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Recent Advances in Extractive Distillation [†]

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Abstract: Distillation is widely recognized as the preferred method for separation due to its operational and control benefits. Traditional distillation processes, however, cannot successfully separate azeotropic mixtures with near boiling points. Numerous special distillation processes have been developed to address this limitation. Extractive distillation, in particular, has gained significant popularity in the chemical, petrochemical, pharmaceutical, and refining industries. This review examines the state-of-the-art advances in extractive distillation. The importance of the proper selection of a solvent was discussed. Several configurations of extractive distillation processes were presented. Additionally, alternative extractive distillation systems have been elaborated. However, significant research gaps remain, such as the need for an exhaustive investigation of various control variables, the impact of certain entrainers on distillation processes, and cost comparisons across specialized distillation systems. Furthermore, process intensification strategies require additional research to solve complexity and operability issues. The integration of energy-efficient technologies, developments in renewable energy consumption, and the development of cost-effective reactive or split distillation columns will shape the future of distillation operations. These advances will help the chemical process sector achieve improved energy efficiency, lower environmental impact, and increased sustainability.

Keywords: extractive distillation; azeotrope; entrainer

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1. Introduction

The benefits of distillation in terms of operation and control make it the most preferred separation method. However, some systems with close boiling points, commonly referred to as azeotropic mixtures, cannot be separated using traditional distillation. This is where special distillation processes like azeotropic distillation, catalytic distillation, extractive distillation, pressure-swing distillation, etc., were developed [1,2]. Among these distillation methods, extractive distillation is commonly used in the chemical, petrochemical, pharmaceutical, and refining sectors.

Conventional extractive distillation involves at least two columns wherein one of the components will go overhead, and the other will go either overhead or at the bottom column, depending on the volatilities of the components . The choice of solvent is a significant additional aspect to consider. It must have a boiling point greater than the components that need to be separated. It must also be miscible and not form an azeotrope.

The high energy demand for extractive distillation technology, like other distillation methods, has an adverse economic and environmental impact [4]. Additionally, improving the extraction method is motivated by the desire to raise the cost, quality, and yield of the extraction process. Numerous improvements have been made over time, either by combining different extraction procedures into a single process, adding more useful techniques, or changing the original methodology .

The ability of extractive distillation to separate azeotropic and mixtures with low relative volatility in various fields has highlighted its significance, resulting in numerous studies . While some processes reduce energy consumption and improve the economy, they frequently complicate the process, making operability and control more challenging. Because feasibility is still a problem, this review paper will thoroughly discuss and evaluate recent advancements in extraction distillation.

2. Selection of Appropriate Solvent

The extractant or solvent is one of the most important parts of extractive distillation. One of the parameters in choosing the perfect extractant includes its effect on the azeotropic system's relative volatility, the intermolecular forces at atmospheric temperature and pressure, and electrostatic potential. The perfect extractant can be easily chosen using these parameters; an extractant should be able to increase the relative volatility of the system; an extractant that has stronger attraction to the undesired substance and weaker attraction to the desired substance, in terms of this article, it is ethanol and ETBE respectively .

The solvent to be used determines how well an extractive distillation process works. The selected solvent needs specific properties that increase the process's feasibility by lowering energy and solvent consumption [9,10]. However, some commonly used solvents have not performed well with mixtures exhibiting azeotropes. Hence, the utilization of ionic liquids (ILs). A low vapor pressure, melting point, and considerable chemical and thermal stability are just a few of the remarkable physicochemical characteristics of ILs . Moreover, it led to using green technologies using non-hazardous solvents or renewable natural resources while retaining high-quality, safe extracts.

Distinct solvents and flow rates have distinct impacts on the components' vapor-liquid equilibrium and volatility order. This may be used to assess solvents' performance and flow rate.

Consider the ternary mixture of acetonitrile, methanol, and benzene, which has three binary azeotropes. Possible solvents include aniline (AN) and chlorobenzene (CB). Three components' pairwise combinations' equilibrium between vapor and liquid is shown. The vapor-liquid equilibrium curves alter upon the introduction of solvents. Methanol, benzene, and acetonitrile are volatile compounds in decreasing order of light to heavy when using AN as the solvent; methanol, acetonitrile, and benzene are volatile compounds when using CB.

2.1. Supercritical Fluid Extraction (SFE)

Advanced extraction techniques were developed to attain high quality and extraction yield . Supercritical Fluid Extraction (SFE) enhances the conventional extraction method by reducing the amount of organic solvent used. SFE starts by heating and pressurizing the fluid to its critical state before entering the reactor. The solute can readily be sorted out by gravity. Therefore, the extracted component can be collected at the bottom of the separator, and the gas can be recycled or released. Despite being more appealing than other organic solvents like acetone, ethanol, or hexane because of its capacity to surpass conventional extraction methods, SFE has a disadvantage because it needs high pressure, which increases the operating cost due to additional safety requirements.

2.2. Extractive Distillation Using Ionic Liquids (ILs)

Various research has been conducted in studying the behavior of ILs when used as a solvent for extractive distillation because of their properties. The separation of benzene and cyclohexane, which have similar boiling points and are inclined to combine into an azeotropic mixture, is one of the most difficult operations in the petrochemical industry.

