



Review

Dehydration of Isopropanol: A Comparative Review of Distillation Processes, Heat Integration, and Intensification Techniques

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Abstract: The dehydration of isopropanol (IPA) is a crucial process in numerous industries, and the optimization of its efficiency and economic viability is essential. This review provides a comprehensive analysis and comparison of various distillation processes, heat integration (HI) strategies, and process intensification (PI) techniques employed for IPA dehydration. The advantages, limitations, and applicability of distillation processes, such as extractive distillation, heterogeneous azeotropic distillation, and pressure swing distillation, are discussed. In addition, this review explores the potential of HI techniques to optimize energy consumption and reduce operating costs of IPA dehydration processes. PI techniques, including thermally coupled arrangements and dividing wall columns, are examined for their ability to improve the process efficiency and sustainability. It is crucial to conduct thorough evaluations, as well as energy and economic analyses, when choosing the appropriate distillation process, HI approach, and PI technique for specific IPA dehydration applications. This review emphasizes the potential for improving the energy efficiency, product purity, and cost-effectiveness of IPA dehydration through the integration of advanced distillation processes and PI techniques.

Keywords: isopropyl alcohol; heat integration; process intensification; heterogeneous azeotrope distillation; extractive distillation; pressure swing distillation



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1. Introduction

Isopropyl alcohol (IPA; IUPAC name: propan-2-ol; common name: isopropanol) is a colorless and flammable liquid with the formula $(\text{CH}_3)_2\text{CHOH}$. IPA was the first commercial synthetic alcohol produced by Standard Oil in 1920 and currently holds significant importance in various industries and applications. IPA serves as a crucial ingredient in the pharmaceutical and cosmetics industries, e.g., as a solvent for various active pharmaceutical ingredients in drug formulations, a carrier for topical medications, and a common component in cosmetics, personal care products, and perfumes [1]. Owing to its ability to dissolve a wide range of substances, IPA is an effective cleaning agent in industrial cleaning processes, in degreasing, and in the electronics industry for cleaning circuit boards and components [2]. The global production of isopropanol was estimated to be approximately 2.21 million tons in 2021 and approximately 2.73 million tons in 2029 [3]. The United States is the largest consumer of IPA, whereas China continues to be the largest capacity holder, accounting for approximately 30% of the global capacity [3].

There are two main methods of producing IPA. The first method, more commonly used in Europe, combines propylene (PP) and water through a direct hydration reaction. Another method involves the production of IPA via hydrogenation of acetone. Nevertheless, this route includes additional steps because acetone is normally prepared from PP via cumene. Subsequently, in both processes, IPA must be isolated from water and other byproducts

by distillation. In summary, IPA production typically involves propylene hydration, IPA preconcentration, and IPA dehydration.

The IPA dehydration step is a major consumer of energy in the IPA production process, mainly due to the critical challenge of separating IPA from water, which forms a challenging azeotropic mixture. According to the Aspen database, IPA and water form a homogeneous azeotrope of 88.25 wt.% IPA at atmospheric pressure. The presence of this azeotrope significantly hampers the direct separation of IPA and water through simple distillation methods [4]. As a result, achieving high-purity IPA is difficult without an effective dehydration process. In particular, the crude IPA stream from the propylene hydration reactor is introduced into the preconcentration step that concentrates IPA to a near-azeotropic composition. The next step involves the challenging dehydration of IPA to achieve a concentration above the azeotropic composition. This process is of significant research interest due to the crucial need for high-purity IPA in numerous industrial applications. By removing water from the azeotropic mixture, IPA dehydration ensures that the final product meets stringent purity requirements.

To address this issue, various advanced separation methods, as well as heat integration (HI) and process intensification (PI) techniques, have been applied to improve the energy efficiency and reduce the environmental impact of production [5–11]. These techniques include azeotropic distillation, extractive distillation (ED), pressure swing distillation (PSD), heat pump-assisted distillation, and dividing wall column (DWC). Note that reactive distillation (RD) stands out as one of the most remarkable intensified techniques and has been reported to significantly enhance the performance of the reaction part in the IPA production process. Chua et al. Presented two alternative intensified processes, namely, the RD-splitter and RD-ED processes, for two different scenarios: excess propylene and excess water, respectively [12]. The results from their study demonstrated that the RD-ED process with excess water exhibited better overall performance compared to the RD-splitter process. These findings further highlight the potential benefits of incorporating reactive distillation as a process intensification technique in the IPA production process. In addition, although plantwide control of the IPA dehydration process is vital for achieving efficient, safe, and reliable operation of the entire IPA production facility, it is out of scope of the present review [13]. In this review article, we explore various IPA separation methods, as well as HI and PI techniques, that have been utilized specifically in the IPA hydration process and examine their impact on process efficiency and sustainability. The challenges and potential solutions associated with IPA production are also discussed.

2. Separation Method for IPA Production

2.1. Heterogeneous Azeotropic Distillation (HAD)

Heterogeneous azeotropic distillation (HAD) is widely used in the industry for the separation of azeotropic mixtures, particularly for IPA production. HAD is a separation technique that involves an entrainer to break the azeotrope between two or more components in a feed mixture [14–16]. The entrainer is added to the mixture to form a new lower-boiling-point azeotrope with one of the components, which can then be separated from the other components by distillation [14]. Figure 1 shows a typical two-column HAD configuration for IPA production. First, the IPA–water mixture and entrainer are introduced into the first distillation column, known as the azeotropic column, to isolate the IPA product (>99.5 wt.%) at the bottom, whereas the ternary azeotrope formed from the entrainer, water, and a small amount of IPA is delivered to the top. The overhead stream is then input into a decanter, which naturally separates the feed into organic and aqueous phases. Subsequently, the organic phase is recycled back to the first column, and the aqueous phase is distilled in the other distillation column that separates the water at the bottom and the IPA–water azeotrope at the top, before recycling this azeotrope to the first column. A careful selection of the entrainer is crucial for the success of the HAD process. Several entrainers have been reported for the IPA process such as benzene [17–19], cyclohexane [17,20–22], isooctane [14,23,24], diisopropylether [25,26], dichloromethane [27], 1,2-dichloroethane [27],

2-methylbutyl acetate [27], 1-butanol [28], 1-pentanol [27], phenylmethanol [27], cyclohexanol [27], 1-methylcyclohexanol [27], dibenzyl ether [27], and octanenitrile [27]. Among these, cyclohexane [17,20–22], benzene [17–19], and isooctane [14] are the most outstanding solvents, as discussed in detail below.

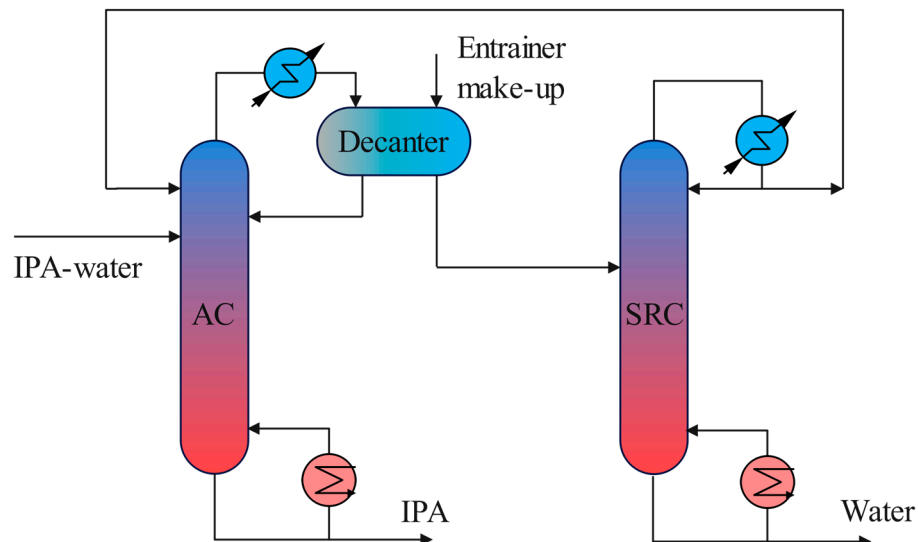


Figure 1. Two-column sequence for heterogeneous azeotropic distillation (HAD-2).

2.1.1. Cyclohexane Entrainer

Wang et al. investigated cyclohexane as an entrainer for IPA dehydration via HAD [20]. A column can produce IPA with higher purity at higher reflux; however, a temperature plateau of 69.3 °C exists because of the formation of an IPA + cyclohexane azeotrope [20]. However, the plateau disappears with increasing the number of stages in a column [20]. This study was one of the earliest to experimentally investigate the behavior of the azeotrope mixture IPA + cyclohexane + water. The regressed parameters from this study have been used multiple times in recent research.

Chien et al. suggested that an HAD two-column sequence (HAD-2) is a more economical and feasible approach than an HAD three-column sequence (HAD-3) [17]. In both sequences, the feed is fed to the first column, from which pure IPA is collected as the bottom product [17]. The top product is then sent to the decanter [17]. The organic phase from the decanter is refluxed to the first column, whereas the aqueous phase is sent to the second column [17]. In HAD-3, the top product of the second column is an IPA–water–cyclohexane azeotrope, which is partially recycled to the decanter, and some parts are refluxed [17]. The bottom product of the second column is sent to the third column [17]. Pure water is collected from the bottom of the third column, whereas the distillate is recycled to first column [17]. In HAD-2, the top product of the second column is partially recycled to the first column, and some parts are refluxed [17]. Pure water is collected as the bottom product of the second column [17]. The results showed that the HAD-2 sequence could considerably reduce TAC as compared to the HAD-3 sequence. Therefore, the compact HAD-2 design was proposed and further explored for dynamic simulation and control strategy developments.

2.1.2. Benzene Entrainer

Cho and Jeon conducted a modeling and optimization study of the IPA process using benzene as an entrainer, producing over 99.9 mol.% IPA from a dilute IPA aqueous stream [18]. A three-column HAD sequence (HAD-3) was designed as shown in Figure 2. The feed was fed to the first column, which behaved as a pre-concentrator column [18] to produce a close azeotrope mixture at the top before being introduced to the second column. Subsequently, azeotropic distillation was performed in the second column to produce the

desired IPA product, and the third column was used to strip benzene and IPA, which were then recycled. The NRTL (non-random two-liquid) liquid activity coefficient model was used to simulate the entire azeotropic distillation unit. The study found that the optimum concentration of IPA at the top of the concentrator that minimized the total heat duty of the reboilers was 38.7 mol.%. However, benzene is a hazardous chemical that can adversely affect human health and the environment. Therefore, its use is regulated or restricted in many countries. Consequently, cyclohexane is more commonly used in the IPA process to mitigate the health and safety concerns associated with benzene.

