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ISOPROPYL ALCOHOL RECOVERY BY HETEROAZEOTROPIC BATCH DISTILLATION

Guy Van Baelen^a, Steven Vreysen^{a*}, Vincent Gerbaud^b, Ivonne Rodriguez Donis^c, Jeroen Geens^d, Bart Janssens^a

^aK.H.Kempen University College, Kleinhoefstraat 4, B-2440 Geel

^bCNRS Laboratoire de Génie Chimique, 5 rue Paulin Talabot, F-31078 Toulouse

^cInstituto Superior de Tecnologías y Ciencias Aplicadas (INSTEC), Cuba

^dJanssen Pharmaceutica, Turnhoutseweg 30, B-2340 Beerse

Abstract

Solvent recovery is becoming a major issue in the pharmaceutical and specialty chemical industries. Solvent recovery by conventional batch distillation is limited by the frequent presence of azeotropes in the used solvent mixtures. Most distillation processes for the separation of azeotropic or difficult zeotropic mixtures involve the addition of an entrainer (homogeneous and heterogeneous azeotropic distillation or extractive distillation).

In this study the recovery of IPA (isopropyl alcohol) from an industrial waste stream (IPA/water mixture) was studied by conventional batch distillation and heteroazeotropic batch distillation, using cyclohexane as entrainer. First the ternary IPA/water/cyclohexane azeotrope (boiling temperature of 64.1 °C), then the binary IPA/cyclohexane azeotrope (boiling temperature of 69.3°C) and finally pure IPA was distilled.

99.96 mass% IPA could be obtained by heteroazeotropic distillation, using cyclohexane as entrainer. By using this procedure the IPA recovery is 97.6%, which is high compared to the conventional distillation techniques. The binary azeotrope could be reused in a subsequent heteroazeotropic batch distillation.

Keywords:

Solvent recovery, batch distillation, heteroazeotropic distillation, isopropyl alcohol, dewatering, residue curve map

INTRODUCTION

Solvent recovery is becoming a major issue in the pharmaceutical and specialty chemical industries. The strongest commercial argument for recovering solvents is the direct cost savings. In some processes with intensive solvent use, the cost of the solvent can be a significant proportion of the overall product cost. Another compelling reason for recovering solvents is the increasing environmental legislation against emissions, some of them being the result of used solvent incineration.

The active pharmaceutical ingredients business is facing all the time 'small volumes' and 'large and continuously changing product portfolio'. These elements make the use of 'optimized continuous distillation' economically unviable. Either this industry considers batch-configurations, either they are forced to waste incineration/discharge.

In waste streams, the frequent presence of azeotropes and zeotropic mixtures with a pinch in the vapor-liquid equilibrium in these streams limit the use of conventional distillation. Most distillation processes for the separation of azeotropic or difficult zeotropic mixtures involve the addition of an entrainer. In azeotropic distillation, the entrainer is added to the charge, whereas it is fed continuously in extractive distillation.

Despite its anteriority to continuous distillation and its interest in high value added industries, batch distillation processes were not devoted as much attention as they should and for long, only homogeneous batch distillation was considered. Homogeneous batch extractive distillation was studied in 1988 by Lelkes et al. [1]; the feasibility of heterogeneous batch distillation processes was described by Rodriguez Donis et al. in 1992 [2]; pressure swing batch distillation was investigated in 2008 in by Lang and Modla [3] and a general criterion for extractive batch distillation was published in 2009 by Rodriguez-Donis et al. [4] and applied to entrainers that form new azeotrope [5]. In these papers, a major advantage of batch distillation over continuous distillation is the ability to drive the composition changes in the column during time thanks to the operating parameters, among which the reflux policy.

In this study the recovery of IPA (isopropyl alcohol) from an industrial waste stream (IPA/water mixture) is studied by conventional batch distillation and heterogeneous batch distillation.

BATCH DISTILLATION PROCESSES.