Adsorption, pervaporation, and liquid-liquid extraction are only a few examples of the many separation procedures that have been attempted. However, extractive distillation employing organic solvents as solvents is discovered to be the most effective method .

Especially to separate hydrocarbons, ionic liquids are used as solvents for they possess a non-volatile nature and high selectivity around aromatic compounds. The performance of seven ionic liquids for C_6H_6 and C_6H_{12} separation by ED was investigated. The optimum solvent for this separation has been determined to be the [4bmpy][TCM]. The C_6H_{12}/C_6H_6, the relative volatility of this ionic liquid, is at its peak at 363.2 K, and even though it is at its lowest at 403.2 K, it is sufficient to carry out the separation satisfactorily. Adding these ionic liquids increases the C_6H_{12}/C_6H_6 relative volatility, reaching values approximating 15, and breaking the azeotrope. The 1-Ethyl-3-methyl-imidazolium-dicyanamide was selected as the solvent in the EDC due to the IL's strong influence on the relative volatility of aromatics-aliphatic mixtures and its high thermal stability . According to the results, liquid-liquid extraction and extractive distillation do not separate.

Some compounds used for various industrial applications require a certain purity level as raw materials. An instance of this is ethanol, which requires 99.5% purity before it can be used for industries such as paint, cosmetics, and perfumery. The use of ILs shows the potential to decrease energy consumption. Compared with conventional extractive distillation, ionic liquid-based extractive distillation (ILED), which produces anhydrous ethanol, uses less energy. The TAC value of $0.73 x 10^6 illustrates how the ILED discovered during the sensitivity analysis for the least energy consumption outperformed alternative setups.

Additionally, much study has been done to compare which IL best suits a specific system. As solvents, 1-Butyl-3-methylimidazolium trifluoromethanesulfonate or [BMIM][CF_3SO_3], 1-Ethyl-3-methylimidazolium tetrafluoroborate or [EMIM][BF4], and 1-Ethyl-3-methylimidazolium methanesulfonate or [EMIM][$MeSO_3$] are used. The best option among all these ILs for extractive distillation is the stripper with 1-Ethyl-3-methylimidazolium methanesulfonate, or [EMIM][$MeSO_3$] . The researchers used three methods: an extractive distillation column, a flash tank, and a stripper. At the EDC, IL raises the relative volatility of ethanol acetate compared to ethanol. Additionally, it causes the ethanol to flow downward and the ethyl acetate to go upward. Due to the lower volatility of the IL, it just flows down the column, leaving the bottom product.

One study employed [MMIM][DMP], 1,3-dimethylimidazolium, to separate the isopropanol-water mixture. The approach using [MMIM][DMP] as a solvent reduced TAC by 7.92%, as opposed to the process using a normal solvent, it was discovered. Because of their outstanding qualities, ILs can be used as better solvents. The success of the ED processes was examined considering the effects on the economy, energy efficiency, and environment using the thermodynamic efficiency index, CO_2 emissions, and TAC [16].

The separation process is generally optimized to improve the EDC's operating conditions and design parameters. Due to a broad selection of potential solvents, extractive distillation works effectively in the chemical industry to separate binary or multiple azeotropes, but it has several drawbacks, including energy consumption. The study offered two solutions for how to do this. The first is process intensification using heat-integrated distillation, divided wall columns, thermal coupling of columns, and heat pump-assisted distillation. The second method involves using a green solvent with great selectivity.

Triethylene glycol (TEG) and the solvents [EMIM][Cl] were used in studies that used the t-butanol dehydration method. According to the findings, utilizing [EMIM][Cl] as an entrainer, as opposed to TEG, could lower the total annual cost (TAC) by 13.9% [16].

2.3. Ionic Liquids-Based Mixed Solvents

Conventional ternary extractive distillation (CTED) uses different solvents, such as EG and ionic liquids. EG and ionic liquids are the common solvents used in extractive distillation, wherein EG significantly impacts relative volatility. Energy consumption and operating cost are one of the disadvantages of extractive distillation. An entrainer was recently developed, combining ionic liquids with another solvent in one shell, which uses a dividing wall column. Conventional ternary extractive distillation (CTED) using EG and ionic liquids solvents give a good outcome, but ionic liquids-based mixed results are better. Conventional ternary extractive distillation, dividing wall column, and extractive distillation column reduce energy consumption and operating cost, but extractive dividing wall column ternary extractive distillation is the most effective in saving energy as it reduces up to 7.81% [17].

3. Optimized Configurations for Extractive Distillation

Since different types of systems can be separated, over the years, researchers have studied various kinds of strategies, and the separation process is not a type of process that applies to all kinds of systems; therefore, all these strategies are efficient in their ways to different kinds of systems [18]. These methods use innovative techniques to provide a more effective way of recovering desired materials without the constraints that are encountered using conventional ways [19].