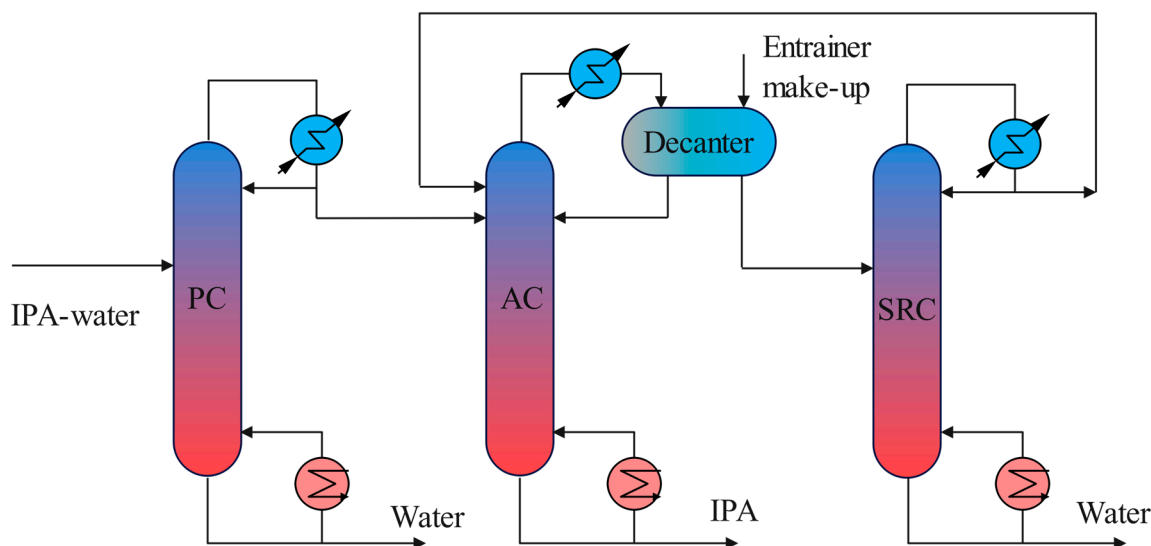


Figure 2. Three-column sequence for heterogeneous azeotropic distillation (HAD-3).

2.1.3. Isooctane Entrainer

Guido et al. presented an entrainer selection step and process simulation for the separation of an IPA + water mixture by HAD [14]. Various candidate entrainers were identified, and their performances were compared using ternary maps [14]. Benzene was found to be the most suitable; however, isooctane was suggested as a feasible and viable entrainer owing to its carcinogenic nature [14]. Once isooctane was identified as the most appropriate solvent for the separation, process simulations were performed using Aspen Plus[®] V11 with the NRTL fluid package. The HAD-2 arrangement was analyzed using an HAD column (30 stages) and a solvent recovery column (SRC) (25 stages) [14]. The feed was fed into the HAD column (third stage), and IPA was collected as the bottom product [14]. The top product of the HAD column, which was close to a ternary azeotrope, was sent to a decanter [14]. The organic phase was returned to the HAD column (first stage), and the aqueous phase was sent to the SRC (tenth stage) [14]. Pure water was collected as the bottom product of the SRC and the distillate was recycled back to the HAD column (second stage) [14]. The results showed that isooctane was a promising entrainer for the IPA dehydration using HAD technique. Specifically, traces of isooctane do not pose a problem in the recovered dehydrated alcoholic product regarding its subsequent use as fuel.

2.2. Extractive Distillation (ED)

Both HAD and extractive distillation (ED) are widely applied techniques for separating azeotropic mixtures in the industry [1,29–33]. In HAD, an entrainer is added to the distillation column along with the feed mixture to form a new low-boiling-point liquid–liquid azeotrope with one or two of the components. The heterogeneous azeotrope is then split using a decanter and purified using another distillation column before being recycled back to the system. However, in ED, a solvent is added to revamp the relative volatility of the components to be separated [1,34]. Unlike the entrainer in HAD, the solvent in ED is

typically miscible with the feed mixture and selectively dissolves one of the azeotropic components, which creates a difference in volatilities of the two components, thereby facilitating separation through distillation. Different solvents can be used depending on the specific mixture to be separated [1]. Figure 3 shows a typical ED configuration for separating the IPA–water azeotrope. The feed mixture and solvent are simultaneously introduced into the first distillation column, where the IPA is collected as a distillate. The bottom stream, containing water and solvent, is delivered to the second column to regenerate the solvent for reuse. Solvent selection plays a crucial role in ED. The selection of the most suitable extractive solvent depends on various factors, such as selectivity, separation efficiency, boiling point temperature, cost, availability, environmental considerations, and ease of solvent regeneration. Several popular extractive solvents used to separate IPA from water are discussed below.

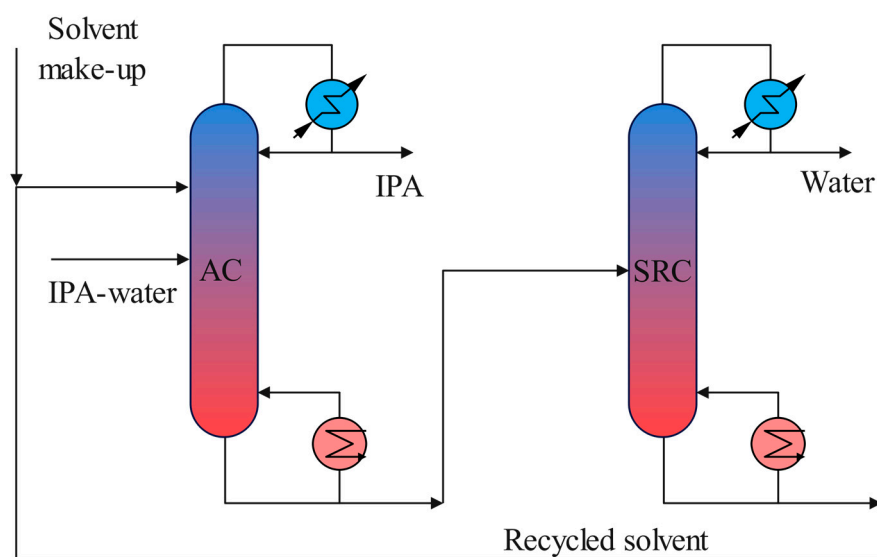


Figure 3. Typical extractive distillation configuration for separating IPA–water azeotrope.

2.2.1. Alcohol Solvents

Thus far, alcohol solvents have played a crucial role in ED for separating the IPA–water azeotrope. Their selectivity toward IPA and ability to adjust the relative volatility considerably enhances the separation efficiency, enabling the production of high-purity IPA.

Hartanto et al. suggested the use of glycerol as a solvent in ED to separate the IPA/water mixture [35]. Glycerol, a byproduct of biodiesel production, is an environmentally friendly chemical [35]. In this study, glycerol was continuously fed to the top stage (second stage) of the ED 25-stage column, whereas the IPA/water mixture was fed to the middle (20th stage) of the column [35]. On the basis of a sensitivity analysis considering factors such as the number of trays, reflux ratio, distillation composition, and energy duties, an optimal process design for ED was determined. The proposed ED design using glycerol allowed for the successful separation of IPA–water azeotropes, resulting in the production of highly pure IPA (up to 99.27 mol.%) and efficient recycling of the solvent. Note that, while glycerol has advantages as an extractive solvent for separating IPA and water, its high boiling point introduces certain drawbacks, including increased energy requirements, potential thermal degradation, equipment design considerations, viscosity effects, solvent loss, and environmental implications. These factors should be carefully evaluated when considering the use of glycerol in ED processes.

Kalla et al. provided insights into the use of ethylene glycol (EG) as an entrainer for IPA–water mixtures and highlighted the importance of sensitivity analysis in process simulations [1]. Aspen Plus was used as a simulation tool to study the temperature,

pressure, and concentration profile of the separation process, and the optimum number of stages for the simulation was 42 [1]. Throughout the sensitivity analysis, the findings revealed that the top of the column exhibited remarkably high-purity IPA, reaching up to 99.97 mol.% purity, highlighting the effectiveness of EG as a solvent for the separation of the IPA–water mixture.

Recently, Cui et al. proposed a mixture of choline chloride/glycerol (1:2) (ChCl–G (1:2)) and ChCl/ethylene glycol (1:2) (ChCl/EG (1:2)) for the separation of IPA–water azeotropes using ED [36]. The advantages of mixed solvents were analyzed and compared with those of traditional solvents in terms of cost, thermodynamic efficiency, and environmental impact. Compared to traditional single solvents, processes employing mixed solvents were considerably economical in terms of equipment costs and energy consumption. Moreover, this process demonstrated improved thermodynamic efficiency, primarily because of the reduced use of extractants. Regarding the environmental impact, a mixture of choline-based and alcohol solvents exhibited favorable environmental characteristics, including simple preparation and strong biodegradability, which are of utmost importance for promoting green practices and the sustainable development of IPA production.

2.2.2. Ionic Liquids

In recent years, ionic liquids (ILs) have gained significant interest as extractive solvents for separating IPA–water azeotropes. This is because the use of ILs offers improved selectivity, a wider operating range, tunability, reduced environmental impact, and potential for reusability, making them promising alternatives to traditional solvents in the IPA process.

1-ethyl-3-methylimidazolium Tetrafluoroborate ([EMIM][BF₄])

Gomey et al. studied the IPA ED process by comparing the extractive solvents of the IL 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄]), ChCl/EG, ChCl/G, and dimethyl sulfoxide (DMSO). The feed and entrainer were fed into the ED column near the bottom and top stages, respectively [37]. The solvent flow rate and reflux ratio were analyzed to determine the desired product purity [37]. [EMIM][BF₄] achieved the lowest reboiler duty and was considered the most promising candidate according to energy consumption.

1-ethyl-3-methylimidazolium Dicyanamide ([EMIM][N(CN)₂])

Ma et al. suggested [EMIM][N(CN)₂], as a more viable entrainer as compared to [EMIM][BF₄], due to the low molecular weight of ([EMIM][N(CN)₂]) [11]. Its feasibility was verified using a residue curve map [11]. Two different process arrangements were proposed using one or two evaporators instead of the SRC [11]. Evaporators were incorporated because ILs have low saturated vapor pressures [11]. When using one evaporator, pure IPA was collected as a distillate, and the bottom product was sent to the evaporator [11]. The pure ILs from the evaporator were recycled in a column [11]. While using two evaporators, pure water was removed from the first evaporator, and the remaining liquid was sent to the second evaporator [11]. The pure IL from the second evaporator was recycled into the column [11]. A multiobjective genetic algorithm was employed to optimize the operating parameters of these processes. The findings indicated that the process utilizing two evaporators outperformed the others, primarily because of its ability to operate at higher pressures. Moreover, the suggested control structure demonstrated excellent resilience against disturbances caused by variations in the feed flow and composition. These results highlight the potential of [EMIM][N(CN)₂] as an extractant for the industrial separation of IPA and water.

