations (8) – (22) can be condensed in the form described by equations (23) and (24).

$$M^{(L)} = \Phi^{(L)}\left(M\right) \tag{23}$$

$$M^{(V)} = \Phi^{(V)}\left(M\right) \tag{24}$$

According to the periodicity condition:

$$M^{(V)} = \Phi^{(V)} \circ \Phi^{(L)}\left(M^{(V)}\right) \tag{25}$$

The problem can be solved by considering $M^{(V)}$ as the unknown of the system described by equation (25) and applying a numerical method for algebraic equations (Newton or Broyden). For finding the initial approximation, an initial state is considered and equations (20) and (21) are applied repetitively.

In order to size and to determine the most efficient column from an economical point of view, the operating characteristics of the cyclic distillation systems has been studied. It is observed that, for a fixed number of trays, the required vapor flow-rate (which is directly related to the energy requirements) depends on the chosen feed tray. The variation of the required vapor flow-rate with the chosen feed tray for a column with 20 trays is presented in Fig. 9.

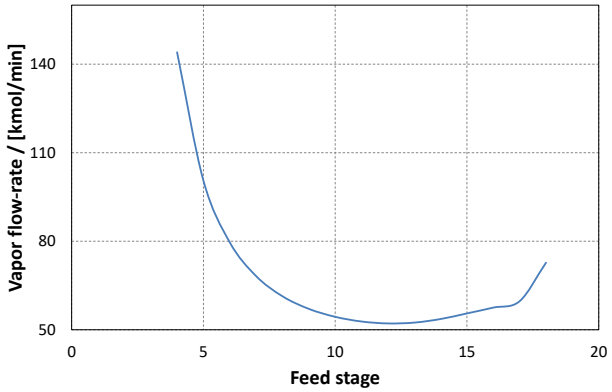

Fig. 9. Dependence of the vapor flow-rate with the feed tray for a 20 trays column

Similarly to the conventional distillation columns, for the cyclic distillation there is an optimum feed tray. The influence of the number of trays on the vapor flow-rate has been investigated by calculating the vapor flow-rate for columns with 20, 25, 30, 35 and 40 trays, fed at the optimal feed tray. The characteristics of the columns are presented in Table 7. The variation of the vapor flow-rate with the number of trays is represented in Fig. 10.

Similar to conventional distillation, the vapor flow-rate decreases with the increase of the number of trays, which indicates the existence of an optimum number of trays. The flow-rate decreases sharply between 20 and 25 trays, followed by a slower decrease between 25 and 40 trays. The variation of the total annual cost with the number of trays is shown in Fig. 11.

Table 7

Operating parameters of various cyclic distillation columns

Number of trays	Optimal feed tray	Molar reflux (kmol/cycle)	Molar vapour flow-rate (kmol/min)
20	12	12.05	52.13
25	16	10.44	46.75
30	20	9.83	44.72
35	25	9.55	43.77
40	29	9.39	43.25

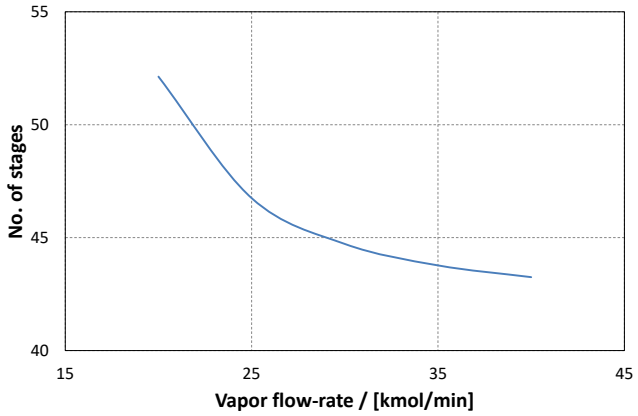

Fig. 10. Variation of the vapor flow-rate with the number of trays

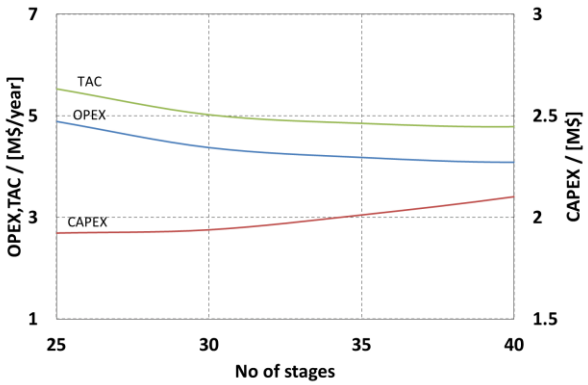

Fig. 11. Total annual cost for the water acetic acid through cyclic distillation column

The total annual cost decreases with the increase of the number of trays. However, the decrease between 35 and 40 trays is very small. For practical reasons, a column with 35 trays is further studied. The variation of the required vapor flow-rate with the bottoms' product purity is shown in Fig. 12.