At atmospheric condition, a binary mixture of IPA and water forms a homogeneous minimum-boiling azeotrope at 87.4–87.7 mass% (68.1–67.5 mole%) and 80.3–80.4°C. Therefore, conventional distillation of a binary mixture Water – IPA will distillate the binary azeotrope.

Many distillation processes have been proposed to separate a pure substance from a mixture. There are two kinds of approaches to obtain a nearly pure IPA using advanced continuous distillation processes. One is to utilize an azeotropic distillation process using benzene or cyclohexane as an entrainer and the other is an extractive distillation process using ethylene glycol as a solvent. In azeotropic distillation, by forming a ternary heterogeneous azeotrope lower than any other binary azeotropic temperatures, a nearly pure IPA can be obtained as a

bottom product of the azeotropic distillation column. In extractive distillation, by adding a solvent exclusively familiar with water like ethylene glycol, IPA can be obtained as a top product of the extractive distillation column [8,9].

In this study the recovery of IPA from an industrial waste stream (IPA/water mixture) was studied by heterogeneous azeotropic batch distillation with cyclohexane. This technique is compared with conventional distillation and salting out methods.

According to experimental data [10], IPA forms a homogeneous minimum boiling azeotrope with cyclohexane at 67.0 mass% (37.8 mole%) and 68.6°C, and a ternary heteroazeotrope at 18.5 mass% (19.1 mole%) and 64.3°C. Finally, cyclohexane forms a heteroazeotrope with water at 8.5 mass% (31.3 mole%) and 69.8°C. The ternary mixture belongs to the 3.1-2 Serafimov's class, the most frequent, accounting for 26% of ternary mixtures [11]. The three pure components, the three binary azeotropes and the ternary azeotrope are stable nodes, saddle and unstable node respectively. Therefore, azeotropic distillation of any ternary mixture water – IPA - cyclohexane will lead to the ternary heteroazeotrope as distillate, which can be further decanted in a cyclohexane-rich phase and in a water-rich phase.