1-ethyl-3-methylimidazolium Acetate ([EMIM][OAC])

Chen et al. suggested [EMIM][OAC], composed of cations (1-ethyl-3-methylimidazolium ([EMIM]⁺), 1-butyl-3-methylimidazolium ([BMIM]⁺), and 1-hexyl-3-methylimidazolium ([HMIM]⁺) and anions (acetate ([OAC][−]) and chloride ([Cl][−]), as an entrainer over ILs [38].

[EMIM][OAC] enhanced the relative volatility of IPA and water the most, even when compared to DMSO [38]. The operating temperature was set to 140 °C, at which the decomposition of [EMIM][OAC] was initiated [39]. Two arrangements were studied [38]. One uses two flash drums in series in addition to the ED column, and the second uses a flash drum and a stripping column in addition to the ED column [38]. Operating conditions of high temperature and low pressure were used to recover pure IL [38]. Consequently, the pressure of the ED column and first flash drum was set to 101.3 and 3.9 kPa in both approaches [38]. The feed was preheated with the recycled IL using an FEHE [38]. Subsequently, feed and IL were fed into the ED [38]. Pure IPA was collected as a distillate [38]. In the first approach, the bottom product of the ED column was passed through two vacuum-operated flash drums to collect pure IL [38]. The pressure of the second flash drum was 0.32 Pa, resulting in the vaporization of the IL, which was recovered using a condenser and was then recycled to the ED column [38]. In the second approach, the vaporized IPA was heated to 244 °C and then directed into the stripping column, where it flowed in a countercurrent manner to the IL stream originating from the bottom of the flash drum [38]. The IPA present in the top product of the stripping column was recovered using a condenser and recycled back to the ED column [38]. The first approach required vacuum conditions with very low pressure [38]. Therefore, the second approach was more feasible, with an 8.36% reduction in TAC compared to the conventional ED that uses DMSO as an entrainer [38].

2.2.3. Deep Eutectic Solvents (DES)

In recent years, deep eutectic solvents (DES) have attracted significant attention for the separation of IPA from water in ED [40–42]. DESs are a class of solvents composed of a eutectic mixture of hydrogen-bond donors and acceptors. Unlike traditional solvents, which are typically composed of a single compound, DESs are formed by the complexation of two or more components through strong hydrogen-bonding interactions. Therefore, DESs are characterized by several distinct features such as low volatility, high thermal stability, ionic conductivity, high viscosity, excellent solubility, and environmental sustainability. They combine the high separation capability of solid salts with the simple handling of liquids, while exhibiting low to negligible vapor pressures and non-flammability [41]. Their unique properties make them attractive alternatives to traditional entrainers, offering advantages in terms of selectivity, energy efficiency, sustainability, versatility, and reusability.

Jiang et al. screened 18 choline-chloride-based DESs using the COMSMO-SAC model for the separation of the IPA and water azeotrope [40]. The results showed that choline chloride/triethylene glycol (ChCl/TEG) and choline chloride/ethylene glycol (ChCl/EG) had the highest capacities and screening indices, whereas the performance index of ChCl/TEG was higher than that of ChCl/EG. ChCl/TEG in a molar ratio of 1:3 was selected and validated by measuring the vapor–liquid equilibrium (VLE) data for the IPA + water + DES system at 1 atm. The measured VLE data were in good agreement with the VLE data correlated with the NRTL model.

Rodríguez and Kroon conducted experiments using two DESs, lactic acid/ChCl (2:1) and glycolic acid/ChCl (3:1), as entrainers for IPA dehydration through ED [42]. Initially, the VLE data of binary mixtures comprising the entrainers, IPA, and water were measured. Both DESs increased the activity coefficients of IPA and water, indicating their potential as entrainers. However, only glycolic acid/ChCl (3:1) at a concentration of 10 mol.% exhibited a greater enhancement in IPA volatility than in water volatility.

Subsequently, the VLE data for the ternary mixture of the entrainers, IPA, and water were measured at DES concentrations of 5 and 10 mol.%. Glycolic acid/ChCl (3:1) at 10 mol.% shifted the azeotrope composition from 0.68 mol.% IPA to 0.89 mol.% IPA; the azeotrope was not completely broken in any case. These findings suggest that glycolic acid/ChCl (3:1) at a higher concentration can effectively modify the composition of the azeotropic mixture, albeit not achieving complete separation.

Neubauer et al. discussed VLE measurements, thermodynamic modeling, entrainer feasibility considerations, and process simulations [41]. A DES can be inputted as a user-

defined component because it is unavailable in commercial process-simulator databases [41]. Scalar thermodynamic properties, such as critical temperature, pressure, and volume, as well as normal boiling point and acentric factor, were either taken from the literature or estimated using a combination of the modified Lydersen–Joback–Reid method and the Lee–Kesler mixing rules [41]. These simulations can optimize the use of DES in extractive distillation by predicting their behavior under different conditions and identifying the most efficient operating parameters for separation [41].

2.2.4. Other Extractive Solvents

Dimethyl sulfoxide (DMSO) is an attractive entrainer for the dehydration of IPA due to its high separation factor [9,10,43–46]. Arifin and Chien investigated the optimal design and control structures of an ED for separating IPA and water with DMSO as the solvent [43]. Initially, the feasibility of DMSO as a solvent for separating the IPA–water azeotrope was confirmed through RCM and equivolatility curve analyses. Subsequently, the process structure was optimized by minimizing the total annual cost (TAC) criterion.

In the optimized ED process, DMSO was continuously fed into the seventh stage of a 41-stage column, whereas the IPA–water mixture was introduced at the 35th stage [43]. The high-purity IPA product was obtained from the top of the column, whereas the bottom product, containing water and DMSO, was fed into the ninth stage of a SRC consisting of 24 stages. The SRC separated DMSO, which was then recycled back to the ED column for further use.

Furthermore, ED using DMSO as the solvent was compared with HAD using cyclohexane as the entrainer. The simulation results demonstrated that the ED process with DMSO achieved a remarkable 32.7% reduction in the TAC compared to the HAD process. These findings highlight the superiority of DMSO as an entrainer for the separation of IPA–water mixtures, in terms of efficiency and cost-effectiveness.

Spatolisano and Pellegrini presented a comprehensive review of the fundamentals of dehydrating IPA and water mixtures and proposed innovative and energy-efficient separation schemes, including HAD with binary azeotropes and liquid–liquid extraction combined with distillation [47]. The proposed schemes involve the use of alternative solvents; DMSO was suggested as one of the most promising solvents in terms of separation selectivity and reduced energy consumption.

Kataria et al. suggested 13 mol.% diaminomethanal as a potential entrainer for the dehydration of IPA using ED [48]. Diaminomethanal is nonvolatile, nontoxic, inexpensive, and widely available [48]. VLE experiments showed that the vapor-phase concentration of IPA increased with increasing diaminomethanal concentration [48].

Kong et al. discussed an ED design strategy for the separation of binary azeotropic mixtures, focusing on its inherent flexibility [49]. This approach allowed external fluctuations to be considered in the early stages of the design, including the ability to adjust and adapt to changes in feed composition or operating conditions without significant modifications or loss of efficiency, leading to better economic efficiency [49]. The control variables were determined and adjusted to analyze the feasibility of the system under the available constraints while maximizing the flexibility index [49]. IPA and water were separated using DMSO and EG as solvents in two case studies. The results showed that DMSO provided lower TAC, whereas EG provided better operational flexibility with a lower TAC trade-off [49].

2.3. Pressure Swing Distillation (PSD)

In addition to ED and HAD, PSD has been suggested as a viable option for IPA dehydration [50]. PSD is a commonly used separation technique for azeotropic mixtures, in which the operating pressure of the distillation column is varied to exploit the differences in vapor pressure between the components. This allows for the selective separation of the desired components by adjusting the pressure, thus overcoming the limitations of traditional distillation methods. A notable advantage of PSD over AD and ED is the

elimination of the need for additional entrainers or solvents, thereby avoiding product contamination. Therefore, to address potential environmental issues, it is important to reduce the use of additional solvents.

Zhai et al. reported that the PSD method could effectively separate IPA from water, and that energy-saving methods could be applied to further improve its performance [50]. On the basis of the feasibility analysis, the PSD process was designed with an LP (low-pressure column operating at 0.2 atm and a HP (high-pressure) column operating at 10 atm (Figure 4). This pressure variation is a promising approach for the effective separation of IPA/water mixtures. The sequence of the process involved initially introducing the feed into the LP column and then feeding the distillate to the HP column. Pure water and pure IPA were collected from the bottom of the LP and HP columns, respectively. Their results demonstrated that the PSD process achieved the desired separation with high-grade IPA product purity.

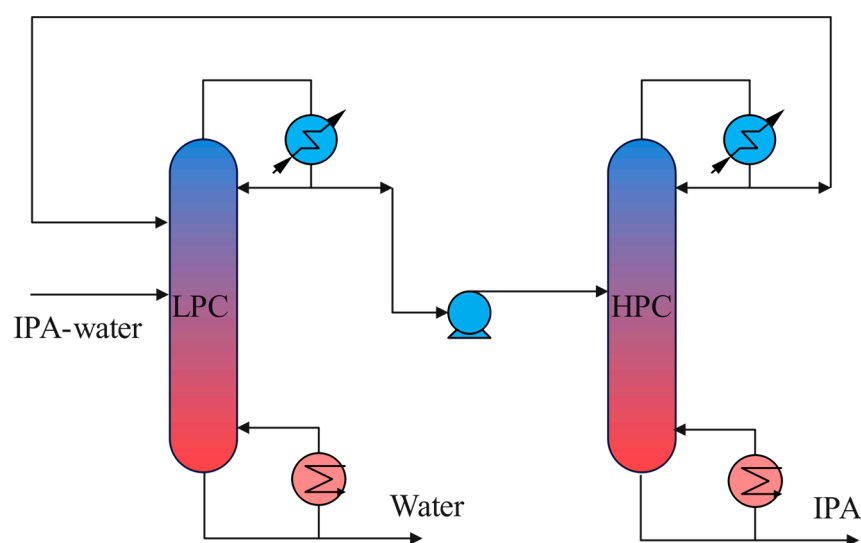


Figure 4. Pressure swing distillation for IPA dehydration.

3. Heat Integration and Intensification Techniques for Improving IPA Dehydration

To further reduce the energy requirements and environmental impacts and improve process performance, numerous HI and PI techniques have been implemented in the IPA dehydration process in recent years [7,8,22,45,50–54]. HI is a common technique that involves the integration of heat exchangers and heat recovery systems within the distillation process. By capturing and utilizing waste-heat streams from different process streams, heat integration reduces the need for external heating or cooling, thereby saving energy. Another approach is PI, which aims to enhance the separation efficiency and productivity of the distillation units. This can be achieved through various means, such as the use of advanced internals (e.g., structured packings, trays) that promote better mass and heat transfer, application of novel column configurations (e.g., dividing wall columns) to improve separation efficiency, and implementation of hybrid separation processes that combine distillation with other separation technologies (e.g., membrane distillation, reactive distillation).