Different methods for achieving energy efficiency are being developed as distillation process designs grow more energy-conscious. Some of the processes used in distillation to become energy efficient are feed flashing, multi-effect distillation, vapor compression, and heat-integrated distillation column. Feed flashing incorporates a feed-splitting vessel that creates a two-phase feed directed to their respective feed plates; this reduces the energy requirement and allows flexibility in variations in thermodynamic modeling. Heat integration can be employed in various ways, such as heat exchange between the feed and rundown or pump-around to optimize heat recovery. Multi-effect distillation integrates the condenser and reboiler of two columns with different operating pressures. This method uses the heat the high-pressure condenser releases to operate the low-pressure reboiler. This method saves 40% of energy costs. Heat-integrated distillation columns operate in a single unit that consists of a high-pressure section (top/rectifying) and a low-pressure section (bottom/stripping); this difference in pressures allows heat transfer between the columns [20,21]. This type of method reduces reboiler and condenser duties and significantly reduces energy consumption down to 50% [22]

Other ways of lowering energy requirements are by intensifying the process of distillation. These include reactive distillation, dividing wall column utilization, and hybrid separation processes. The wall columns separate the feed, side stream, and product streams. The product is extracted at the top of the column, and the feed and side streams are on each side of the wall, preventing contamination. This intensification method reduces capital costs and energy by up to 45%. A hybrid separation method combines two distinct units into a single process. This is applied to a design wherein one unit overcomes the limitation of the other working in a mutually beneficial relationship [23]. In azeotropic distillation, commonly used methods include extractive and pressure-swing distillation is required, which are energy-intensive processes. In these cases, hybrid distillation is recommended.

3.1. Classic, Modified, and Intensified Extractive Distillation

Several separation techniques while concentrating on extractive distillation, which is thought to be the most researched type of distillation employed in the manufacture of bioethanol [18]. The classic extractive distillation configuration is shown in Figure 1.

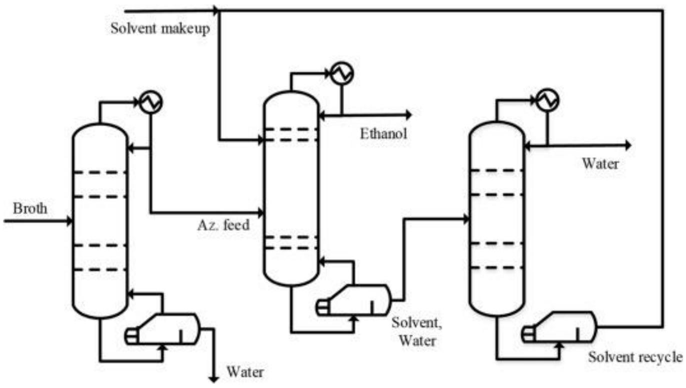


Figure 1. Classic Extractive Distillation. Reprinted with permission from [18]. Copyright (2022) Elsevier.

There are alternatives to the classic ED that had a higher recovery by using a recycle stream in the solvent recovery column. (Figure 2). This set of configurations was the starting point for creating various complex designs. Thermally coupled systems and extractive divided wall columns (DWC) were produced from these. These types of extractive distillation have been studied since 2012, and reports and comparative analyses have been written. Figure 3 shows an example of intensified extractive divided wall configuration wherein it utilizes a reduced number of columns compared to the classic configuration, which uses three columns; the intensified DWC uses only two or one. In a 2-column configuration, the separation and solvent recovery occur on the second column using an extractive DWC; the distillate is collected in the partition and flows through a recycle stream back to the first column. This configuration ensures there are no ethanol losses and provides a higher recovery. Moreover, it reduces capital costs by 23% while having the same energy consumption as a regular configuration.

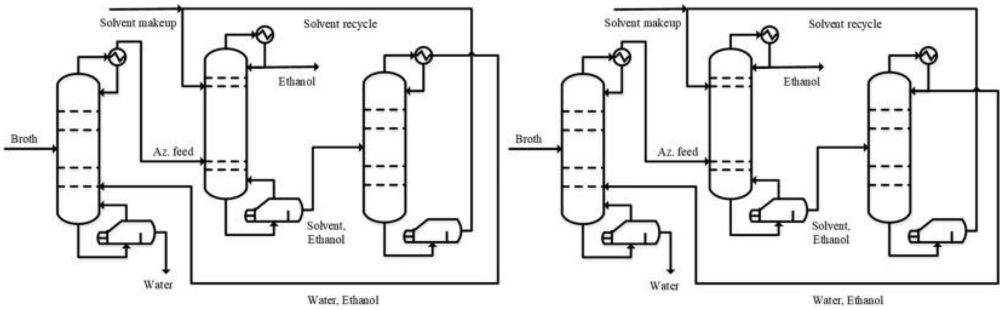


Figure 2. Modified Extractive Distillation. Reprinted with permission from [18]. Copyright (2022) Elsevier.

