Azeotropes for Waste Recovery

Subjects: Others

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Aiming for more sustainable chemical production requires an urgent shift towards synthetic approaches designed for waste minimization. In this context the use of azeotropes can be an effective tool for “recycling” and minimizing the large volumes of solvents, especially in aqueous mixtures, used. This review discusses the implementation of different kinds of azeotropic mixtures in relation to the environmental and economic benefits linked to their recovery and re-use. Examples of the use of azeotropes playing a role in the process performance and in the purification steps maximizing yields while minimizing waste.

Keywords: azeotrope ; waste minimization ; solvent recovery ; azeotropic distillation ; process design

1. Introduction

By following the EPA policy for waste minimization, when the “redesign” of a process is not possible or complicated, recovery and reuse of solvent waste is crucial. An option could be distillation under different pressures, however, the risk of product degradation and also economic disadvantages, may lead to the definition of azeotropic distillation as an alternative effective route [1]. Azeotropic distillation may also involve an entrainer (E) which changes the volatility of the components of the azeotrope forming a new azeotrope. The azeotropic distillation can be homogeneous or heterogeneous, depending if it involves a liquid−liquid separation of the new azeotrope. When the entrainer is substituted with a solvent, the distillation is named extractive distillation: the solvent interacts with one or more components and changes their fugacity without forming any new azeotrope [2]. By combining the extractive distillation with heterogeneous azeotropic distillation a hybrid extractive-heterogeneous azeotropic distillation was proposed in 2004 [3]. One of the most important advantages of this hybrid distillation technology is that no additional solvents are added, and no new azeotropes are formed. Generally, water is present as auto-entrainer.

2. Homogeneous Azeotropic Distillation

The first production of anhydrous ethanol with azeotropic distillation was dated 1902 and was proposed by Young [4]. The addition of benzene to an ethanol−water mixture forms a three-component azeotrope which boils at 64.85 °C. This lower boiling point, compared with the ones of ethanol−water azeotropes, allowed the distillation of the novel azeotrope formed by removing water from ethanol. In addition, the excess of benzene could be easily separated from the alcohol by using *n*-hexane. Although this method proved to be efficient and opened the way for the development of different azeotropic distillation procedures, nowadays the use of benzene is unappealing and, generally, it should be avoided.

In this context, a practical example of waste minimization deals with the nitrocellulose manufacturing facility of Taiwan described by Liu in 2003 [5]. The waste minimization assessment plan applied at the satellite plant in Taiwan allowed for the reduction of waste at source and minimized waste, resulting in increased productivity of the facility. The alcohol rectification by azeotropic distillation was part of the recovery/recycle program. In 1978, ethanol was replaced with isopropyl alcohol (IPA) as a dehydrating agent. After concentration of the spent IPA by the two-phase column system, the formation of ternary azeotrope water−IPA−benzene allowed the recovery of up to 4 tons of IPA (99%+) daily. From 1990 to 1996 several alternatives were evaluated, and a novel rectification unit was built due to both increased production and the toxicity of benzene. The new rectification plan adopted from the task force replaced benzene with cyclohexane and the benefits from this decision allowed the recovery in two years of the USD 260,000 invested for the new rectification unit.

In 2018, You and coworkers proposed and compared by technoeconomic analyses different azeotropic distillation designs to separate light oil waste into single components [6]. Light oil is an organic waste from Nylon plant production and is composed of *n*-pentanol, cyclohexanone and cyclohexene oxide, compounds that are difficult to separate using conventional distillation due to their similar boiling points.

By using water as entrainer, the authors designed six different configurations for azeotropic distillation and carried out rigorous simulations, making use of the Aspen Plus software platform. The composition of the light oil was set as 35.4% of *n*-pentanol, 31.8% of cyclohexanone, and 32.8% of cyclohexene oxide in accordance with data from Yueyang Branch of Sinopec Corp. Strict parameters about purity degree of the recovered chemicals (more than 95%), their amounts (more than 92.5%) and amount of the entrainer (at least 98%) needed to be fulfilled when designing the process separation. With the results obtained from the simulations and technoeconomic analyses, it emerged that azeotropic distillation may save around 7% of the total annual costs in comparison with conventional distillation.

3. Heterogeneous Azeotropic Distillation

In cellulose acetate manufacturing, an important operation is the dehydration of acetic acid. Water and acetic acid do not form an azeotrope, and their boiling points are very similar, making conventional distillation too expensive for accomplishing the recovery of pure acetic acid. For this reason, several studies have been performed using heterogeneous azeotropic distillation [7][8]. Although these studies were focused on an optimization of the process design, an evaluation of operating costs and control of azeotropes are needed for a more comprehensive definition of a sustainable protocol. Indeed, process design and product design must be performed interactively to give a global evaluation of costs and the environmental quality of the entire process.