In the upcoming sections, we examine the recent advancements in HI and PI techniques as they apply to three commonly used methods for separating mixtures of IPA and water: ED, HA, and PSD. These techniques have been employed to enhance the efficiency and performance of separation processes. We explore the specific applications of HI and PI in each method, highlighting their contributions to improving energy utilization, reducing costs, and optimizing separation efficiency.

3.1. HI and PI Techniques on HAD

3.1.1. HAD Incorporated with Stripping Columns

Chang et al. reported a novel scheme for the dehydration of IPA, which consisted of three columns using two stripping columns instead of the conventional distillation columns with cyclohexane as the entrainer, as shown in Figure 5 [51]. The feed was fed into a preconcentration stripping column to remove pure water as the bottom product [51]. The distillate from the preconcentration stripping column was fed to a heterogeneous azeotropic stripping column to collect pure IPA as the bottom product [51]. The distillate from the heterogeneous azeotropic stripping column was fed to a decanter [51]. The organic phase from the decanter was recycled into a heterogeneous azeotropic stripping column as reflux [51]. The aqueous phase was fed to the solvent recovery stripping column to remove pure water as the bottom product [51]. The distillate was then recycled into a heterogeneous azeotropic stripping column [51]. The results showed that the proposed scheme could reduce both the energy requirements and the TAC compared with other configurations, and the IPA purity in the product stream was greater than 99.99985 mol.%.

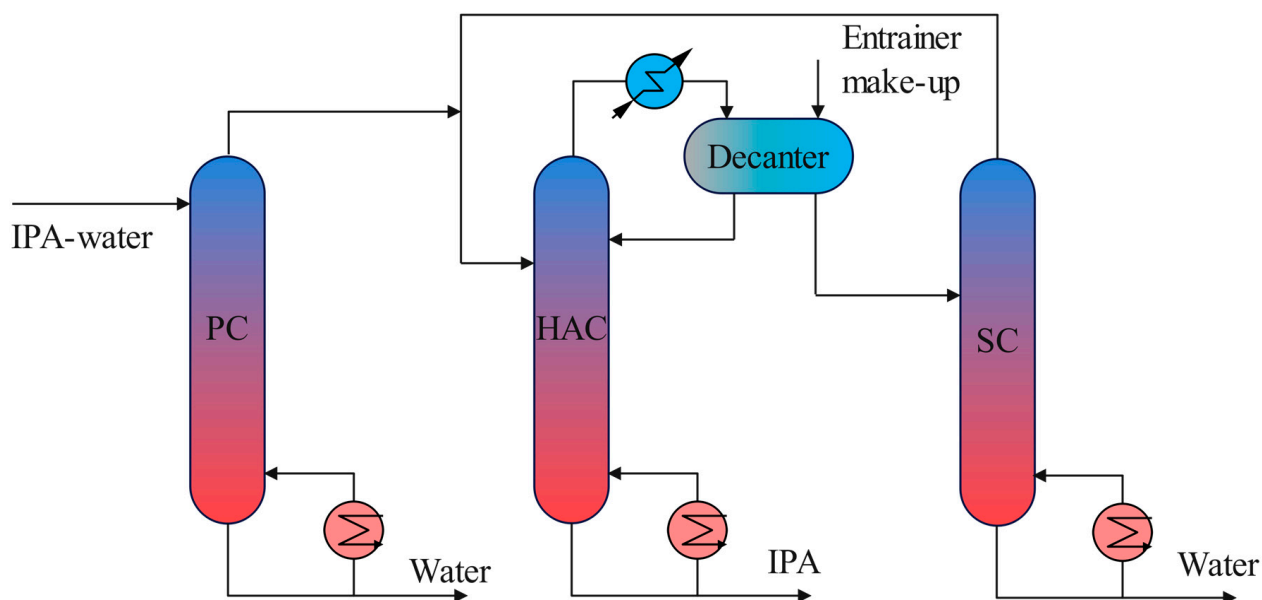


Figure 5. Heterogeneous azeotropic distillation incorporating with stripping columns. Adapted with permission from [51]. Copyright 2012 American Chemical Society.

3.1.2. HAD Incorporated with Combined Pre-Concentrator and Recovery Columns

Arifin and Chien suggested an HAD process incorporating combined pre-concentrator and recovery columns using cyclohexane as the entrainer, as shown in Figure 6 [22]. In the proposed scheme, the feed was fed to a SRC, which functions as a recovery and preconcentration column [22]. Pure water was obtained as the bottom product [22]. The distillate from the SRC was fed to a HAD column [22]. Pure IPA was collected as the bottom product of the SRC, and the distillate was fed to a decanter [22]. The aqueous phase from the decanter was supplied to the SRC, and the organic phase was fed to the HAD column for reflux [22]. The simulation results showed that the TAC was reduced by 7% and 5% compared with the conventional two-column and conventional three-column sequences [22].

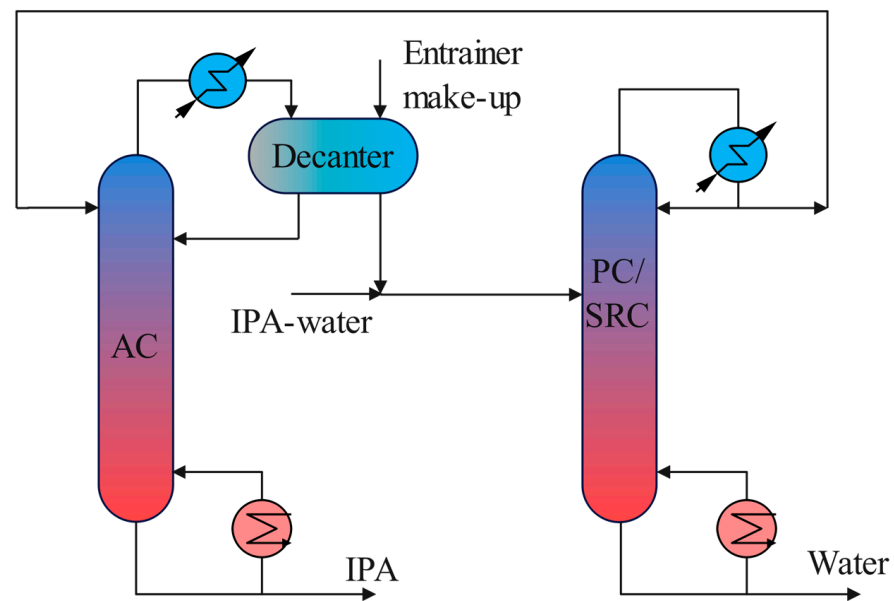


Figure 6. Heterogeneous azeotropic distillation incorporating combined pre-concentrator and recovery columns. Adapted with permission from [22]. Copyright 2007 American Chemical Society.

3.1.3. HAD Incorporated with DWC

Wang et al. used cyclohexane as the entrainer and investigated the incorporation of one and two dividing walls into a column, as shown in Figures 7 and 8, respectively [8]. In both arrangements, the dividing walls were placed at the bottom of the column.

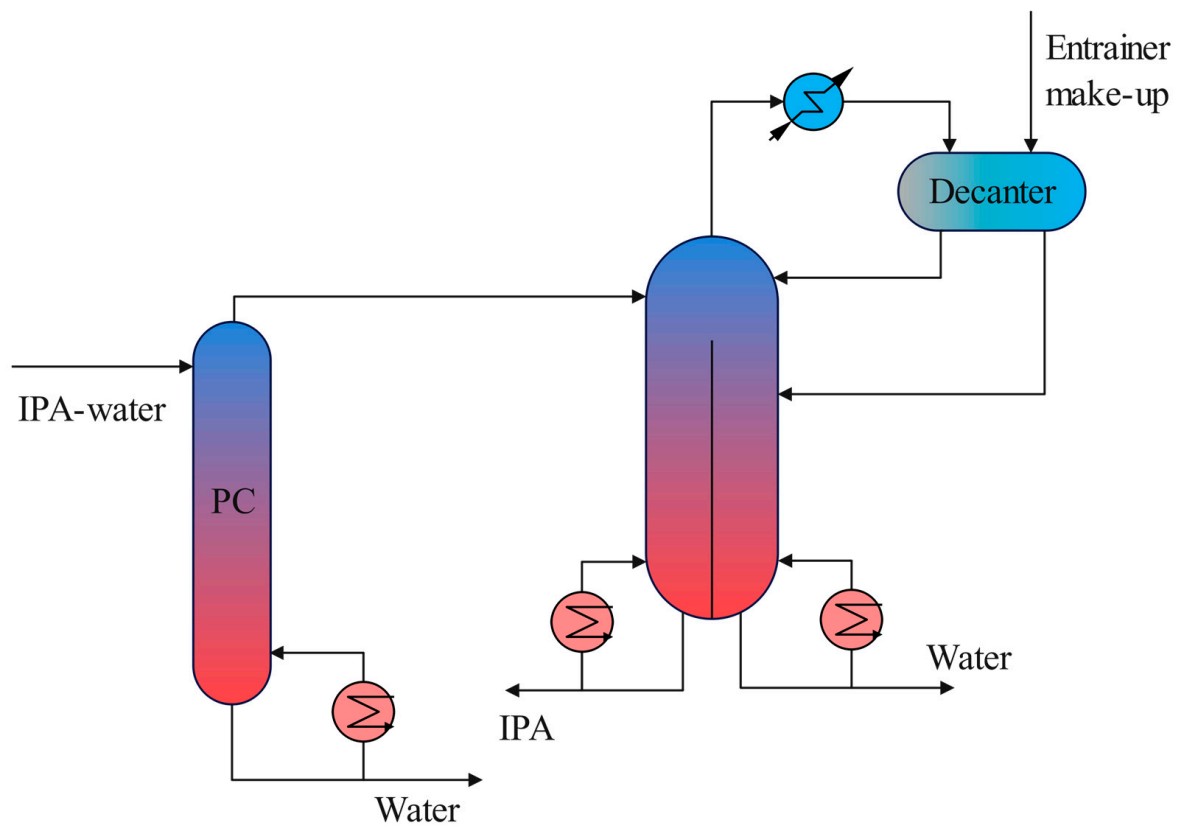


Figure 7. Heterogeneous azeotropic distillation intensified by a single-dividing-wall column.