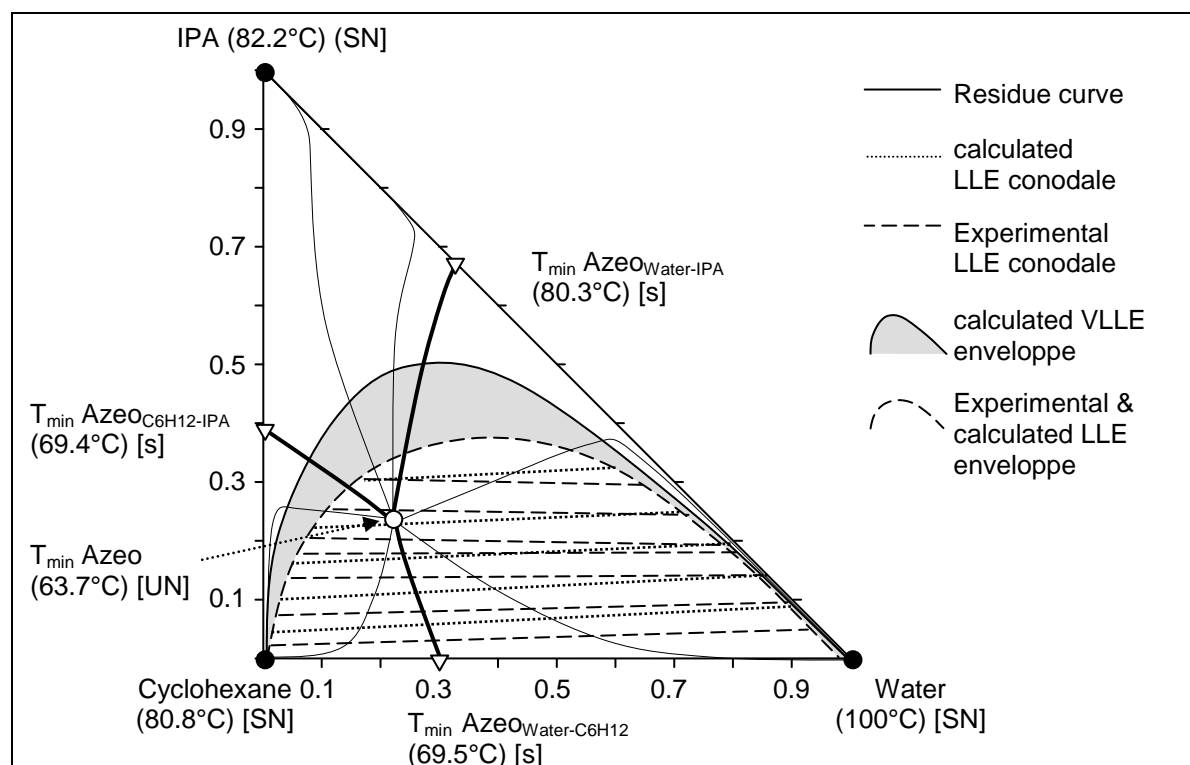


Figure 1: Residue curve map of the water – IPA – cyclohexane mixture

Figure 1 displays VLE calculations using the NRTL model and VLE binary parameters from Dechema [12] and LLE calculations using UNIQUAC with LLE parameters published in the Dechema [13]. The LLE conodale slopes at 25°C are reasonably predicted but do not capture the solutrope LLE behavior of the mixture. The VLE calculations agree fairly well, although they slightly overestimate the IPA fraction in the ternary azeotrope.

According to the precepts of heterogeneous batch distillation [1, 6, 7], several reflux policies can be used. Mode I policy refluxes all the decanter content to the column. Mode II policy has several sub-modes. Usually all the entrainer-rich phase is refluxed, possibly with some of the product-rich phase in order to maintain the demixtion in the decanter longer. Besides both phases in the decanter can be accumulated or depleted during the process. In this study the simpler complete entrainer-rich phase only reflux policy is achieved.

EXPERIMENTAL METHOD

An industrial IPA/Water mixture with an IPA content > 97 mass% was used. The IPA was previously dewatered by sodium hydroxide. The goal is to purify it with less than 0.1% water. Cyclohexane with a purity $\geq 99\%$ was used.

The water content of the samples was measured with an automatic Karl Fisher titration. The cyclohexane and IPA content were measured by gas chromatography using pentane as an internal standard.

CONVENTIONAL DISTILLATION

All conventional distillation tests were executed with a fractioned distillation column with 28 theoretical plates. The adiabatic column with a length of 105 cm and a diameter of 3 cm is filled with metal rashig rings.

780 g of an IPA/water mixture, which contained 2.00 mass% water was distilled with the conventional distillation column. The reflux ratio was ∞ until steady state conditions were reached at the top of the column (boiling temperature of binary IPA/water azeotrope). The IPA/water azeotrope was distilled with a reflux ratio of 30:2.

SALTED-OUT DISTILLATION

In a second experiment MgSO_4 was added as a drying agent to a known amount of IPA/Water mixture (2.47 mass% water). This mixture was mixed during 0.5h. A small amount of the salt dissolved in the mixture. The mixture was distilled with the conventional distillation method, with a reflux ratio of 20:2, when equilibrium conditions were reached.

In a third experiment the added MgSO_4 was filtered off prior to distillation. The water content of the initial IPA/water mixture was 1.75 mass%.

HETEROAZEOTROPIC DISTILLATION

The heteroazeotropic distillation is performed on a Heckman column with 30 real plates. 50L of an IPA/water mixture, which contained 0.83 mass% water and 2.5L of cyclohexane were added to the reboiler. This cyclohexane amount is slightly larger than the total holdup of the column (2250 mL). Preliminary test showed that this was the optimal entrainer volume. The vapor flow rate was set at 0.23 kmol/h.

