

OPTIMISATION, DYNAMICS AND CONTROL OF A COMPLETE AZEOTROPIC DISTILLATION: NEW STRATEGIES AND STABILITY CONSIDERATIONS

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ABSTRACT

Heterogeneous azeotropic distillation process is widely used in industries to separate non-ideal mixtures in order to obtain high purity components. In this work it was studied an important aspects of this process were made: layouts, optimisation using factorial design, dynamic simulation and a new control strategy which avoids the problem of multiple steady states. Ethanol dehydration was used as case study. Simulations were performed using Hysys.Plant commercial simulator Version 2.2 , 2000 (AEA Technology).

Keywords: Heterogeneous azeotropic distillation, Factorial Design, Distillation Control, Ethanol dehydration

INTRODUCTION

In chemical and petrochemical industries, the task of separating close boiling point and azeotropic mixtures is very common. Three processes, normally, are used for these kinds of separation: heterogeneous or homogeneous azeotropic distillation and liquid-liquid extraction processes. Heterogeneous azeotropic distillation operations represent the most complex behaviour and this reflects in difficulties of convergence, mainly when the complete process is considered and, also, depending on the characteristics of the entrainer.

In this work, the complete process for heterogeneous azeotropic distillation applied to the ethanol dehydration problem was studied. Ethanol is used as a gasoline additive for octane enhancement and, due to the high production costs, this process has been studied for many years. Any improvement resulting in even few cents per gallon produced represents a significant incentive for its renewable fuel use. Extensive works concerning ethanol recovery have been published [1, 2, 3]. Furthermore, the studied process and the results can be generalised for other application of the heterogeneous azeotropic distillation process.

In this work, the results of the process using cyclohexane (a clean solvent) as entrainer were compared with the azeotropic distillation using benzene, the conventional entrainer. A methodology to simulate this process using a commercial simulator was developed. The model was validated with experimental data from the literature and from a real industrial plant. Steady state modelling was used to establish the flowsheet topology, the specifications and all process conditions necessary to achieve the desired product. Before comparing different alternatives of layout, it is fundamental to assure that each one is on its best design and operating configuration. Therefore, the processes were optimised in terms of energy consumption using factorial design and Response Surface Methodology. These techniques are important not only for optimisation, but also for knowing the effect of each operational variable on the energy consumption. Besides the economical aspect, it will be also considered the environmental restrictions. Other important aim of this work is to get products with high purity in all exit streams. Finally, the dynamic modelling is considered to evaluate the process stability and a new control scheme is proposed to maintain the desired specifications when disturbances are introduced. The azeotropic distillation control is a hard task due to the multiple steady state phenomena that can occur in this column. In this new strategy, the undesired steady state can be avoided controlling the temperature in a strategic point identified in the temperature profile and in situations of emergence, the ratio of the feed plus the recycle from the recovery column to the organic phase must also be controlled. So, it is important to study not only the azeotropic column, but the whole process, which includes the decanter and the solvent recovery column, what is commonly made in the works found in the open literature.

STEADY STATE PROCESS SIMULATION

Azeotropic Distillation Process Description

When ethanol is produced by fermentation, the concentration in the outlet of the reactor is about 10% in mass. This mixture is concentrated near to the azeotropic point (89% in mole concentration) in a conventional column and, then from that, it is necessary to use other separation methods to break the azeotrope and to produce pure ethanol. Formally, the azeotropic distillation process, which needs a mass separating agent is used. Figure 1 shows the ethanol/water vapour(y)-liquid(x) phase equilibrium representation at 1 atm.

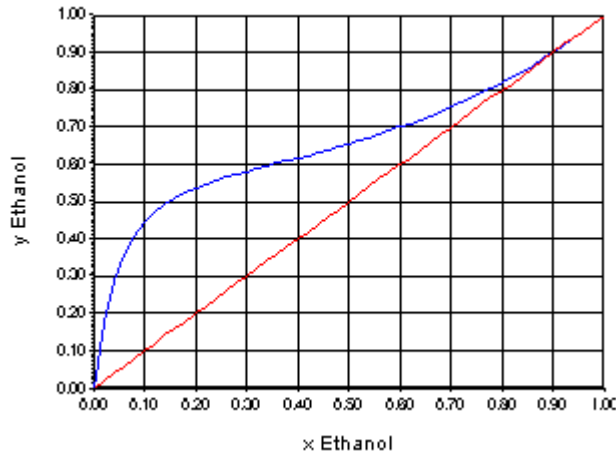


Figure 1 – Vapour-liquid equilibrium for ethanol/water system at 1 atm (x is the mole fraction in the liquid phase and y is the mole fraction in the vapour phase).

The mass separating form a new minimum boiling point and a heterogeneous azeotrope. Taking this and the waste minimisation into account, cyclohexane is a convenient entrainer. Figure 2 shows the ethanol/cyclohexane vapour-liquid behaviour and Table 1 shows the azeotropes in the ethanol/water/cyclohexane system.

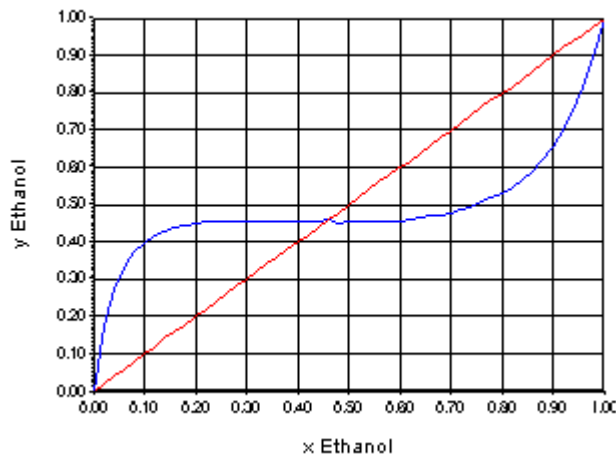


Figure 2 – Vapour-liquid equilibrium for ethanol/cyclohexane system at 1 atm.