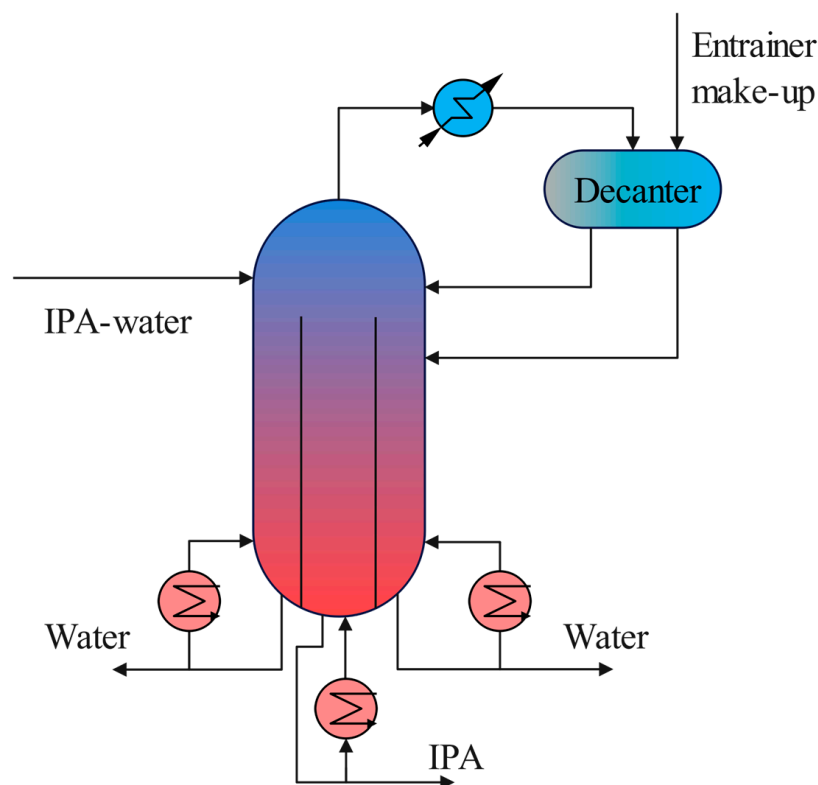


Figure 8. Heterogeneous azeotropic distillation intensified by double-dividing-wall column.

The feed was initially fed to the preconcentration column in an azeotrope DWC (ADWC) with a single-dividing-wall column. The distillate from the preconcentration column was then sent to the left side of the dividing wall of the ADWC. The overhead vapor from the ADWC was sent to the decanter [8]. The organic phase received from the decanter was recycled to the ADWC as reflux [8]. Simultaneously, the aqueous phase was recycled to the right of the dividing wall of the ADWC. Pure IPA and pure water were collected as the bottom products from the left and right sides of the dividing wall, respectively, in the ADWC.

In an ADWC with a double-dividing-wall column, the liquid leaving the top stage was sent to the decanter [8]. In total, 99.97% of the organic phase was recycled to the middle portion, whereas only 0.03% was recycled to the right side of the column. The aqueous phase was recycled to the right side of the column. The right side of the first dividing wall was similar to the ADWC used with a single dividing wall, whereas the left side of the first dividing wall behaved as a preconcentration column. Pure water was collected as the bottom product from the left and right sides of the column, and pure IPA was collected as the bottom product from the middle portion of the column. The findings highlighted the superiority of DWC techniques, as both HAD processes with one or two dividing walls could save approximately 6% of the TAC compared to the three-column sequence with two stripping columns by Change et al. [51].

3.1.4. Heterogeneous Azeotropic Dividing Wall Column (HADWC) Incorporated with Vapor Recompression

In a heterogeneous azeotropic dividing wall column (HADWC), the condenser duty is typically high, allowing it to offset the duties of one or both reboilers [7]. The condenser facilitates compensation by recompressing the top vapor of the column. Intermediate heat exchangers are employed to enable heat exchange between the condenser and reboiler. Heat exchange occurs between the condenser and high-duty reboiler when there is a significant difference in reboiler duties [41]. Conversely, if the reboiler duties are similar, the condenser

exchanges heat with both reboilers [41]. This approach can optimize energy utilization and enhance the efficiency of HADWC.

Shi et al. proposed two approaches for incorporating vapor recompression (VR) into HADWC for IPA dehydration using cyclohexane as an entrainer [7]. The column included 19 and 9 stages in the azeotropic and recovery sections, respectively, which were separated by a dividing wall. The feed was fed to the top stage. The distillate was then transferred to a decanter. The organic phase was refluxed at the top of the column and the aqueous phase was refluxed on the right side of the dividing wall. The two-stage compressor was utilized to compress vapor from 1.05 atm to 2.23 atm and then to 2.41 atm. In the first approach, as shown in Figure 9, the compressed vapor was directly condensed in the left section of the reboiler. The recompressed overhead vapor could supply all the heat requirements of the reboiler in the right section; however, the heat duty of the heat exchanger was specified as 1372 kW to prevent stage drying. In the second approach, as shown in Figure 10, heat exchange occurred by condensing the top product directly in both reboilers. The results demonstrated significant reductions in TACs of 34.54% and 25.58% for the first and second approaches, respectively, compared with conventional HADWC. The use of compressors to compress and reuse the overhead vapor resulted in substantial energy savings for the reboilers and condensers. However, further research is required to address the complex process dynamics and operational challenges associated with the practical implementation of additional compressors. Resolving these challenges is crucial for ensuring the successful and efficient implementation of these energy-efficient techniques.

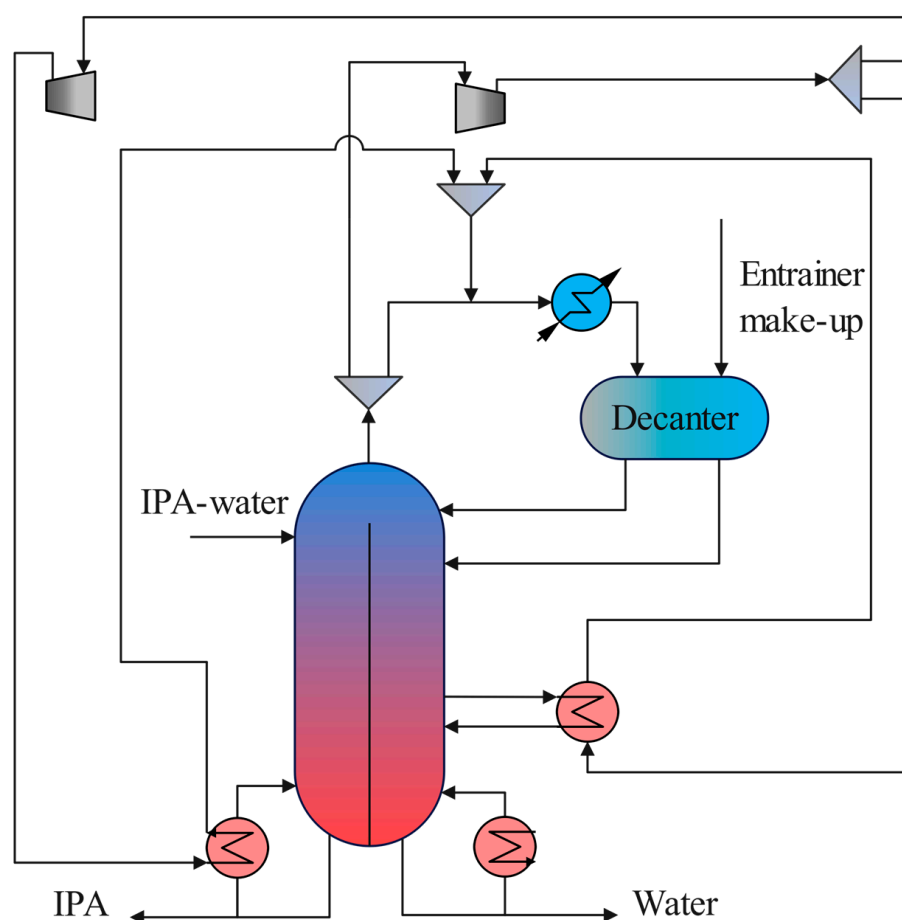


Figure 9. Heterogeneous azeotropic dividing wall column incorporating vapor recompression (first approach). Adapted with permission from [7]. Copyright 2015 American Chemical Society.

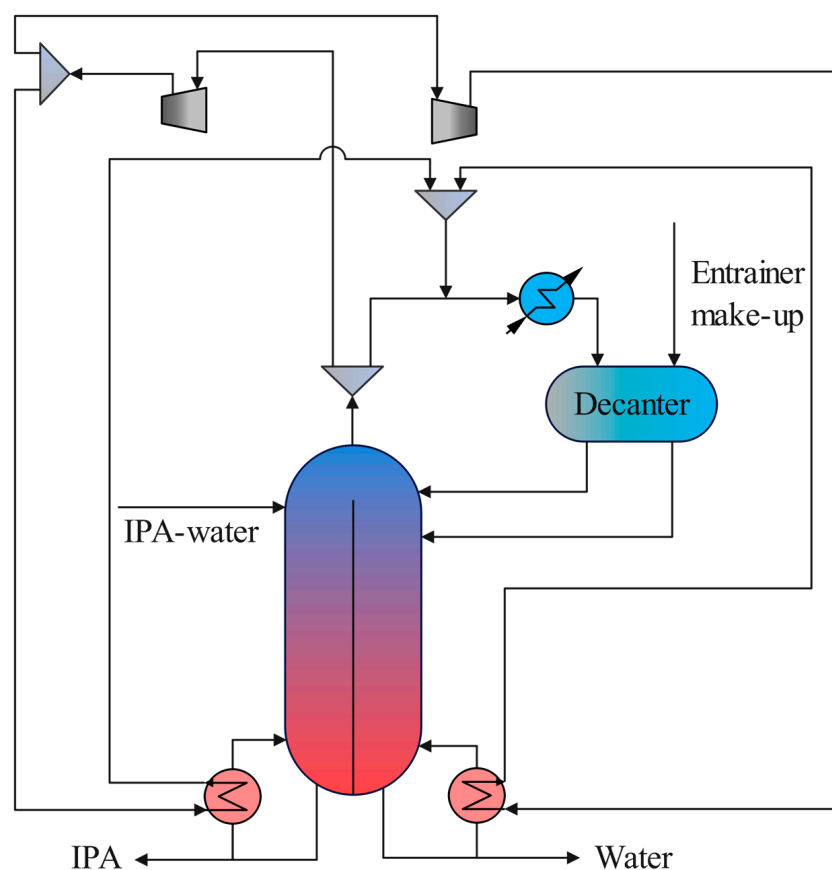


Figure 10. Heterogeneous azeotropic dividing wall column incorporating vapor recompression (second approach). Adapted with permission from [7]. Copyright 2015 American Chemical Society.