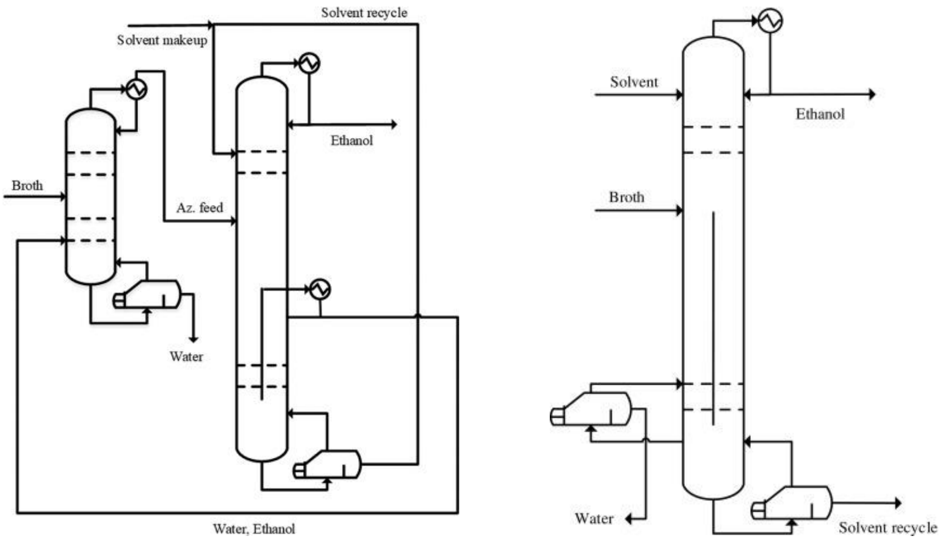


Figure 3. Intensified Extractive Distillation. Reprinted with permission from [18]. Copyright (2022) Elsevier.

3.2. Assisted Single-Column Extractive Distillation with Heavy Entrainer

Figure 4 proposes an extractive distillation with one column and a heavy entrainer (FT-SCED) [24]. It allows pure light and heavy compounds to be produced from the flash tank and column overheads. In this review study, we will concentrate on the proposed design in the first case, which is the separation of an ethanol and water mixture with a heavy entrainer, ethylene glycol. In comparison to extractive distillation with dividing wall columns and conventional two-column extractive distillation, it was determined that the new process had high energy efficiencies and low investment costs. A control study also revealed that the FT-SCED process could be effectively managed. When ±20% feed flow rate and ± 10% composition disturbances were introduced, the purities of the product returned to its original setting for about 10 hours, indicating its effectiveness.

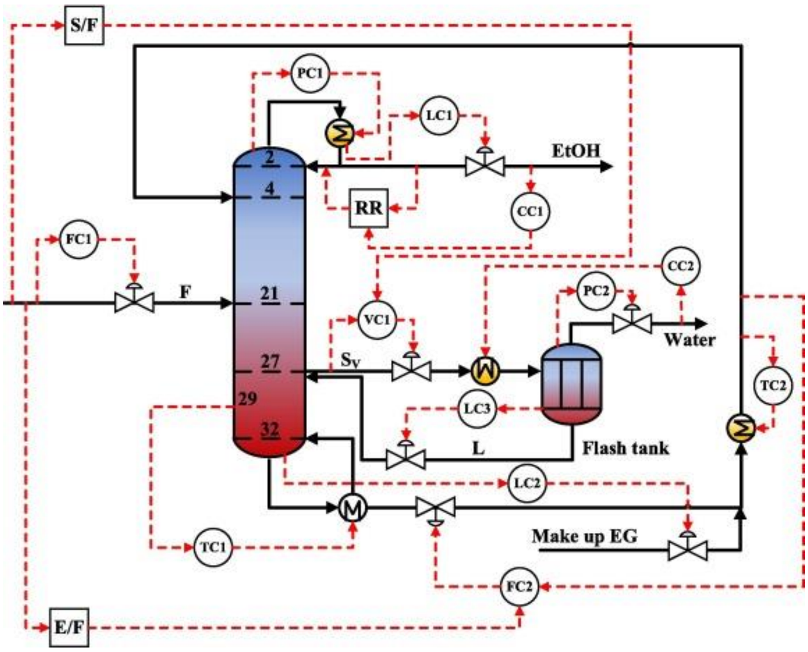


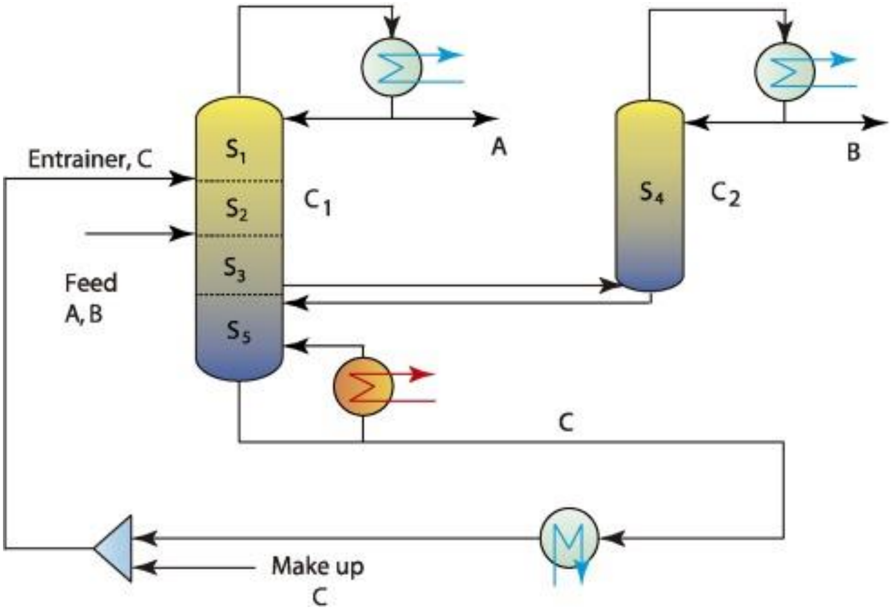
Figure 4. Proposed single-column extractive distillation. Reprinted with permission from [24]. Copyright (2023) Elsevier.