Table 1 – Azeotropes in ethanol/water/cyclohexane system.

Azeotrope / components (mole fraction)	Boiling point (°C) at 1 atm	Type
Ethanol/water (0.890/0.110)	78	Homogeneous
ethanol/cyclohexane (0.449/0.551)	65	Homogeneous
Water/cyclohexane (0.301/0.699)	70	Heterogeneous
Ethanol/water/cyclohexane (0.318/0.180/0.502)	62	Heterogeneous

Figure 3 shows a schematic flowsheet for the ethanol dehydration. The stream feed composition coming from the fermentation reactor is about 10% ethanol and 90% water mole basis. Column 1 is a stripper (vapour is fed at the bottom of the column and remove the excess of water). The top product is hydrated ethanol (89% ethanol, mole basis). This stream goes to column 2 (azeotropic column); this column is already fed by a stream containing the entrainer (organic phase recycled from the decanter). The top product composition is near to the ternary azeotrope formed by ethanol, water and the entrainer and the bottom product is pure ethanol. The vapour from the top is condensed and goes to a decanter, where the liquid phase splits into organic and aqueous phases. The organic phase, rich in the entrainer, is recycled to column 1 as reflux and the aqueous phase goes to a recovery column (column 3), where pure water is removed at the bottom and the top product containing ethanol, water and the entrainer is recycled back to the azeotropic column. Different configurations will be discussed later.

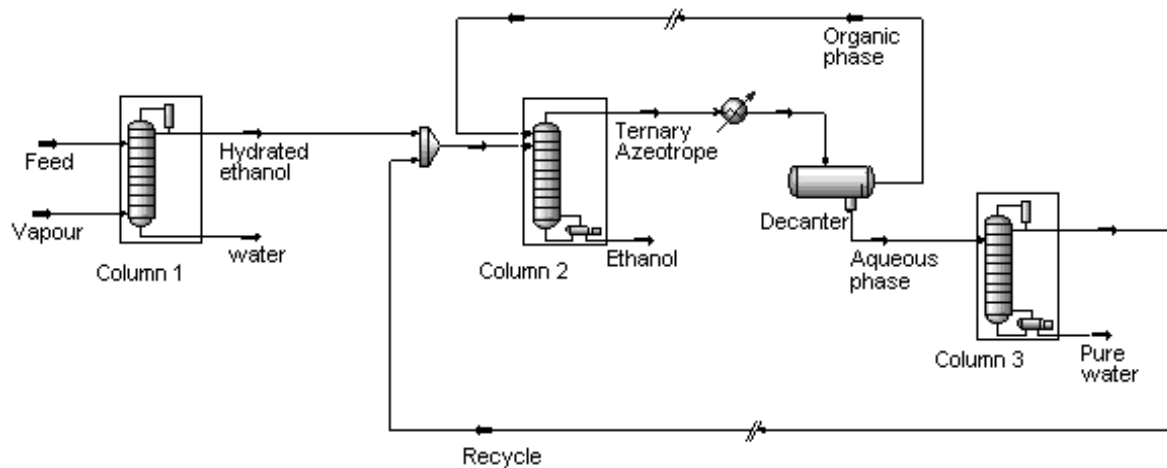


Figure 3 – Flowsheet of the azeotropic distillation

Process simulation

In this work, the complete process is being considered: the azeotropic column, the decanter and the recovery column. The pre-concentration system (column 1) is omitted in the following schemes, due to its simplicity when compared with the integrated process. The majority of the works about this process emphasises only the azeotropic column, but it is important to evaluate also the recovery column, since the top product is recycled back to the azeotropic tower. All equipments (distillation columns and decanter) are strongly integrated due to the recycle streams.

The start point to obtain a representative model is a reliable database for physical properties and for thermodynamic parameter calculations. In the azeotropic distillation process, this step must be carefully taken into account, because the vapour-liquid equilibrium (VLE), vapour-liquid-liquid equilibrium (VLLE) and liquid-liquid equilibrium (LLE) must be considered. In this way, it must be used different parameters for the decanter and for the distillation columns. If the parameters were not well adjusted, the results will be far from the reality. The data for ethanol/water/benzene system (benzene was the entrainer used so far for the

ethanol dehydration) is widely studied in different operational ranges and the HYSYS data bank was able to reproduce results found in the literature [4]. For the ethanol/water/cyclohexane system, there is a lack of published data [4,5]. Some sets of parameters were tested in order to obtain the ones that could reproduce industrial data. The thermodynamic model used for activity coefficient calculations was the NRTL (Equations 1 to 3). Tables 2a and 2b show, respectively, the a_{ij} and α_{ij} parameters for the NRTL model for the liquid-liquid equilibrium used to supply the Hysys values. These values were obtained from [5].