Liu et al. presented another approach for incorporating VR into an ADWC by utilizing a single-stage compressor [53]. In this configuration, the top vapor was recompressed and utilized to power the side reboiler. The findings reveal that the proposed VR + ADWC configuration has the potential to decrease operating costs while increasing capital costs. Therefore, this configuration should be carefully considered when considering long-term returns on investment. Further analyses and evaluations are required to assess the economic feasibility and overall benefits of this approach.

3.2. HI and PI Techniques on ED

3.2.1. Combining Pre-Concentrator and Recovery Columns in ED

The conventional ED process consists of three distillation columns: pre-concentration, extraction, and solvent recovery columns. Liang et al. suggested a two-column ED process that combines pre-concentrator and recovery columns, as shown in Figure 11 [52]. IPA hydration using DMSO as the entrainer was selected as a case study. To satisfy the energy requirements in the pre-concentration stage, a side reboiler was incorporated. Both the conventional ED process and the proposed two-column process were simulated and optimized using the total annual cost (TAC) as the objective function. The results demonstrated that the proposed process achieved energy savings of 13.7% and reduction of 12.1% in TAC compared with the conventional approach. Moreover, the new process exhibited versatility and could be applied to separate other azeotropic and close boiling point systems, provided that the bottom product of the pre-concentration column and the top product of the entrainer recovery column met the same composition specifications.

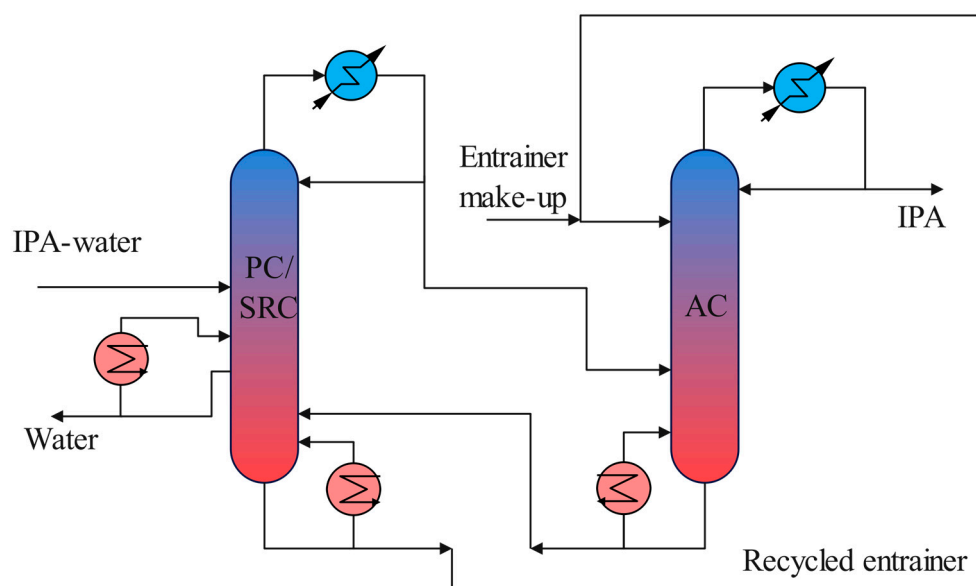


Figure 11. Combination of pre-concentrator and recovery columns in extractive distillation. Adapted with permission from [52]. Copyright 2014 American Chemical Society.

3.2.2. Side-Stream Extractive Distillation (SED)

To enhance the process performance of ED, a simple modification involving the addition of a side stream in the extractive column can be implemented [44]. Han et al. introduced a side-stream extractive distillation (SED) process utilizing ChCl/EG (1:2) as the solvent for separating IPA and water, as shown in Figure 12 [55]. In the extractive column, the side stream is extracted from the stripping section and directed to the SRC as the feed stream, whereas the bottom stream is recycled back to the column as the solvent. This straightforward modification allows the SED to achieve a 5.9% reduction in TAC compared with the conventional ED process.

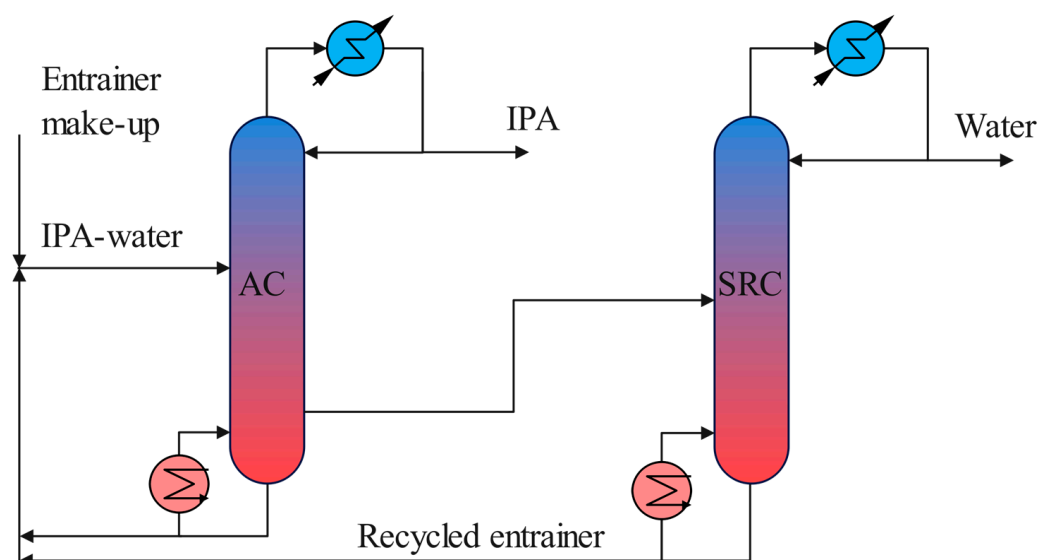


Figure 12. Side-stream extractive distillation process.

3.2.3. Heat-Integrated ED (HI-ED)

Over the years, researchers have shown significant interest in heat integration (HI) techniques for ED processes. Duan and Li conducted a detailed analysis and comparison of three multi-effect HI schemes and five solvent sensible heat recovery schemes for a

three-column ED process, focusing on the dehydration of IPA as a case study [45]. Their study explored the utilization of latent heat from the condenser of the ED column and SRC to recover the reboiler duty of the preconcentration column. Additionally, they preheated the feed streams in all the columns using a recycled solvent, enabling the recovery of the reboiler duty of the pre-concentrator and ED column. Figure 13 shows the optimized HI configuration in which the latent heat from both the ED column and the SRC condensers is integrated to recover the reboiler duty of the pre-concentrator. Furthermore, the feed to the ED column is preheated by exchanging heat with the recycled solvent. The implemented HI measures resulted in a remarkable 52.5% reduction in energy requirements and a 30.3% reduction in TAC compared with the conventional ED process.

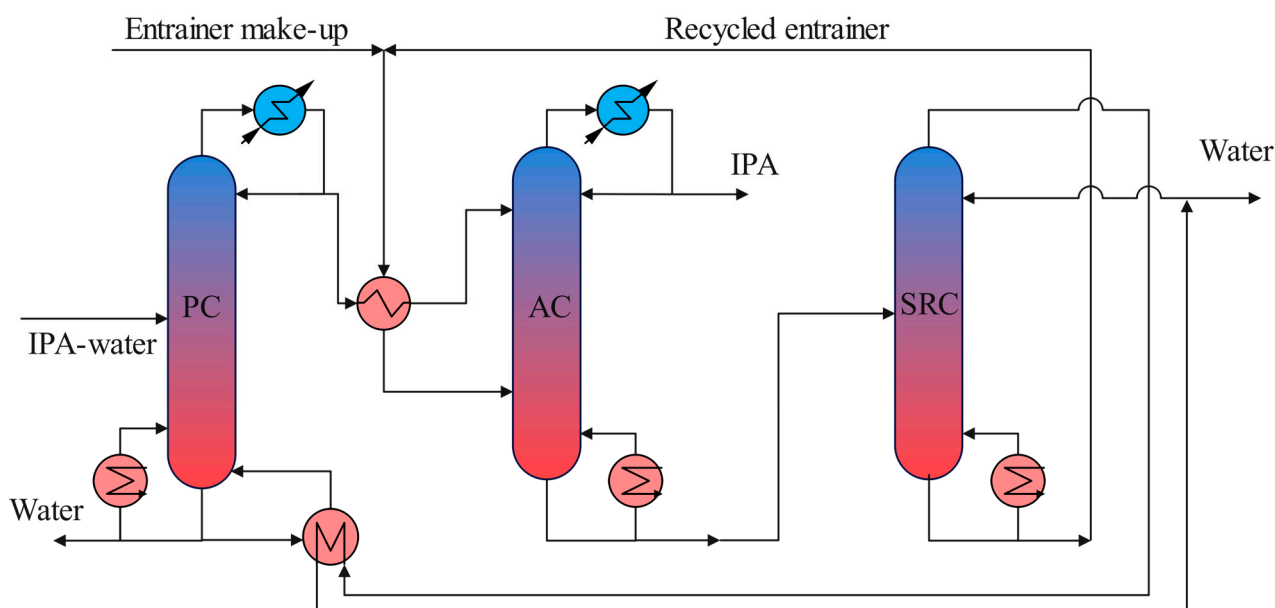


Figure 13. Heat-integrated extractive distillation column.

3.2.4. ED Incorporated with Heat Pump (HP)

Cui et al. incorporated HP into an extractive column in the ED process for IPA dehydration using ChCl/EG (1:2) as a solvent [36]. Figure 14 shows a schematic of the HP-incorporated ED process. The top vapor of AC was recompressed and supplied heat to the AC bottom stream while the recycled solvent having a high boiling point was utilized to preheat the AC feed. The results showed that significant cost reduction of 36.2% was achieved in the overall heat pump process. Additionally, this approach improved the thermodynamic efficiency of the process.

Liu et al. recently introduced an HP-assisted ED (HP-ED) process for the dehydration of IPA using EG as the solvent [6]. In their proposed configuration, the top vapor product from the preconcentration column was compressed from 1 bar to 2.5 bar, and its latent heat was utilized to reduce the reboiler duty. Similarly, the top vapor product of the EDC column was compressed from 1 bar to 2.3 bar. The results of this study demonstrated remarkable energy reduction with the HP-ED process, achieving a 37.7% reduction in energy consumption compared with the conventional ED process. By employing the HP system and leveraging the latent heat of compressed vapors, the HP-ED process demonstrated improved efficiency in IPA dehydration.