3.3. Ternary Extractive Distillation

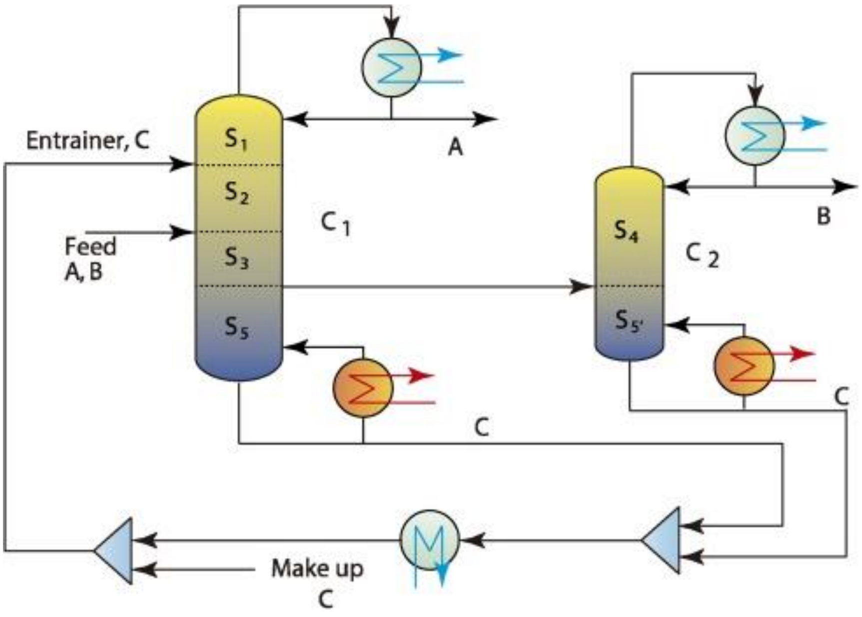
Conventional distillation (CD) systems are inefficient in terms of energy due to the remixing of the components [17]. Numerous research has recommended the use of thermocouples to address this issue. The first column of the distillation is then proposed to be managed by thermally coupled systems with side rectifiers and dividing-wall columns. Operating issues are unavoidable; hence a modified extractive distillation structure with thermal couplings (TCD) was proposed to address probable issues.

3.3.1. Alternative Extractive Distillation Systems

Extending the previously mentioned ideas, which are depicted in Figure 5a, an alternative system (AD) was proposed, which is depicted in Figure 5b, does not have a thermocouple. In the alternative configuration, a second column with one feed was used in place of the vapor-liquid interface, and a stripping section was added to the side rectifier to complete the separation process. While the second column (C2) creates the intermediate as the top stream, the first column (C1) becomes the side stream column, where the light component is eliminated as the distillate. The solvent is then recycled to help with the separation and is present in the bottom streams from the C1 and C2. Thermally coupled and conventional distillation are reported to have five parts; however, the alternative system has six sections. The goal of this additional section, designated as S5 in Figure 5b, is the same as the task of the bottom part of the TCD system, which is purification.



(**a**)