The reflux ratio was ∞ until steady state conditions were reached at the top of the column where the recorded temperature was that of the boiling ternary IPA/water/cyclohexane

azeotrope. Then the reflux ratio of the column was set at 30:1. In a second step, the ternary IPA/water/cyclohexane heteroazeotrope was collected, cooled with ice and transferred to a separatory funnel. The water phase was collected and the organic phase was completely refluxed at the top of the column. This was continued until separation of the two phase became difficult because of the water removal. Then homogeneous distillation proceeded.

RESULTS AND DISCUSSION

CONVENTIONAL DISTILLATION

Figure 2 shows the temperature of the top vapor and the water content (mass %) of the residue as a function of the volume distillate. After 27% of the initial volume was distilled with a conventional distillation, the temperature of the top vapor was 81.9 °C, which corresponds to pure IPA. The water content of the residue reached the specification of 0.1 mass%.

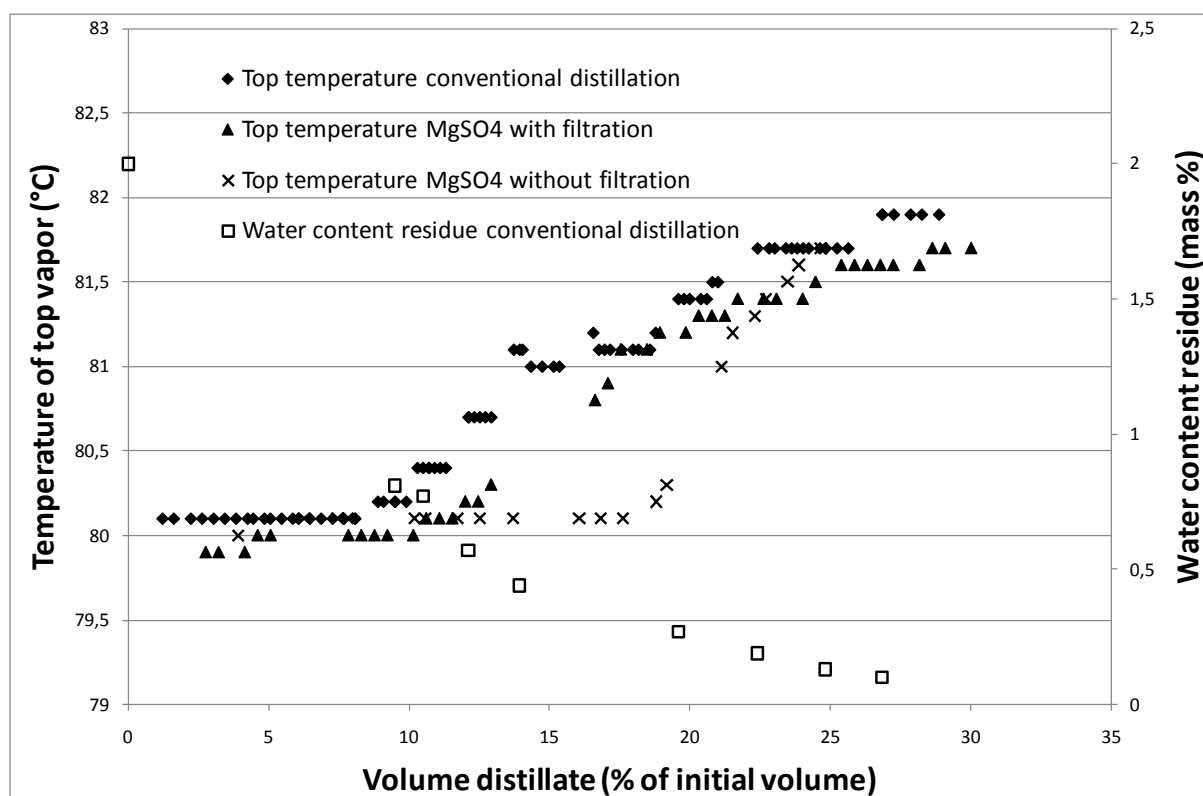


Figure 2: conventional distillation temperature of the vapor overhead and water content of the residue as a function of the volume distillate (% of initial volume)