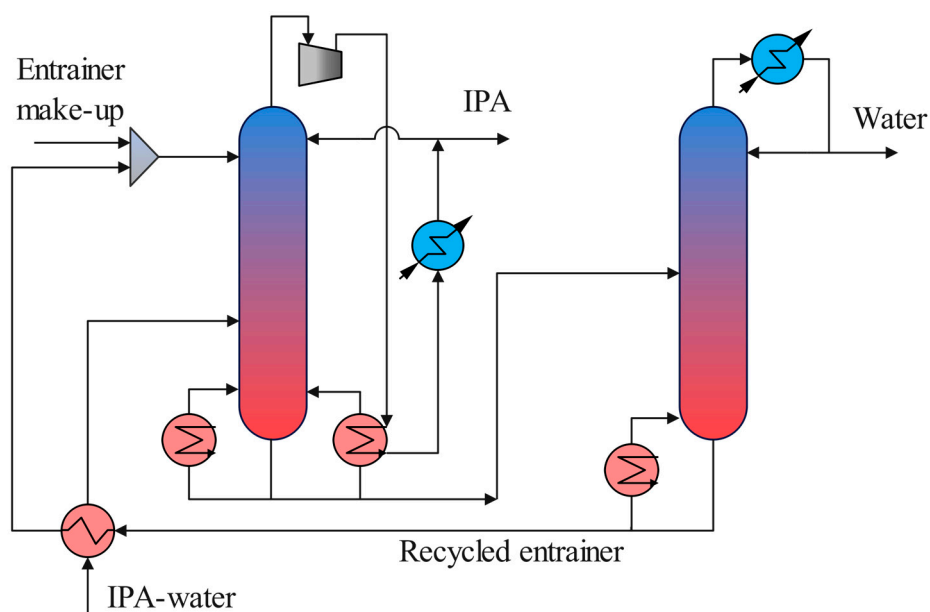


Figure 14. Heat pump incorporated extractive distillation process. Adapted with permission from [36]. Copyright 2020 American Chemical Society.

3.2.5. Extractive Dividing Wall Column (EDWC)

A recent study introduced an energy-efficient extractive DWC (EDWC) for the dehydration of IPA using EG as a solvent [6]. This arrangement effectively transformed the column into a preconcentration column on the left side of the wall and an SRC on the right side (Figure 15). In this configuration, the feed was introduced in the top stage of the preconcentration column, whereas EG was introduced in the fifth stage of the EDWC. The liquid bottom product from the extractive section was directed entirely to the solvent recovery section. The EG collected from the bottom of the EDWC was recycled back into the column after undergoing heat exchange with the fresh feed.

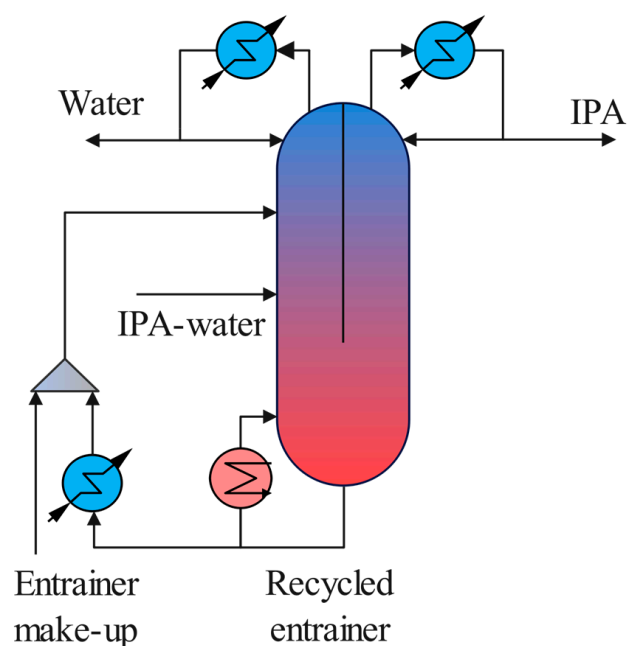


Figure 15. Extractive dividing wall column. Adapted with permission from [5]. Copyright 2013 American Chemical Society.

By integrating multiple functions into a single unit, the EDWC eliminates the need for intermediate separation steps and reduces the number of reboilers required. Unlike the conventional sequence, the remixing of solvent EG and water in the DWC design was avoided, thus considerably increasing the thermodynamic efficiency of the DWC. Consequently, it improved the energy efficiency and offered cost savings in terms of capital and operating expenses. The findings of this study demonstrated that the EDWC achieved significant energy savings of 40% compared with the conventional ED process [6].

Wu et al. investigated the energy-saving potential of the EDWC design for the separation of IPA–water using DMSO as an entrainer [5]. As depicted in Figure 15, the EDWC design combines two reboilers, while two condensers remain at the same position in the conventional sequence, as the dividing wall is installed at the top of the EDWC column. However, the results showed that, although reboiler duty savings of 5.1% could be achieved with the EDWC design, there was a significant increase of 24.8% in the steam cost, leading to a 16.9% increase in the TAC. This could be attributed to the use of DMSO as a heavy entrainer. In the conventional ED, the first and second columns operate at bottom temperatures of 152 °C and 196 °C, respectively, while the EDWC operates at a bottom temperature of 196 °C. The LP steam can be used in the first column of the conventional configuration, whereas the EDWC requires a more expensive HP steam. Consequently, despite the reduction in reboiler duty, the total steam cost significantly increased.

3.2.6. Thermally Coupled ED

Wu et al. proposed a thermally coupled ED arrangement as an alternative to the conventional ED arrangement for IPA dehydration using DMSO as an entrainer [5]. The thermally coupled ED configuration comprised two distillation columns. The feed was introduced into the extraction column, in which pure IPA was obtained as a distillate. Unlike conventional arrangements, the extractive column had no reboiler. The bottom liquid from the extractive column was directed to the SRC, whereas the vapor stream was withdrawn from the stripping section of the SRC and fed back into the extractive column. The pure DMSO collected from the bottom of the SRC was recycled into the ED column. Although the total reboiler duty was reduced by 6.84% in the thermally coupled ED arrangement; there was a 14.55% increase in the TAC compared with the conventional ED. This higher TAC was attributed to the exclusive use of HPS in thermally coupled ED instead of medium-pressure steam, which could be used in the first column of the conventional ED process.

3.2.7. HP-Assisted EDWC (HP-EDWC)

Liu et al. proposed the integration of an extractive dividing wall column (EDWC) with an HP to improve IPA dehydration using EG as the solvent [6]. The HP-EDWC configuration (Figure 16) involves compressing the top vapor from the EDWC from 1 bar to 2.3 bar. In addition, a side reboiler was installed in the stripping section of the preconcentration side to enhance the overall energy efficiency. The heat exchange between the condenser of the EDWC and the side reboiler further contributed to energy reduction.

The results of the study demonstrated that both the EDWC and HP-EDWC processes offered substantial energy savings, with reductions of 40.0% and 56.4%, respectively, compared with the conventional ED process [6]. By incorporating the HP system, the HP-EDWC process achieved additional energy savings of 25.6% compared with the EDWC process. However, it is worth noting that the implementation of compressors may introduce process complexity and operational challenges.

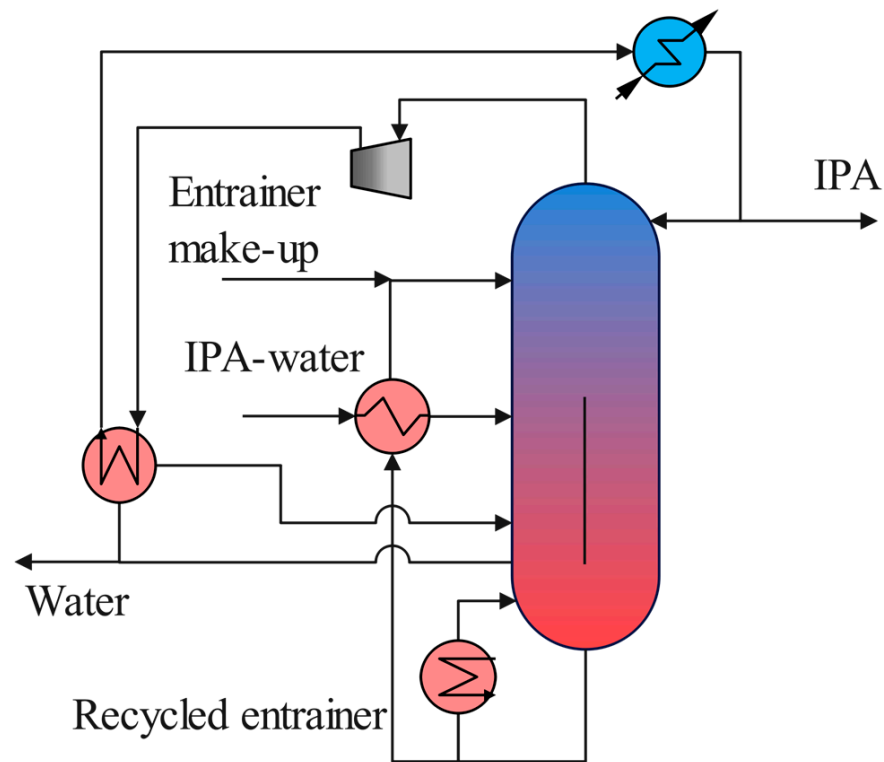


Figure 16. Extractive distillation incorporated with DWC and HP.

3.3. HI and PI Techniques on PSD

3.3.1. PSD with HI and HP Techniques

Zhai et al. focused on the effective separation of IPA and water using the pressure swing distillation (PSD) method and explored energy-saving techniques to enhance its performance [50]. To achieve energy and economic savings, they proposed the following three intensified schemes as alternatives to conventional PSD: heat integration of PSD (HI-PSD), HP-assisted PSD (HP-PSD), and combined heat integration and HP-assisted PSD (HI-HP-PSD).

Feasibility analysis and temperature-enthalpy diagrams were used to assess the energy consumption and reliability of the compression process. The HI-PSD scheme involved HI, utilizing the thermal exchange between the condenser of the HP column and the reboiler of the LP column. The HP-PSD scheme incorporated a HP to enhance energy efficiency. Furthermore, the HI-HP-PSD scheme combined both HI and HP technologies to explore their synergistic energy-saving potential, as shown in Figure 17. In this configuration, the top vapor of the HP column was split into two streams: one stream directly exchanged heat with the reboiler of the LP column, and the other stream recompressed and exchanged heat with the reboiler of the HP column. The compressor ratio and split flow rate were optimized to minimize the energy requirements.

The study demonstrated significant energy and cost savings by comparing the proposed intensified configurations with the conventional PSD. The HI and HP techniques achieved savings of 31.44% and 51.30% in TAC, respectively, with a capital payback period of three years [50]. Although the HI-HP-PSD showed slightly lower heat savings than the HP-PSD, it exhibited a better TAC and achieved a 38.30% reduction compared with the conventional PSD. It is worth mentioning that the intensified designs were expected to yield even greater cost savings over longer payback periods.