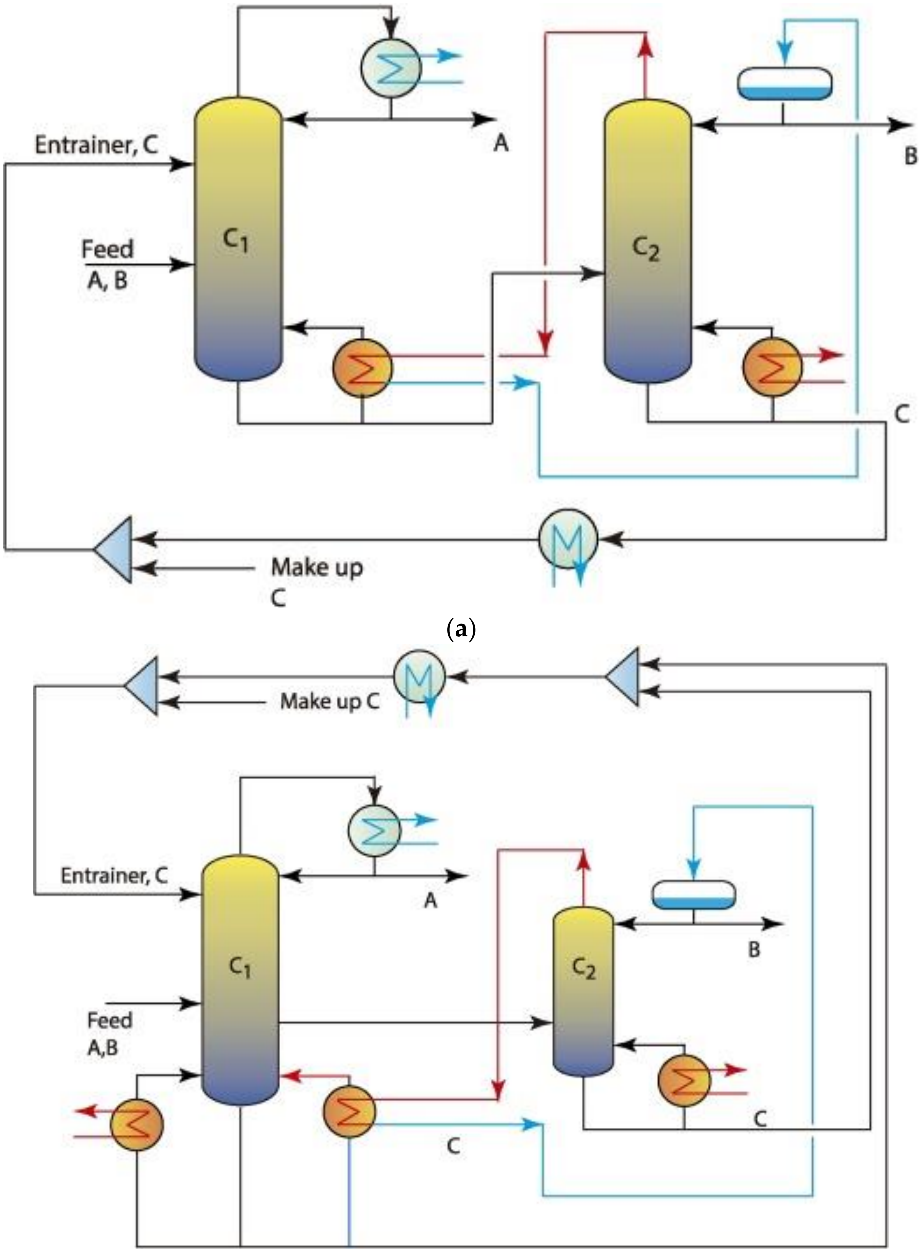


(**b**)

Figure 5. (**a**) Extractive distillation system with thermal coupling system and side rectifier (**b**) Proposed alternative extractive distillation system. Reprinted with permission from [4]. Copyright (2017) Elsevier.

The new alternative system was applied to three case studies to prove its efficiency: ethanol dehydration, heptane-toluene-aniline mixture, and acetone-methanol-water system. In the first case, it was determined that AD is advantageous to CD and TCD because it saves 13.50% more energy, resulting in a 12.40% reduction in the total annual cost. Also, CO_2 emissions are reduced by 10.60% compared to the CD and 3.20% compared to TCD. Similar outcomes were also seen in the other two cases, demonstrating that AD can be more energy-efficient and offer a more sustainable alternative when compared to CD and TCD.

A structure that implements heat integration between columns for additional energy and CO_2 emissions saving was also proposed [4]. It was implemented in AD and CD, as seen in Figure 6a,b. The results showed that the AD system had a superior potential for energy integration since it resulted in a reduction in energy consumption compared to the CD system and a reduction compared to the conventional system with heat integration. Such an effect leads to a decreased annual total cost. When heat integration between AD columns is used, CO_2 emissions are reduced by 11% compared to the CD with heat. This is equivalent to a 39% reduction compared to the CD that is not integrated for extractive distillation.



(**a**)

(**b**)

Figure 6. Heat integration: (**a**) Conventional System; (**b**) Alternative System. Reprinted with permission from [4]. Copyright (2017) Elsevier.

3.3.2. Three-Column Extractive Distillation

A three-column extractive distillation (TCED) is usually used to separate azeotropic mixtures. TCED processes work in two types: XYX and XXY. The difference between the two types is shown in Figures 7 and 8, wherein D3 and B1 are equal for XYX, and D3 and B1 for XXY are not equal. As shown in both figures, condenser 1 has lots of roles.

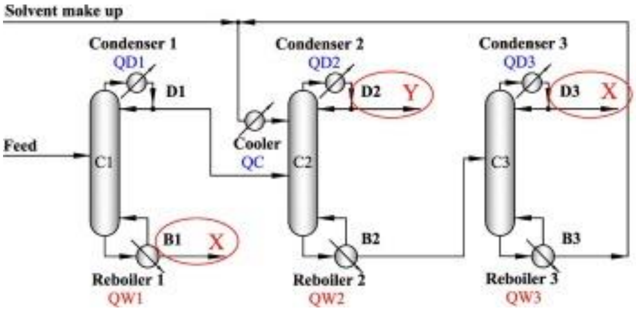


Figure 7. XYX Type**.** Reprinted with permission from [27]. Copyright (2022) Elsevier.