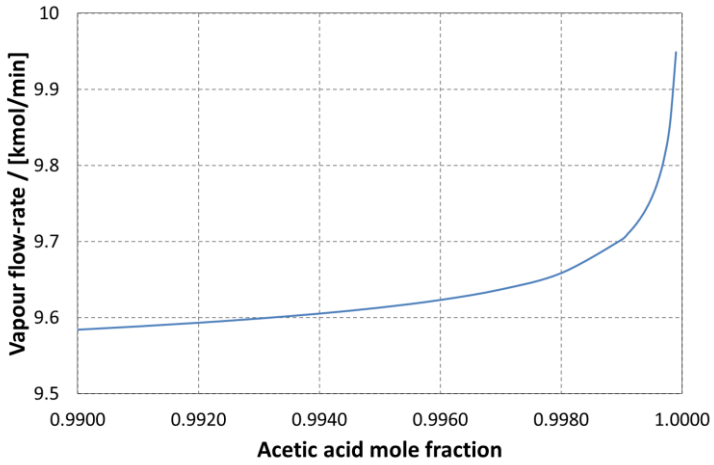

Fig. 12. Variation of the vapour-flow-rate with the bottoms stream purity

The equilibrium and operating curves for the 35 trays column are shown in Fig. 13. In the tangent pinch region, the equilibrium and operation curves are still very close to each other, similar to conventional distillation.

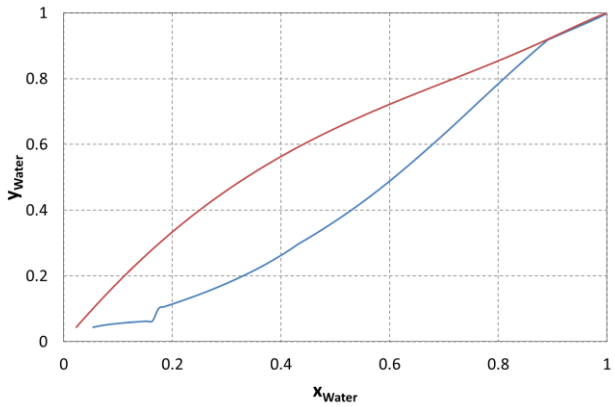

Fig. 13. Equilibrium and operating curves for a 35 tray cyclic distillation column

The mass balance of the cyclic distillation column is shown in Table *8*. The characteristics of the column are shown in Table 9. Table 10 summarizes the cost of the column.

Table 8

Mass balance of the water - acetic acid cyclic distillation column

Stream	Feed	Distillate	Bottoms
Flow-rate / [kmol/h]	477.31	424.76	52.55
Water mole fraction	0.8919	0.9982	0.0230

Acetic acid mole fraction	0.1081	0.0018	0.9770
Water mass fraction	0.7100	0.9940	0.0070
Acetic acid mass fraction	0.2900	0.0060	0.9930

Table 9

Characteristics of the water – acetic acid cyclic distillation column

Number of trays	35
Feed tray	25
Diameter / [m]	3.7
Height / [m]	22.2
Reboiler duty / [kW]	17037
Condenser duty / [kW]	12957

Table 10

Cost summary for the water acetic acid cyclic distillation column

Column / [10^3 $]	806
Trays / [10^3 $]	142
Reboiler / [10^3 $]	758
Condenser / [10^3 $]	397
CAPEX / [10^3 $]	2102
Cooling water / [10^3 $/year]	269
Steam / [10^3 $/year]	3817
OPEX / [10^3 $/year]	4087
Total annual cost (10^3 $/year)	4787

7. Conclusions

Even though possible from a theoretical point of view, separation of water and acetic acid through binary distillation is unpractical. A very large number of trays is required in the rectifying section, in order to overcome the tangent pinch formed by the two components. Through cyclic operation, the number of trays is reduced to half and slightly lower energy consumption (therefore a lower total annual cost) is required for the same distillate purity and a higher purity of the bottoms' product.

The azeotropic distillation remains the preferred separation technique, for applications in which contamination with small amounts of i-butyl acetate is

acceptable. This technique makes the separation possible for a total annual cost which is half of the cost of cyclic distillation.

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