Figure 2 also shows that the distillation curve of the IPA/Water mixture with the addition of MgSO₄ as a drying agent is similar to the distillation curve of the conventional distillation. The water content of the residue was 0.14 mass%. When the MgSO₄ salt was filtered prior to the distillation, the curve in the distillation line is more pronounced. The water content of the residue in this case is 0.02 mass%. However, the volume of distillate before the temperature of the top vapor equals the boiling temperature of IPA is again 25 – 30 %. The IPA recovery is thus 75 – 70 %.

HETEROAZEOTROPIC DISTILLATION

Figure 3 shows the temperature at the top of the column as a function of time. Because of the applied reflux policy (total reflux of organic rich phase), it is impossible to plot the top temperature as a function of volume distillate.

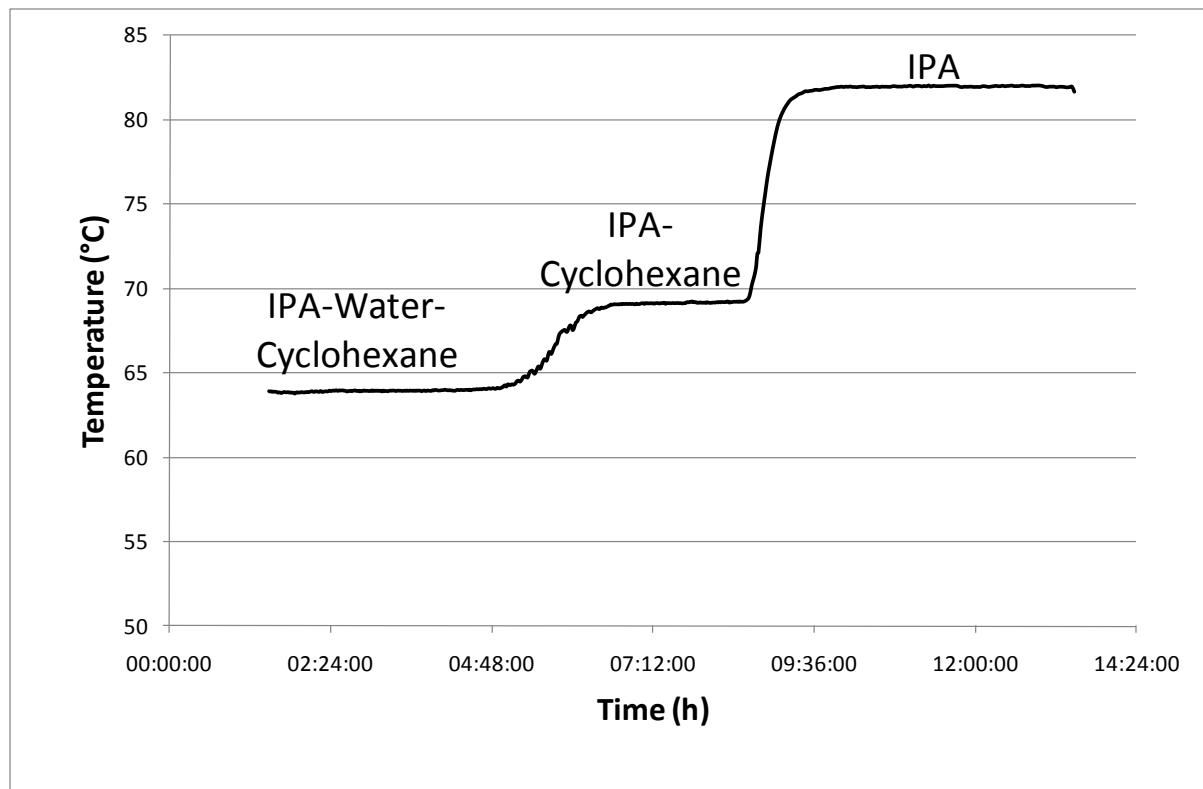


Figure 3: heteroazeotropic distillation temperature of the vapor overhead as a function of time