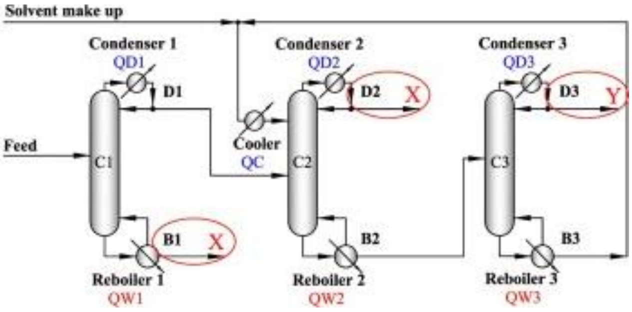


Figure 8. XXY Type. Reprinted with permission from [27]. Copyright (2022) Elsevier.

The feed split method is developed to help the distillate flow, feed flow, and the role of the reboiler to work together, which lessens the work for condenser 1. The applicability and feasibility of the feed-split method work in cases. XYX has six cases (EG, DMSO, and cases concerning the value of δF) and two common cases for XXY (using DMSO and NMP). These different cases give the result if the feed-split method is applicable. It found out that this method works in adverse outcomes for XYX and can be used for saving energy as per XXY type [27].

3.3.3. Comparison of Conventional Ternary Extractive Distillation and VRHP

Conventional ternary extractive distillation (CTED) works directly (DCED) and indirectly (ICED). These two CTEDs are usually used to separate binary azeotrope, which is considered expensive. Based on the calculation in this study, economic and environmental ICED performance is much better than DCED. Since it is expensive, a new method known as a vapor recompression heat pump (VRHP) is being studied to improve economic efficiency and environmental performance. [28] VRHP works directly (VRHP- DCED) and indirectly (VRHP-ICED). The calculation for ICED and CED does not correlate with VRHP-DCED and VRHP-ICED, wherein six different separation sequences for both VRHP are determined. For VRHP-DCED, sequence V gives the lowest steam costs, and four sequences (I, II, III, IV) are much better in terms of annual cost than CED sequences, and four sequences (I, II, III, IV) are better for environmental efficiency. However, II′ and IV′ made VRHP-ICED more environmentally efficient than CED sequences andI,′ IV,′ and VI′ sequences [25].

3.3.4. Extractive Distillation with Two Columns and Rectifier

The dynamics of a traditional three-column configuration are compared with a non-conventional two-column configuration with a side rectifier since a conventional ternary extractive process requires three columns but thermally coupled side stream/rectifier columns have demonstrated to have economic advantages. Furthermore, it is necessary to investigate dynamic controllability because process disruptions are unavoidable and may affect product quality, safety, and environmental concerns.

Both feed flow rate and feed composition disturbances are compared between the conventional and non-conventional configurations. A 1-minute dead time was employed, and a disturbance of ±10% was introduced. The non-conventional process's dynamic response was observed to be inferior to the conventional process. concluded that although the non-conventional process has a lower energy cost than the conventional process, it still needs to be studied because of how poorly it responds dynamically to disturbances.

3.3.5. Comparison of Heterogeneous Azeotropic Distillation and Extractive Distillation Methods for Ternary Azeotrope Ethanol/Toluene/Water Separation

Comparisons are made between two techniques for separating the ternary azeotrope ethanol/toluene/water. These processes are extractive distillation and heterogeneous azeotropic distillation. The study covered four solvents for extractive distillation, including ethylene glycol, glycerol, N-propylbenzene, and n-butylbenzene. The authors' solvent of choice was glycerol. Due to the immiscibility of water and toluene, only two columns are needed after selecting the solvent [29].

It was discovered that ED had a lower cost of energy than HAD. To be more precise, 18.8% and 39.3%, respectively [16]. Overall, it was found that in terms of economics, ED is more desirable than partially heat-integrated HAD.

3.4. *Hybrid Reactive-Extractive Distillation Configurations*

Three processes were used in this study [7], namely the common process (CP), reactive extractive dividing wall process (REDWP), and reactive extractive distillation process (REDP). The process design optimization was created using a simulation software called Aspen. The diagrams of each process discussed above are shown below respectively.

The common process (Figure 9) utilizes three distillation columns. The REDP (Figure 10) is a modified process of the classic one, where the distillation and reactor columns are combined to form a device with azeotropic distillation. The REDWP (Figure 11) uses a single column for the azeotropic and extractive distillation process. Economic optimization results showed that the REDWP outperformed the REDP and CP, which held a total cost of 15% and 9% less than the REDP and CP, respectively. In terms of environmental optimization, REDWP again stood higher against its counterparts, showing overall remarkable results regarding greenhouse gas emissions and water pollution and environmental benefits such as lower biological toxicity. Regarding exergy losses REDP and REDWP showed that these processes had great thermodynamic efficiency and less exergy loss.

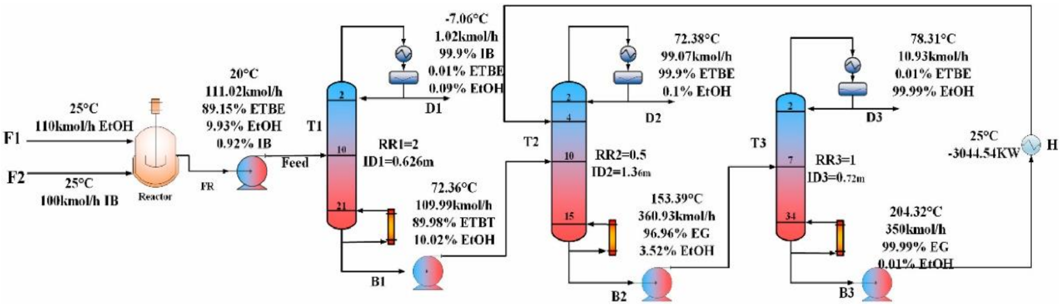


Figure 9. Common process of ethyl tert-butyl ether production. Reprinted with permission from [7]. Copyright (2022) Elsevier.