NRTL Model for Activity Coefficient

$$\ln \gamma_i = \frac{\sum_{j=1}^n \tau_{ji} x_j G_{ji}}{\sum_{k=1}^n x_k G_{ki}} + \sum_{j=1}^n \frac{x_j G_{ij}}{\sum_{k=1}^n x_k G_{ki}} \left(\tau_{ij} - \frac{\sum_{m=1}^n \tau_{mj} x_m G_{mj}}{\sum_{k=1}^n x_k G_{ki}} \right) \quad (1)$$

$$G_{ij} = \exp[-\tau_{ij} \alpha_{ij}] \quad (2)$$

$$\tau_{ij} = \frac{a_{ij} + b_{ij} T}{RT} \quad (3)$$

γ_i = Activity coefficient of component i

x_i = Mole fraction of component i

T = Temperature (K)

n = Total number of components

a_{ij} = Non-temperature dependent energy parameter between components i and j (cal/gmol)

b_{ij} = Temperature dependent energy parameter between components i and j (cal/gmol*K)

α_{ij} = NRTL non-randomness constant for binary interaction ($\alpha_{ij} = \alpha_{ji}$)

R = Universal gas constant (1.987 cal/gmol K)

Table 2a – NRTL a_{ij} parameters for LLE

	ethanol	water	cyclohexane
ethanol	---	1431.10	1091.63
water	-2537.70	---	483.55
cyclohexane	772.98	3396.90	---

Table 2b – NRTL α_{ij} parameters for LLE

	ethanol	water	cyclohexane
ethanol	---	0.300	0.463
water	0.300	---	0.210
cyclohexane	0.463	0.210	---

Usually, the algorithms used for conventional columns can not support azeotropic distillation. The algorithm used to perform the simulations was the 'sparse continuation solver', recommended by [6]. It supports two liquid phases on the trays of the column and its main use is for solving highly non-ideal chemical systems and reactive distillation.

After the selection of appropriated database, thermodynamic model and solution algorithm, the simulation of an existing process will depend on practical information, such as: operating pressures, temperatures, number of stages and feed position of the columns and reflux flow. There are some information that are not measured, such as the composition and flow rate of the recycle streams. These are points that difficult the solution of the complete process simulation. To proceed with the column simulation, values must be estimated for the flow and for the composition of the recycle streams and these are essential for the column convergence. This task, usually, takes time to be achieved. Even after the convergence of the individual columns, it is not simple to close the recycles. If the calculated values are far from the estimated values, the recycle operation can not be readily installed. The recycle loops are the last work of the simulation. If we are dealing with a new process, the complexity is even higher.

Model Validation

Actual industrial data from a distillery were obtained and the measured values were compared with the simulation results. The design parameters for the process are described in Table 3.

Table 3 – Parameters of an industrial process.

Number of stages azeotropic column	42
Number of stages recovery column	21
Bottom pressure	1.4 atm
Feed flow rate	8600Kg/h
Feed composition	93% ethanol (mass basis)

This system were simulated and Table 4 shows the results comparing the measured data and the values obtained from simulations for the azeotropic column. It was used an efficiency of 60% (25 theoretical stages) was used to represent the azeotropic column).

Table 4 – Model validation

Parameter	Industrial data	Simulation results
Temperature tray 42 (°C)	83.30	84.91
Temperature tray 28 (°C)	73.20	73.00
Temperature tray 9 (°C)	66.00	66.60

It was also reproduced an experimental data reported by Muller and Marquardt [7] in a laboratory scale column.

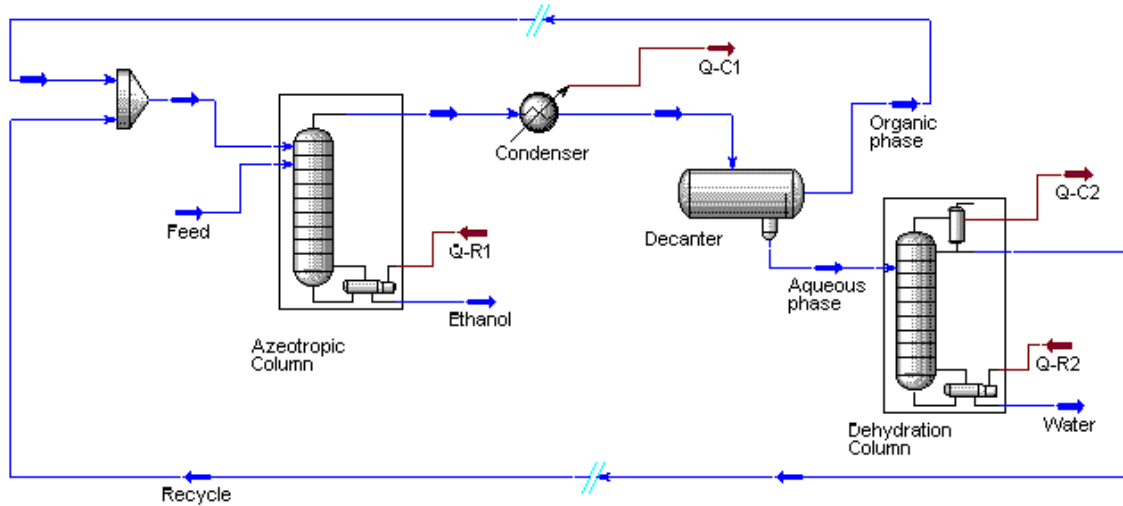


Figure 5 – Configuration 2. Recycle stream is mixed with the organic phase and it is entering in the first stage of the column