In 2005 Diwekar and Xu conducted a multiobjective optimization combining process and product design to evaluate the operability of the system and the environmental impact (EI) based on LD_{50} (lethal dose for 50% of the tested population) and LC_{50} (lethal concentration for 50% of the tested population) for the continuous separation of an acetic acid−water mixture using heterogeneous azeotropic distillation [9]. The authors selected seven different environmentally benign entrainers (ethyl acetate, propyl acetate, isopropyl acetate, methyl propyl ketone, methyl isopropyl ketone, diethyl ketone, and methyl propionate) for the formation of minimum boiling point azeotropes. By considering different objectives and solvents different distillation schemes were given. The results obtained evidenced that the highest amount of recovered acetic acid was obtained by using methyl isopropyl ketone, while the best EI for LC_{50} and LD_{50} was obtained with methyl propionate and isopropyl acetate, respectively.

Chien and coworkers focused their attention on the selection of the best entrainer for acetic acid recovery in different percentages, considering the impact on total annual costs [10][11]. In 2004 the authors selected the best entrainer for the separation of an acetic acid−water mixture 1:1 [10]. Between ethyl acetate, iso-butyl acetate, and *n*-butyl acetate the authors selected the latter as best entrainer for the high ratio and purity of the acetic acid obtained. The implementation of this heterogeneous azeotropic distillation reduced the total annual cost by 55% of the value obtained for conventional distillation. Although the results obtained in this study were interesting, a typical waste stream still contained a low amount of acetic acid. For this reason, the authors in 2006 designed an alternative system for a more reasonable 8:2 water−acetic acid mixture [11]. The need for a preconcentrator column was also investigated and its impact on total annual costs evaluated. Indeed, in industrial processes, the addition of a preconcentrator column in combination with the heterogeneous azeotropic distillation is common. After careful evaluation of different parameters and configurations, the optimal design consists of a single azeotropic distillation column with aqueous reflux stream. In this configuration a decrease in total annual costs of about 25% has been reached in comparison with the preconcentrator design.

As above mentioned, the pharmaceutical industry produces the highest amount of solvent waste and a typical example of this waste stream treatment consists of the recovery of ethyl acetate-isooctane mixture. This mixture features a low boiling point azeotrope (76.3 °C). In 2014, Gerbaud and coworkers screened 13 entrainers, among 60 candidates, for the recovery of high purity compounds through heterogeneous azeotropic distillation [12]. Among these, only acetonitrile and methanol were selected as effective entrainers for heterogeneous azeotropic distillation in a rectifying column configuration. After evaluating of the miscibility gap of the heterogeneous azeotrope, the composition of the entrainer−isooctane azeotrope and the temperature differences between the other possible azeotropes, acetonitrile was selected as the best entrainer. Indeed, acetonitrile allows a decrease in operational time with an increment in yield. This study was the first example of heterogeneous azeotropic distillation for the recovery of ethyl acetate-isooctane mixture. Furthermore, the authors validated the method in a batch distillation column configuration at laboratory scale.

Another growing industry at a global scale concerns the production of semiconductors for screens. One of the major contributors to waste associated with these processes, consists of the photoresistor thinners, i.e., propylene glycol monomethyl ether (PGME) and propylene glycol monomethyl ether acetate (PGMEA). Although these components are generally retrieved by distillation, the formation of their azeotropes with water makes the recovery of these representative photoresistor thinners difficult and energy demanding. In 2016, Lee and coworkers proposed the combination of heterogeneous azeotropic distillation with a dividing wall column (DWC) [13] technology for the purification and recovery of

PGME and PGMEA [14]. The authors investigated several configurations before selecting the heterogeneous azeotropic dividing wall column as the most energy and cost saving system for recovery of the photoresistor thinners. Indeed, they were able to save 33.1% of energy with an impact on the total annual costs of about 20% [14]. The energy savings in the combination of DWC technology with azeotropic distillation had already been observed, also in the dehydration of ethanol [1], bioethanol [2], acetic acid [3] and in the separation of pyridine−water−toluene mixtures [15].

4. Hybrid Extractive-Heterogeneous Azeotropic Distillation

A more complex industrial issue is related to the separation of nonideal quaternary mixtures. The waste streams studied by Mizsey in 2004 were six different nonideal mixtures composed of ethanol (EtOH), ethyl acetate (EtOAc), isopropyl acetate (IPOAc), methyl-ethyl-ketone (MEK), iso-propanol (IPOH), acetone and water (H_2O) [16]. These solvents generate binary and ternary azeotropes and have been divided into three groups (**Table 1**). The authors gave general important guidelines for separating each group by using water as auto-entrainer with hybrid extractive-heterogeneous azeotropic distillation.

Table 1. Groups of nonideal mixtures with number of azeotropes formed.