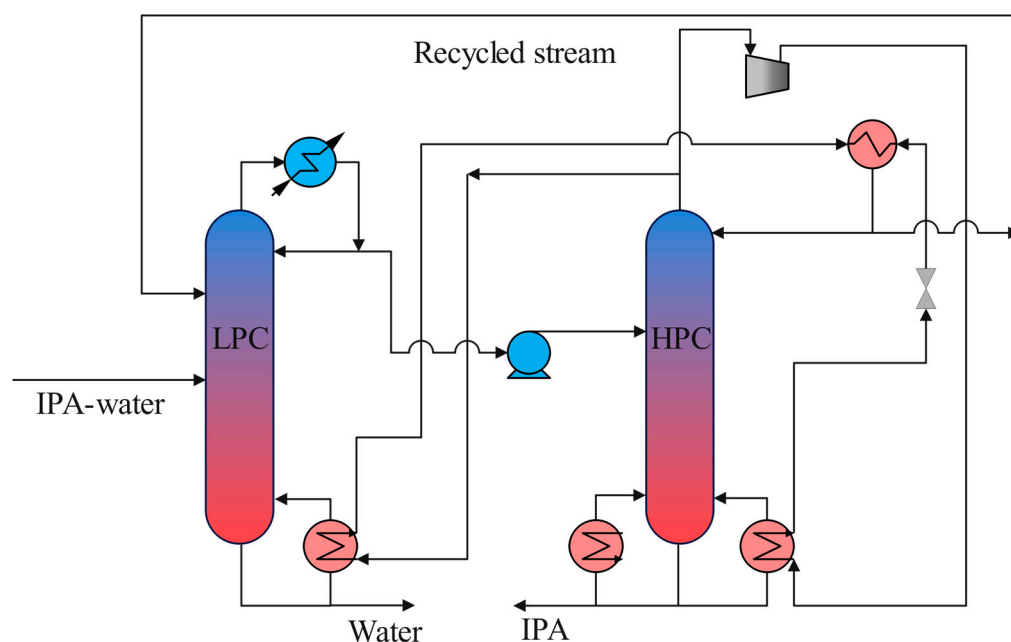


Figure 17. Pressure swing distillation incorporated with heat integration and heat pump.

3.3.2. Heat Integration of Extractive Pressure Swing Distillation

Qin et al. studied the extractive PSD (EPSD) process using tetrahydrofuran (THF) as a solvent [10]. By varying the pressure from 101.3 kPa to 638.3 kPa, changes in the azeotropic composition of the IPA–water mixture from 35.3 mol.% to 32.2 mol.% water, and the water–THF mixture from 21.3 mol.% to 37 mol.% water were achieved. Two different column arrangements including low–high sequence (LH-EPSD) and high–low sequence (HL-EPSD), were discussed.

In the LH-EPSD arrangement, water was removed from the bottom of the LP column, and IPA was collected from the bottom of the HP column. THF was recovered as the distillate from the HP column and recycled into the LP column. In contrast, in the HL-EPSD arrangement, IPA was collected from the bottom of the HP column, and water was removed from the bottom of the LP column. THF was recovered as a distillate from the LP column and recycled into the HP column. HI was implemented between the condenser of the HP column and reboiler of the LP column in both arrangements, as shown in Figure 18. The results showed that the HI of the LH-EPSD process reduced the TAC by 7.04% and CO₂ emissions by 4.27% compared with the LH-EPSD process. One of the advantages of EPSD is its flexibility in column sequence, operating pressure, and selection of entrainers or solvents. This flexibility allows the customization of the process to meet specific separation requirements and optimize performance. However, it should be noted that the use of EPSD is limited in certain cases because the conventional ED process often outperforms EPSD in terms of TAC. The results of this study indicated that the conventional ED process with a two-column sequence using DMSO as an entrainer exhibited a lower TAC than the EAPSD process.

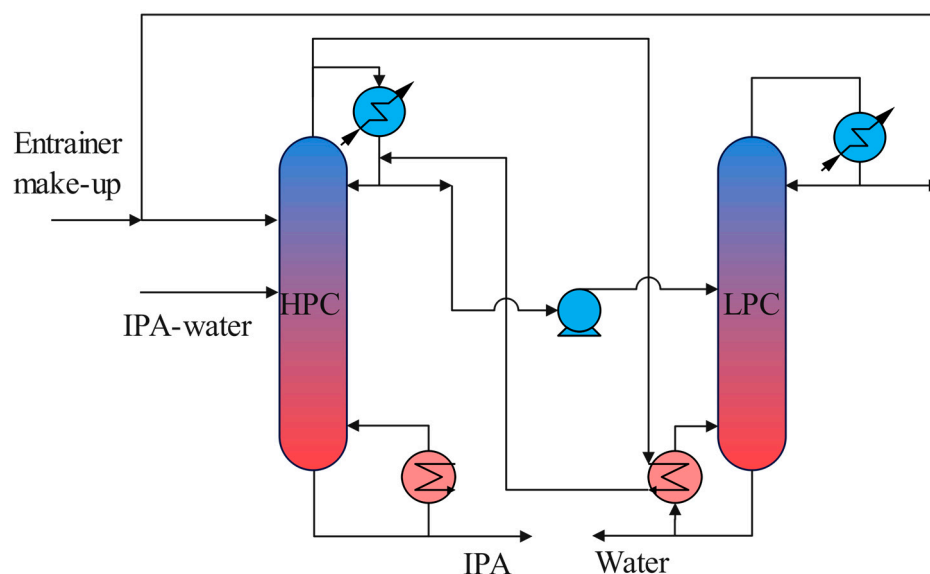


Figure 18. Heat integration of extractive pressure swing distillation.

4. Challenges and Suggestions

Table 1 provides a summary of distillation-based separation methods and the applications of HI and PI techniques investigated in recent years to enhance the IPA dehydration process. Dehydration of IPA poses a significant challenge owing to the formation of an azeotropic mixture with water, which complicates the separation process using conventional distillation methods. To overcome this challenge, alternative separation techniques including ED, HAD, and PSD have been employed. However, it should be noted that the IPA–water azeotrope is not highly sensitive to pressure changes; therefore, the effective application of PSD to IPA dehydration is challenging. Consequently, only a limited number of studies have conducted feasibility analyses for separating IPA–water mixtures using PSD.

The common methods to separate IPA–water mixtures are ED and HAD. The choice of the solvent or entrainer used in these methods plays a crucial role in the separation efficiency and overall process performance. By selecting a suitable solvent with favorable thermodynamic properties, such as high selectivity for water and low affinity for IPA, the separation efficiency can be enhanced, leading to reduced operational costs. Recently, various new solvents including ILs and DESs have been proposed for this purpose. However, the successful application of these solvents to industrial-scale operations may present significant challenges.

HI and PI techniques have been widely applied to reduce the energy requirements and production costs of the IPA dehydration processes. These techniques have shown promising results in terms of improving process efficiency and sustainability. However, future research in IPA production should aim to explore the entire process, including the crucial reaction part. The reaction part constitutes the initial step of IPA production, wherein raw materials such as propylene undergo hydration to form IPA. This chemical reaction is a crucial and energy-intensive process, making it an essential aspect of the overall IPA production. Heat integration and process intensification techniques can be more effective when applied in conjunction with optimized reaction conditions. Continued research and development efforts should focus on exploring innovative HI and PI techniques that encompass the entire IPA production process and integrate all process components. This holistic approach can potentially enhance the overall efficiency, sustainability, and economy of IPA production.

Table 1. Different techniques proposed for IPA dehydration available in literature.

Method	Entrainer	Referenes	Property Model	HI & PI
HAD	Isooctane	[14]	NRTL	
	1-Methyl-N-butyl ether	[47]	UNIFAC	
	Benzene	[18]	NRTL	
	Cyclohexane	[17]	NRTL	
		[22]	NRTL	
[8]		NRTL	ADWC	
[7]		NRTL	HI, ADWC, VRHP	
[53]	NRTL	ADWC, HP		
ED	1-Methyl-N-butyl ether	[47]	UNIFAC	
	[EMIM][BF ₄], ChCl/glycerol and ChCl/EG, DMSO	[37]	NRTL	HI
	Glycerol	[35]	NRTL	
	ChCl/glycerol (1:2), ChCl/EG (1:2)	[36]	NRTL	HP
	ChCl/EG1:2	[55]	NRTL	SED, EDWC
	[EMIM][N(CN) ₂]	[11]	NRTL	HI
	EMIMOAC	[38]	NRTL	
	ChCl/triethylene glycol 1:3	[40]	NRTL	
	Lactic acid/ChCl (2:1), glycolic acid/ChCl (3:1)	[42]	NRTL	
	DMSO	[9]	NRTL	
		[45]	NRTL	
		[46,49]	NRTL	
		[52]	NRTL	HI
[5]		HI, EDWC		
EG	[49]	NRTL		
	[6]	NRTL-RK	EDWC, HP	
	[1]	NRTL		
Diaminomethanal	[48]	NRTL		
Cyclohexane	[51]	NRTL		
PSD	Tetrahydrofuran	[10]	UNIQUAC	HI
		[50]	NRTL	HI, HP

5. Conclusions

IPA dehydration is a critical process in various industries, and numerous distillation processes and HI and PI techniques have been explored to enhance its efficiency and economic viability. In this study, we reviewed various distillation processes, such as ED, HAD, and PSD, as well as their respective advantages and limitations in IPA dehydration. PSD can be applied; however, IPA–water azeotropes are not very sensitive to pressure, necessitating a more sophisticated design and operation, which increases the complexity of the system. In contrast, ED and HAD offer effective separation capabilities but may require additional entrainers or solvents, leading to higher operating costs and potential product contamination.

HI and PI techniques have been investigated to address these challenges and improve the overall efficiency of IPA dehydration. These techniques aim to optimize the energy

consumption, reduce operating costs, and enhance the sustainability of the process. HI involves maximizing the exchange of thermal energy within a system, whereas PI techniques aim to combine multiple functions into a single unit, reducing the need for intermediate separations and improving the overall process efficiency.

In this review, we observed that HI and PI techniques such as HPs, thermally coupled arrangements, and DWCs have shown significant potential for improving the energy efficiency and economic viability of IPA dehydration processes. These techniques reduce the energy requirements, enhance product purity, and decrease capital and operating costs. Nevertheless, it is important to note that the selection of the most suitable distillation process and HI and PI techniques for IPA dehydration should be based on careful evaluation and consideration of the specific requirements, constraints, and economic factors associated with the process.

With this comprehensive review, the authors aim to fill the knowledge gap by bringing together existing research and developments related to IPA dehydration, offering a consolidated and in-depth analysis of the available HI and PI techniques and strategies. Accordingly, it may inspire renewed interest and novel inventions, driving the development of more efficient and intensified IPA processes, and bringing the field into the spotlight it truly deserves.

Author Contributions: L.C.N. and N.A. contributed equally to this work by designing the study, performing process simulations, and writing the manuscript; M.L. conceptualized the core research and provided academic advice. All authors have read and agreed to the published version of the manuscript.

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