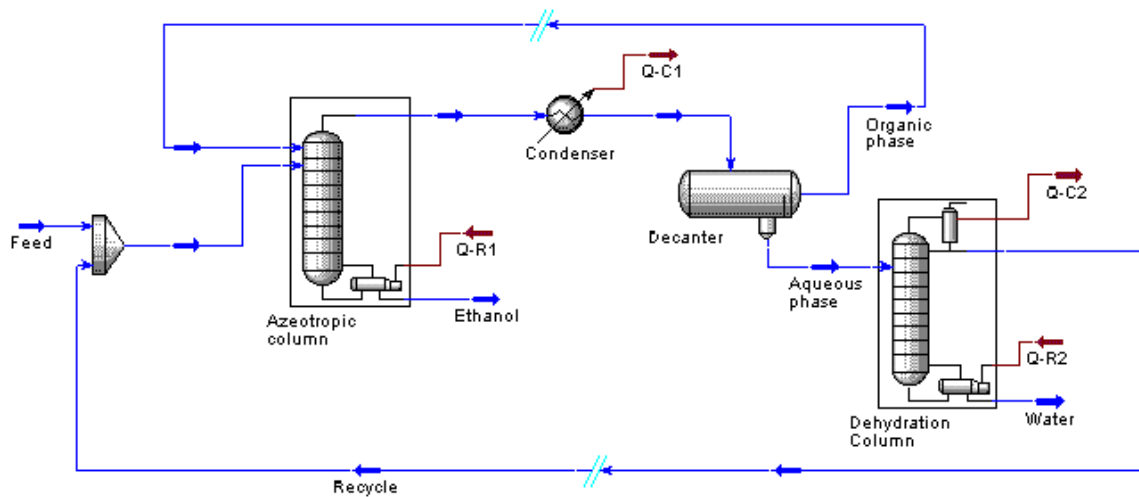


Figure 6 – Configuration 3. Recycle stream is mixed with the fresh feed.

The results reported on Table 5 shows that configuration 1 has the highest energy consumption. Note that the energy consumption in configurations 2 and 3 are very close, but only configuration 3 does not present liquid split in the internal trays of the column.

Table 5 – Energy consumption and phase split for the three configurations studied

Configuration	Energy consumption (KJ/h)	Liquid phase split
1	19.76×10^7	tray 1 to 16
2	2.35×10^7	tray 1 to 12
3	2.39×10^7	-

It is observed that the recycle stream composition is near to the feed composition, so the disturbance in the azeotropic column in configuration 3 is lower than when any other configuration is used. This is a good improvement for the column performance

and, also, for the column stability, since it is avoiding plate liquid phase split. Taking these results into account, it was decided to consider configuration 3 for the following studies.

Residue curve map analysis

Residue curve maps play an important role in interpreting the behaviour and feasibility of distillation column sequences. Figure 7 shows the residue curve map for the system ethanol/water/cyclohexane. There are three distillation regions. To obtain pure ethanol, the initial conditions for the distillation (global feed composition) must lie region II. Points F1 and F2 are the feed composition entering on the azeotropic and dehydration columns respectively.

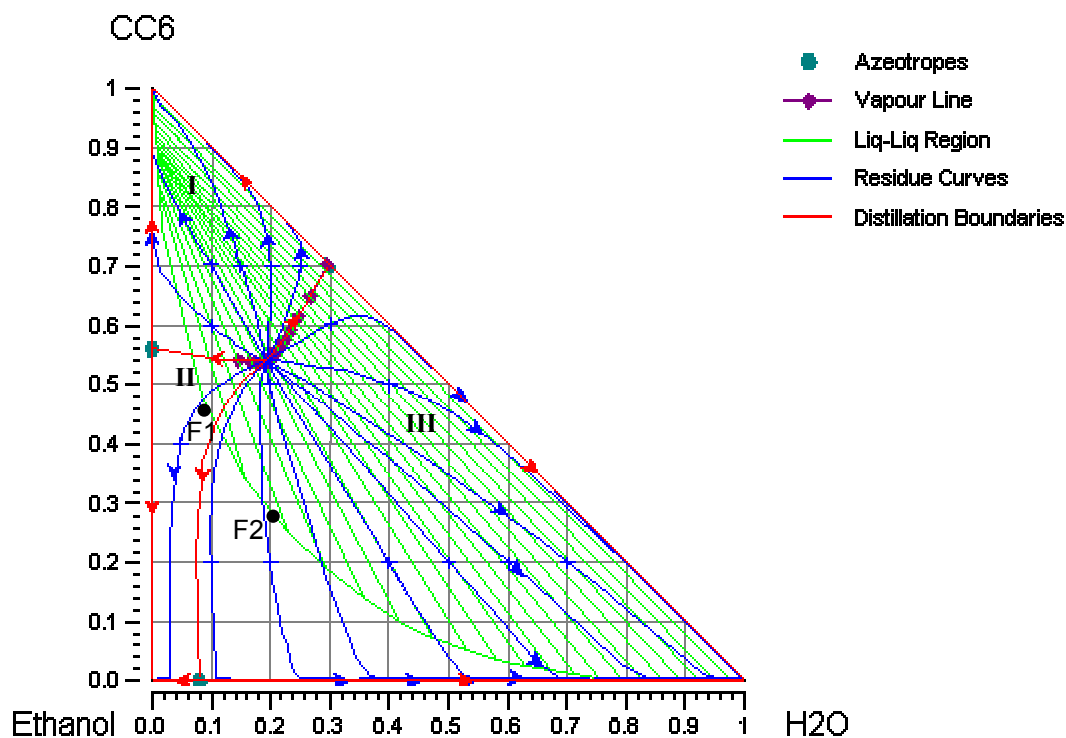


Figure 7 – Residue curve map for the ethanol/water/cyclohexane system at 1 atm.

In reference [8] authors have discussed the feasible and infeasible entrainers and column sequences using residue curve maps. They have analysed different configurations for the system ethanol/water/benzene, which is similar to the ethanol/water/cyclohexane system. All of the configurations presented in this work presented the azeotropic column global feed composition on the appropriate region to make the separation possible and the values were very close (point F1).

Benzene versus Cyclohexane as entrainer

Benzene is the mass separating agent normally used in the publications on ethanol dehydration. But, due to its high toxicity, alternatives have been proposed to its substitution [10, 11] or even changing the whole azeotropic process by extractive distillation or liquid-liquid extraction [12, 13, 14]. Following, a comparison between benzene and cyclohexane performances as entrainer in the azeotropic distillation process is carried out.