As predicted from the residue curve map analysis, figure 3 shows that first a distillate with boiling temperature of 64.1 °C, close to the ternary azeotrope composition is distilled. After collection 1.69L water phase (at a temperature of 65.2 °C), the separation of the two layers became difficult. At this point, the decanter is useless and conventional distillation proceeds. The boiling temperature of 69.3°C indicates that the binary IPA/cyclohexane azeotrope is distilled until the top temperature was 82.1°C. The total amount of binary azeotrope recovered was 4L. Finally 500 mL pure IPA is further distilled.

During the transitions between the ternary azeotrope and the binary IPA/cyclohexane azeotrope, the composition likely moves along the distillation boundary displayed in figure 1.

Table 1 shows the molar fraction and mass percentage of each component in the different collected samples. The water content in IPA decreases from 0.63 mass% to 0.04 mass%. IPA with a purity of 99.96 mass% can be obtained. The IPA recovery is 97.6%.

The binary CyH/IPA azeotrope can be reused in a subsequent batch distillation. The CyH in the water phase cannot be recovered. The total CyH recovery is 90.0%.

Table 1: Molar fraction and mass% of the collected fractions

Products	Amount (mol)	Molar fraction	Mass%
Aqueous phase decanter	33.34	x_{IPA} 0.451	65.2
		x_{CyH} 0.070	14.1
		x_{water} 0.479	20.7
Distillate binary azeotrope	46.34	x_{IPA} 0.587	52.2
		x_{CyH} 0.376	46.8
		x_{water} 0.037	1.00
Distillate final	6.54	x_{IPA} 0.999	99.96
		x_{CyH} 0.000	0.00
		x_{water} 0.001	0.04
Final still	615.47	x_{IPA} 0.998	99.95
		x_{CyH} 0.000	0.00
		x_{water} 0.002	0.05

Table 2 shows the component molar mass balance of the main streams. The deviation of molar amount of IPA and water (1.98% and 2.75% relative to the initial composition) is within the experimental error. The deviation of the molar amount of CyH is larger (-14.97% relatively to the initial composition). This can be explained by the CyH loss by evaporation, since the organic and aqueous phase were decanted manually.

Table 2: Component molar mass balance of the main streams of the process

Component	Input (mol)	Output streams			Balances		
		Aq. phase decanter	Distillates	Final still	Total in	Total exit	Deviation
IPA	650.320	15.052	33.734	614.430	650.320	663.215	12.895
CyH	23.207	2.331	17.402	0.000	23.207	19.732	-3.474
Water	18.247	15.961	1.742	1.044	18.247	18.748	0.501
Total	691.774	33.343	52.878	615.474			

CONCLUSIONS

99.96 mass% IPA was obtained by heteroazeotropic distillation of an industrial IPA/water mixture, using cyclohexane as entrainer. By using this procedure an IPA recovery of 97.6% is obtained. This is a high IPA recovery, compared to the conventional distillation techniques (with and without $MgSO_4$ addition). The binary azeotrope can be reused in a subsequent heteroazeotropic batch distillation.

The IPA recovery could be improved by selecting an entrainer, which does form a minimum boiling heteroazeotrope with water, but not a ternary azeotrope. Alternatively, according to literature, recovery could be also improved by refluxing part of the water-rich phase in order to keep the phase separation longer.

Finally, other processes could be investigated, such as extractive distillation [1,4,5]. The entrainer is then removed from the mixture by a second distillation step. Both options will be the topic of future research.

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