	Mixture	n. Binary Azeotropes	n. Ternary Azeotropes
Group 1	Water, EtOH, MEK, acetone	3	1
	Water, EtOH, EtOAc, acetone	3	1
Group 2	Water, EtOH, EtOAc, IPOAc	5	2
	Water, EtOH, MEK, IPOAc	5	2
Group 3	Water, EtOH, EtOAc, MEK	6	3
	Water, IPOH, EtOAc, MEK	6	3

Below are listed the general strategies for each group without considering dehydration of EtOH and IPOH:

- Group 1: acetone does not form any azeotropes with other components; from the economic point of view it is preferable to separate it with conventional distillation before proceeding through extractive heterogenous distillation to separate the remaining solvents by using additional water as auto-entrainer.
- Group 2: when a couple of solvents which do not form azeotropes, but their azeotropes are present with other components, extractive-heterogeneous azeotropic distillation with two subsequent conventional distillations is the preferred way to recover single components.
- Group 3: when a binary azeotrope is present between the components of the mixtures, the best way for solvent separation is two extractive-heterogeneous azeotropic distillations with subsequent conventional distillation.

This novel hybrid distillation allows the separation of complex mixtures and is a promising tool for the recovery of solvents from the waste stream with a reduced environmental impact.

To better understand the role of this new hybrid azeotropic distillation, a comparison with the conventional treatment, i.e., recovery or incineration, has been reported by the same authors in 2006 considering both environmental and economic impact [17]. A life-cycle assessment (LCA) consideration was expanded for different options of treatment of a nonideal mixture (EtOH, EtOAc, IPOAc, water) from a printing company by using Eco-indicator 99 life-cycle impact assessment methodology [18]. This method allows the assignment of a single score to the environmental impact. Focusing only on incineration and recovery by conventional distillation alternatives, economic and environmental impacts are not in agreement. Indeed, from the economic point of view, recovery is the preferable option, however, the high energy demand for separating this nonideal mixture is too high to be considered sustainable. This contradictory evidence is the driving force of green engineering to design more sustainable recovery processes. On the other hand, from these calculations, emerges the only option which leads to both economic and sustainability benefits: extractive-heterogeneous azeotropic distillation [17].

Extractive-heterogeneous azeotropic distillation is not only limited to the separation of minimum boiling point azeotropes but is useful also when those with maximum boiling points are present. Based on industrial problems, Toth and coworkers investigated the separation of two nonideal mixtures containing chloroform [19]. Chloroform generates maximum boiling

point binary azeotropes both with acetone and EtOAc. After careful simulation and experimental verifications, the authors proved for the first time in 2019 the efficiency in separation of maximum boiling point azeotrope recovering chloroform at 99.5% purity.

5. Azeotropes and Membrane Technologies in Water-Containing Waste Treatment

Wastewater treatment is a complex common issue for several industries and it is also linked to the worldwide increasing demand for fresh water. Industrial wastewater comes from reverse osmosis of brine and requires the employment of membrane technologies [20][21]. Among these technologies, pervaporation is also widely employed in the removal of volatile organic compounds (VOC), dehydration of organic solvents and separation of organic mixtures [22][23][24][25][26][27]. In addition, the pervaporation approach has many advantages in the sustainable dehydration and recovery of solvents (e.g., avoids the use of entrainer, high selectivity), although a major limit can be related to the relatively high costs of membranes.

To solve this issue, hybrid technologies have been developed [28][29][30].

In 2018 a study by Andre and coworkers about the separation of an isobutanol−water mixture, emerged that the choice of a separation process strictly depends on the product composition requirement [31]. Moreover, the ranking position of a separation technology cannot be easily standardized due to social and technological factors. The authors compared different separation methods and also their combination: azeotropic distillation, azeotropic distillation extended with heat integration, pervaporation, distillation assisted pervaporation and distillation assisted pervaporation with heat integration. Multi-Criteria Decision Analysis, comprehensive of Political, Economic, Social and Technological (PEST) analysis, gave similar results to those obtained from LCA considerations. Besides considering 98.8 *w*/*w*% of isobutanol it is clear how pervaporation is the favorable choice in comparison with azeotropic distillation, by increasing to 99.9 *w*/*w*% their relative ranking position is unclear, while the hybrid combination of distillation-assisted pervaporation with heat integration is without any doubt the most convenient separation alternative in both cases.

In 2019 similar considerations have been highlighted by Toth for the selection of the separation technology of an ethyl acetate−ethanol−water highly nonideal mixture [29]. Four different combinations of separation techniques have been economically compared considering the total annual costs (TAC). Hybrid extractive-heterogeneous azeotropic distillation allowed a reduction of the energy requirement in combination with pervaporation confirming the importance of the combination of different methodologies for saving money and energy in waste purification. Recently this combination has shown itself to be efficient also in the separation of other nonideal three-component mixtures: ethyl acetate−methanol−water and isobutyl acetate−methanol−water [30].

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