Table 6 shows the number of trays and energy consumption for the azeotropic and the recovery columns. There are two important points to be observed when benzene is substituted by cyclohexane:

1. the recovery column needs more trays;
2. the total energy consumption is higher.

Table 6 – Comparison between benzene and cyclohexane for the ethanol dehydration process

	Benzene	Cyclohexane
Number of trays of the azeotropic column	30	30
Number of trays of the recovery column	10	16
QR1 (KJ/h)	1.069×10^7	1.217×10^7
QR2 (KJ/h)	1.875×10^6	9.187×10^6
QR1 + QR2 (KJ/h)	1.256×10^7	2.135×10^7

The liquid phase split were compared for the process using benzene and cyclohexane. Tables 7 and 8 show, respectively, the component mole flows of the organic phase and of the aqueous phase leaving the decanter. When using benzene, the quantity of ethanol in the organic phase is higher than when using cyclohexane. On the other hand, when using cyclohexane, the aqueous phase is rich in ethanol, so that the flow rate going to the recovery column is higher. Increasing the feed flow (of the recovery column) the energy consumption increases too, because all ethanol from this stream is recovered as top product and recycled to the azeotropic column.

Table 7 – Organic phase component mole flows (kmol/h)

Component \ Entrainer	Benzene	Cyclohexane
Ethanol	89.54	28.62
Water	13.79	2.44
Entrainer	163.17	163.49
Total	266.50	194.56

Table 8 – Aqueous phase component mole flows (kmol/h)

Component \ Entrainer	Benzene	Cyclohexane
Ethanol	16.38	99.95
Water	16.16	38.26
Entrainer	1.33	53.75
Total	33.88	190.96

Even being economically favourable, benzene is not used anymore due to environmental aspects. In this work, we emphasise the process using cyclohexane due to the wide use in industries and due to the fact that new process implementation implies in large investment costs.

OPTIMISATION

Factorial design is a powerful tool in process optimisation, although it is often used to obtain the optimal conditions for experimental works, when there is no mathematical model. One advantage of this method is the possibility to evaluate the influence of process variables on the response. When using an algorithm to proceed with the optimisation (for example the SQP – Sequential Quadratic Programming) the result is only the optimal point, there is no information about process behaviour and variable interactions. Besides this, when changes are made, if the simulation can not converge with the initial estimates, the optimisation algorithm will fail. Due to the complex behaviour of azeotropic columns, the initial profile is important to obtain convergence and, therefore, numerical optimisation does not have good performance. For this reason, factorial design was used. Some works have already used this procedure for nonideal distillation columns [15, 16].

Optimisations for structural and operational variables (number of trays, feed position, reflux temperature, position of recycles and split of the reflux stream from the decanter) were performed. The objective of the optimisation is to minimise the energy consumption in the reboiler of the two columns, maintaining the specifications of ethanol purity and recovery.

In this study, the response was the energy consumption. The purities of ethanol and water were specified and, in all cases, the recovery of ethanol was very close to 100%. The independent variables were:

- number of stages in the azeotropic column (NS1)
- feed position (FP1) in the azeotropic column
- decanter temperature (TD)
- the number of stages in the recovery column(NS2)
- feed position in the recovery column (FP2)
- reflux ratio (RR) in the solvent recovery column

Firstly, a fractional factorial design was proposed to verify which variables have the main effects on the response. The low level (-1) and the high level (+1) are presented in Table 9. The number of simulations necessary to the fractional factorial design with six variables is 64 (2^6). This number of runs could be reduced using a fractional factorial design, but it was decided to use the full design. For the process using benzene, the mean value of the runs was 1.459×10^7 KJ/h for the energy consumption and the variables main effects are shown in Table 10.

Table 9. Levels for the independent variables to the factorial design

Variable	-1	+1
NS1	30	50
FP1	4	10
TD	30	60
NS2	10	20
FP2	4	8
RR	0.8	2.0

Table 10. Main effect

Variable	Effect
NS1	0.030
FP1	-0.010
TD	0.188
NS2	-0.016
FP2	-0.016
RR	0.148

It can be observed that the decanter temperature presents the largest effect on the energy consumption. It was verified that increasing the decanter temperature, the energy consumption decreases. An analysis changing the decanter temperature was made in order to verify the component distribution in the organic and aqueous phases. The results are presented in Tables 11 and 12. Increasing the temperature, the composition of ethanol in the organic phase increases. As the aqueous phase flow is reduced, the energy consumption in the recovery column decreases. In many works, the decanter temperature is about 25 – 30°C, what represents an increase in the reboiler duty and, even, in the cooling water.

Table 11. Organic phase composition – mole flows in kmol/h

Organic phase	30°C	60°C
Ethanol	77.27	89.54
Water	7.75	13.79
Benzene	161.28	163.17

Table 12. Aqueous phase composition – mole flows in kmol/h

Aqueous phase	30°C	60°C
Ethanol	27.01	16.38
Water	19.08	16.16
Benzene	2.50	1.33

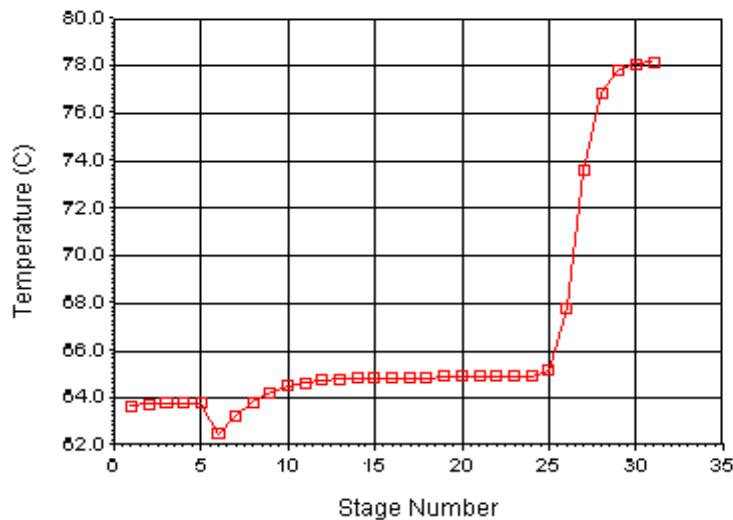
The same procedure was used to optimise the process with cyclohexane.