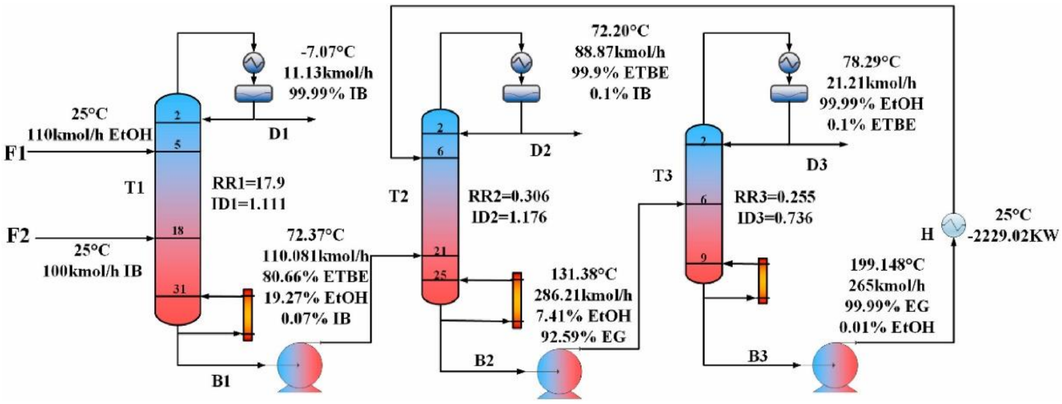


Figure 10. Reactive Extractive Distillation Process. Reprinted with permission from [7]. Copyright (2022) Elsevier.

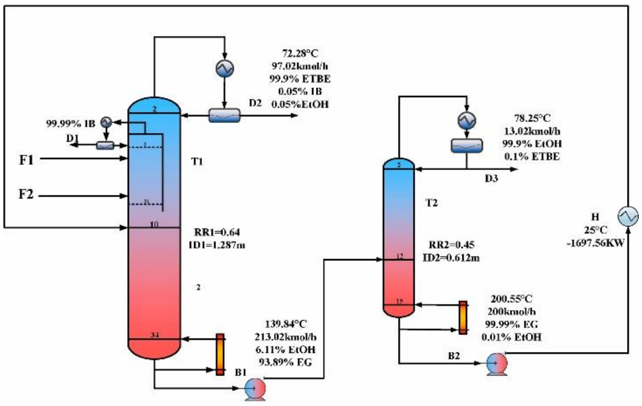


Figure 11. Reactive Extractive Dividing Wall Process. Reprinted with permission from [7]. Copyright (2022) Elsevier.

4. Research Gaps

Although several authors have investigated various grounds for studying, some space remains left for further research. For one, there is usually a lack of parameters to put under study. For instance, the optimization process only focused on a single factor, such as pressure [8]. [15] one article only reported on the reduced capital costs by utilizing different configuration configurations of extractive distillation columns. One could further obtain data and information on the differences in process controls, parameters, and detailed information on recovery. [30] another one is that an article discussed entrainer selection; however, there is a lack of research on how a specific entrainer affects the distillation process [24].

One study showed that [11], even though computer-aided molecular design is a new method for efficiency, two aspects must be considered in screening solvents: price and source. Intensification and integration techniques are used for capital cost and energy consumption but are much more complex than traditional processes. Another one is in a study where it resulted that [24] a vapor recompression heat pump (VRHP) is better than conventional ternary extractive distillation. As specialized distillations are created, a comparison of specialized and vapor recompression heat pumps should be made regarding their financial costs and environmental performances.

With regards to process intensification, a study showed that [2] even though some process intensification technologies increase economic efficiency and reduce energy consumption, they also make the process more complex than it would otherwise be and make it harder to operate and monitor. Another is that [31] different special distillations reduce energy consumption using inorganic salts as the entrainer. More research should be conducted regarding thermally coupled distillation columns with inorganic salt entrainers.

5. Future Outlook

Choosing the right control variables is crucial since any changes in feed flow rate or composition lead to undesirable product purities because of material imbalances in the system. Further research is required in this area because there is still an issue with introducing ± 20% feed disturbances.

As the battle with climate change further intensifies, process designers are more energy-conscious, and novel energy-efficient methods and distillation processes are pushed further to advance. In the future, it is said that more of these types of methods will be incorporated into the chemical process industry. More so, designers will find a way to create reactive or divided distillation columns with less expensive materials and be able to marginalize the use of these energy-efficient methods. Renewable energy will also play its part in the chemical process industry and significantly reduce the use of fossil fuels and be able to lessen the harmful emissions as a by-product of the process.

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