MULTIPLE STEADY STATES

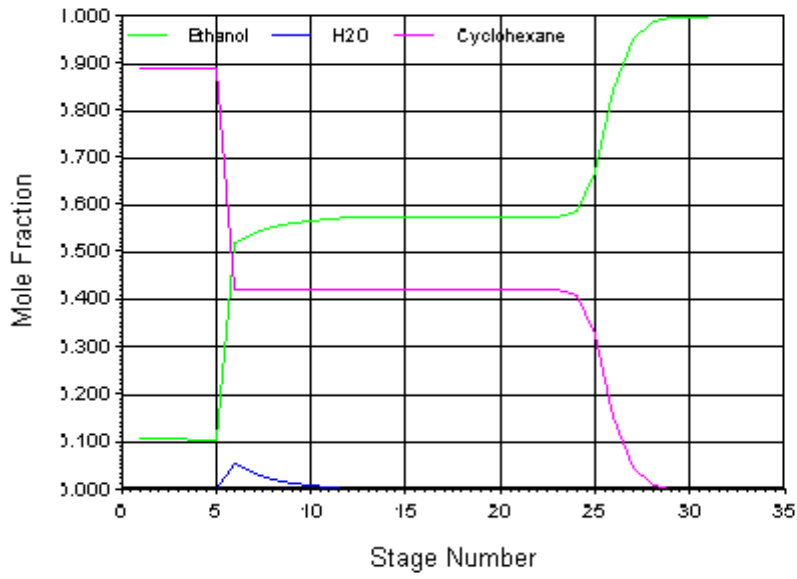
Azeotropic distillation columns are not simple to operate. Among their complex features, they can exhibit two or more different steady states for the same set of operating conditions. This phenomenon is named multiple steady states and they are classified in output multiplicity and state multiplicity. In the output multiplicity, columns with the same operating conditions (reflux, product flow rates, energy, feed flow rate and composition) present more than one output (product composition and internal profiles). State multiplicity refers to the columns with the same operating conditions and outputs, but with different profiles. In this work, we are discussing only the first case.

The multiple steady states phenomena in heterogeneous azeotropic columns have been studied by many authors using residue curve maps or simulation [17, 18] and, recently, experimental works were reported proving the existence of output multiplicity in these columns [19, 20]. In this work, simulations were performed reproducing the behaviour obtained experimentally by Muller and Marquardt [20].

Figures 8a and 8b show the temperature and the liquid composition profiles for the azeotropic column (using cyclohexane) with high purity ethanol production and Figures 9a and 9b show the process behaviour for the same input data (feed and reboiler duty), but with low purity of ethanol as result.

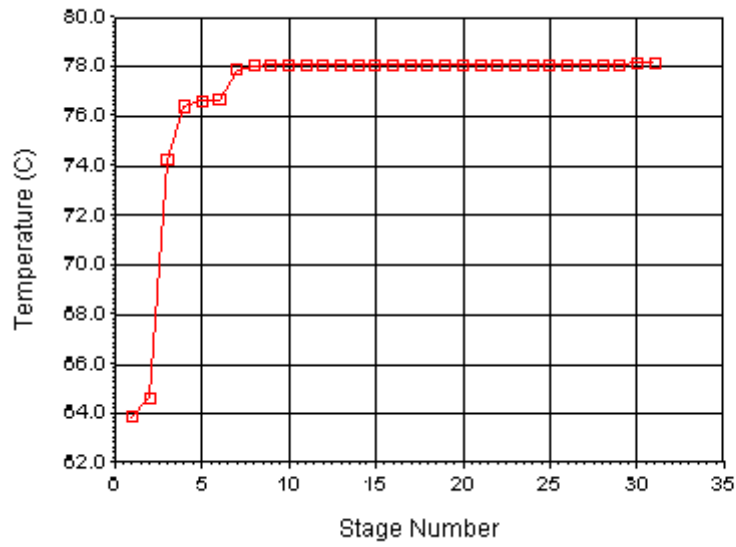


(a)

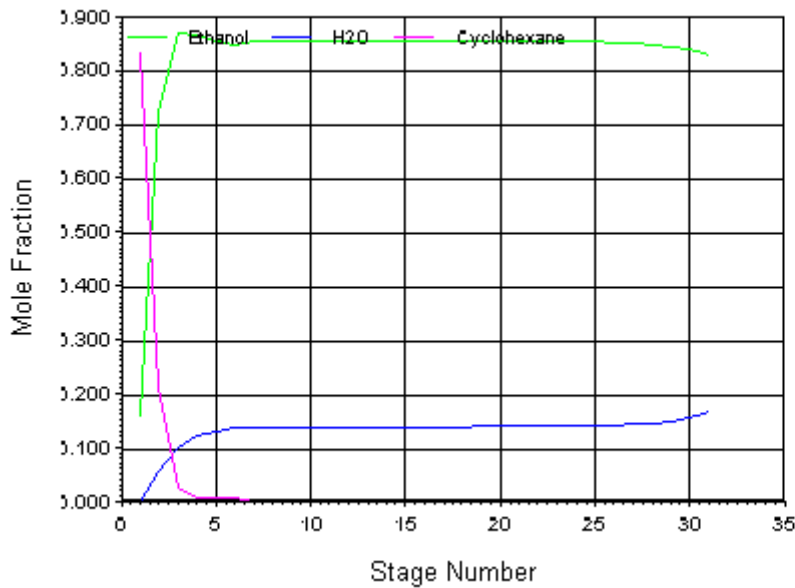


(b)

Figure 8. Temperature (a) and liquid phase composition (b) profiles for the azeotropic column using cyclohexane as entrainer with high purity ethanol production.



(a)



(b)

Figure 9. Temperature (a) and liquid phase composition (b) profiles for the azeotropic column using cyclohexane as entrainer with high purity ethanol production

It is important to introduce an efficient temperature control to assure that the ethanol purity is at the desired value. Another important observation is that the temperature to be controlled must not be the one at the bottom, since in both situations it is near to 78°C (pure ethanol boiling point = 78.25°C and ethanol/water azeotrope boiling point = 78.09°C)

DYNAMIC SIMULATION AND CONTROL

The dynamic simulation and the control of the heterogeneous azeotropic distillation process are difficult tasks and have been recently discussed for many authors [21, 22, 23, 24, 25]. The main difficulty to control an azeotropic column is due to the strong parametric sensitivity to small variations on corresponding operating conditions.

Practical industrial situations often lead the column to run at conservatively high organic reflux flow rate and, consequently, high energy consumption is necessary. In this paper, the aim is to maintain the process operating near to the optimal point. It was proposed a simple, but efficient, control loop using PID controllers. It was evaluated not only the azeotropic column, but also the decanter and the recovery column. Both flow rate and composition of the feed stream were disturbed in order to test the proposed control scheme. The following controllers were implemented:

Azeotropic Column

- Reboiler level control by manipulating the ethanol stream flow rate (LIC-100)
- Pressure control by manipulating the vapour leaving the top of the column (PIC-100)

- Temperature control by manipulating the reboiler duty (TIC-100)

Decanter

- Level control for the aqueous phase manipulating the aqueous phase flow rate (LIC-101)
- Level control for the decanter manipulating the organic phase flow rate (LIC-102)

Recovery Column

- Level control for the reboiler by manipulating the bottom product stream flow rate (LIC-103)
- Level control in the reflux vessel manipulating the distillate flow rate (LIC-104)
- Reflux flow rate control (FIC-100)
- Temperature control (TIC-102) by manipulating the reboiler duty
- An on/off controller (FIC-101) was settled to maintain the ratio of the sum of the fresh feed and the recycle per organic reflux flows lower than 1.6. This value was determined by changing the stream flows. It was observed that when this value is larger than 1.6, even maintaining the temperature profile, the purity of ethanol is out of specification (which is 0.999). It will be used in extreme situations, where the organic flow decrease abruptly or the feed flow increases strongly (about 100 Km³/h to 167 Km³/h).

When dynamic simulations are performed using HYSYS.Plant, it is used hydrodynamic equations to describe the pressure profile. This means that the pressure drop in the column is being considered. All equipment were sized and the temperature profile, taken into account the pressure drop, is shown in Figure 10. It can be observed that the values are slightly higher than those presented in Figure 8a, when the pressure drop was neglected.

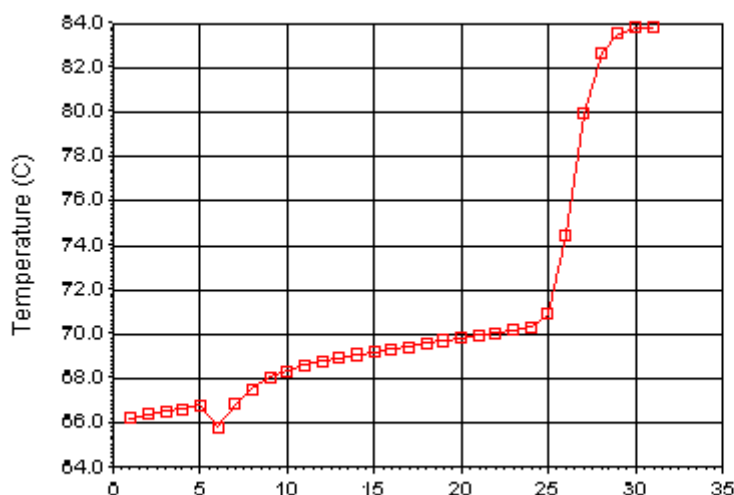


Figure 10 – Temperature profile considering the pressure drop in the azeotropic column.

Figure 11 shows the process behaviour when the feed flow is increased from 100 Km³/h to 120 Km³/h (time about 10 minutes). Figure 12 shows the reboiler duty variation.

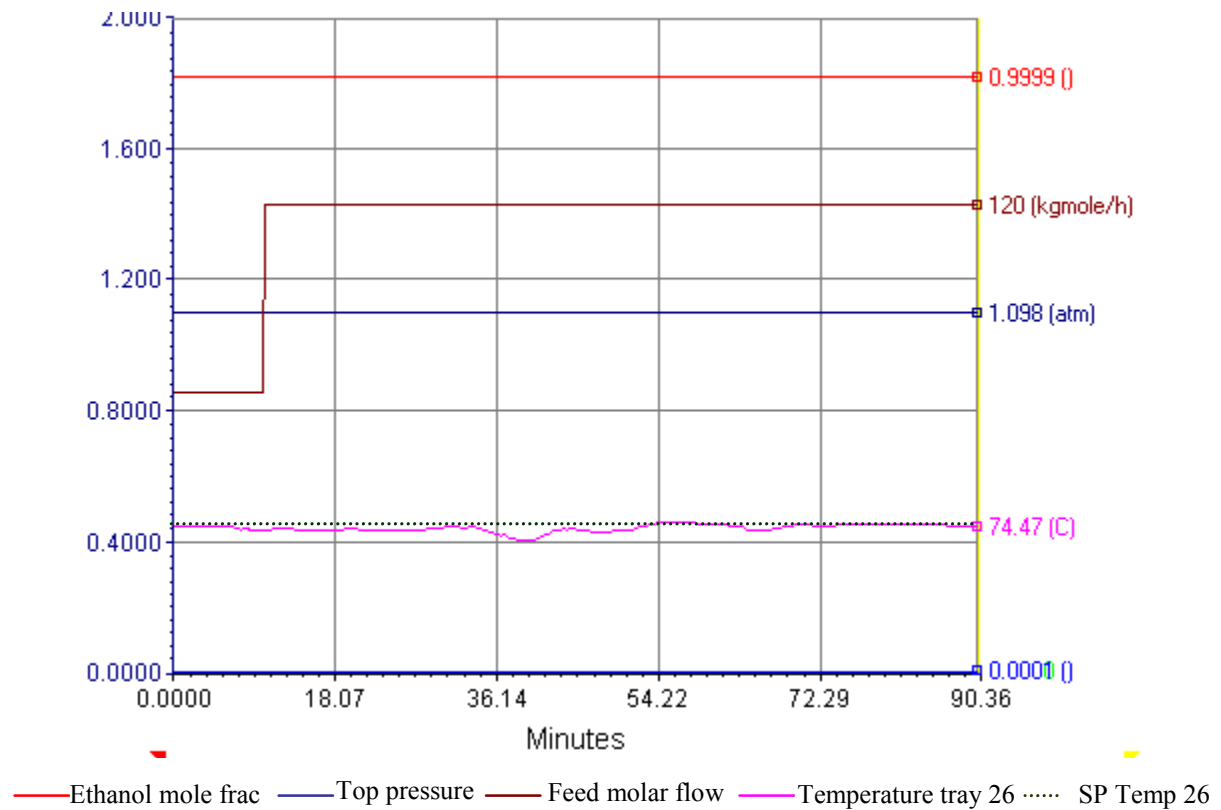


Figure 11 – Process variables when feed flow changes from 100 kmol/h to 120 kmol/h.

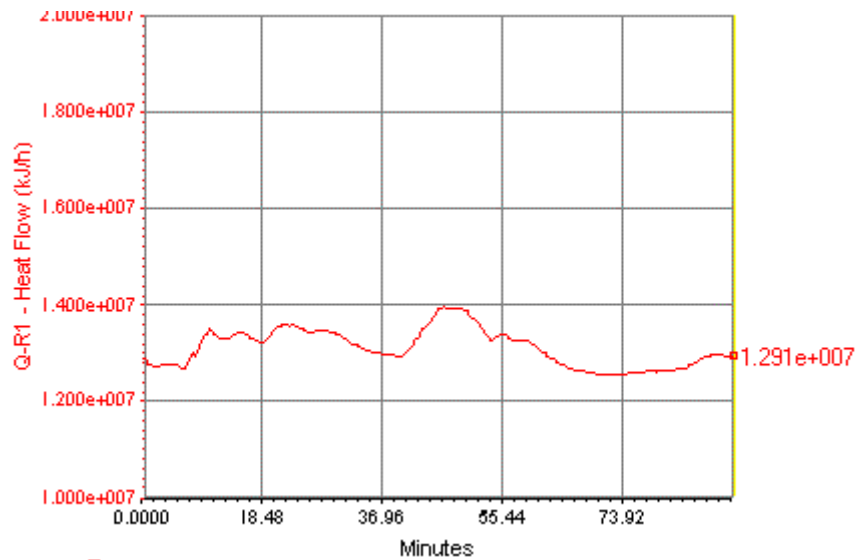


Figure 12 – Reboiler duty

Table 13 presents the values for the tuning parameters for the PID controllers used in the azeotropic column. This is the most difficult task to maintain the column stability

and, also, to have a good controller (which can not send abrupt variations to the control valves).

Table 13 – PI parameters to the azeotropic column controllers

Controller	Kc	Ti	Td
LIC – 100	0.5	2	-
PIC – 100	1	5	-
TIC – 100	2	6	0.001

CONCLUDING REMARKS

This paper presents studies on the heterogeneous azeotropic distillation process using as case study the dehydration of ethanol. It was discussed the process simulation, thermodynamics, flowsheet and the model was validated with industrial data. It was made a comparison between two separating agents: benzene and cyclohexane. It was verified that the behaviour of the process is quite different when using cyclohexane instead of benzene. The main difference is concerned with the organic and the aqueous phases leaving the decanter, due to the higher ethanol concentration in the aqueous phase. When using cyclohexane, the energy consumption is higher. It was proposed to use factorial design as optimisation tool due to convergence problems, what make deterministic optimisation algorithms, like SQP difficult to use. Furthermore, this method allows not only the optimisation, but also to have additional information on the process behaviour. It was discussed and verified by simulations the multiple steady state phenomena in azeotropic columns. It was observed that with the same reboiler duty and bottom temperature, two different profiles can be achieved, which lead to high purity of ethanol or to an undesirable condition. Finally, it was studied the control problem of this system. It was possible to maintain the process under the specifications using only PID controllers with a rigorous control in the stage 26 (determined by the analysis of the temperature profile). The presented results, mainly the choice of the best configuration and the control strategy, are important matter to maintain the azeotropic column stability, what is a complex problem in distilleries and other industries, which uses heterogeneous azeotropic distillation process.

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