5 Process synthesis and intensification of hybrid separations

Abstract: Hybrid flowsheets are defined, in the context of process intensification, as alternatives suitable for replacing energy-intensive separation methods through the combination of more than one unit operation. Distillation is one of the first options considered for achieving a required separation; therefore, this chapter examines distillation-based hybrid alternatives. Due to the extent of the topic, this analysis is limited to the separation of bioalcohols utilizing pervaporation and liquid–liquid extraction as assisted distillation methods. For each case, different hybrid flowsheets are reported and commented on. The corresponding distillation-based processes are considered for comparison. Synthesis of the possible hybrid flowsheets appears to be important, especially when multicomponent mixtures are considered. This aspect is discussed for the combination of liquid–liquid extraction and distillation as applied to the separation of biobutanol from its fermentation broth. The synthesis of alternative hybrid flowsheets is reported, showing that one configuration can realize a 43% reduction in the total annual cost.

Bioalcohol production by fermentation perfectly represents the case where distillation alone is penalized by the thermodynamics of the mixture, but its applicability can be extended using valid alternative hybrid flowsheets.

Keywords: Hybrid flowsheet, process intensification, distillation, bioethanol, biobutanol

5.1 Introduction

There are many possible definitions of crisis, but Coyne [1] stated, “A crisis is an unexpected event that creates uncertainty and poses a direct or perceived threat to the goals and norms of an organization or society.” Offe [2] pointed out that crisis are “processes in which the structure of a system is called into question.” Being specific, by coupling the words “energy” and “crisis,” the latter acquires the metaphorical meaning of “some turning point in energy resources” [3]. Events like the 1973 Arab oil embargo, the 1976/1977 shortage of natural gas, and the 1977 New York blackout (even if they were not the result of a resource crisis) impacted all levels of society, from governments to citizens. Is our energy availability unlimited? Even if insulation is cheaper than heat, is it sustainable to keep wasting energy? Are we spoiled energy users? Can we change into wise energy users without compromising our habits?

These questions, together with increases in the cost of energy, swiftly reached the industrial sector, where a change in the energy price can determine production prof-
Itability. Therefore, great research efforts were focused on rational energy usage and on developing alternative production methods. One of the first results of this approach was introduction of pinch technology [4, 5]. This method is based on the second law of thermodynamics and aims to determine the best heat exchanger network for reducing utility consumption. Since 1983, pinch technology has achieved energy savings in the range of 10–70%, reductions in the capital cost of new plants of up to 25%, increased process capacity by the removal of bottlenecks, and greater flexibility and operability. In particular, cost-savings associated with crude oil units were quantified at 1.75 million US$, with a payback time of 1.6 years [6]. Pinch analysis still represents a valid design and retrofit methodology and has achieved outstanding results in industries such as biofuel production [7, 8] and food processing [9].

Since the time of the energy crisis, society has faced different issues associated with energy price, energy availability, environmental quality, and control or process risk due to dangerous or toxic substances. All these drivers have merged into a new approach for process development, called process intensification. A commonly accepted definition of process intensification is difficult, or maybe impossible, to report, but does not limit the importance of process intensification within the chemical engineering community [10]. Stankiewicz and Moulijn [11] defined process intensification as “the development of novel apparatus and techniques that, compared to those commonly used today, are expected to bring dramatic improvements in manufacturing and processing, substantially decreasing equipment-size/production-capacity ratio, energy consumption, or waste production, and ultimately resulting in cheaper, sustainable technology.” This approach defines two main dimensions: (1) the possibility to reduce equipment size (process-intensifying equipment), microreactors and divided wall columns being excellent examples [12, 13]; and (2) the possibility to develop multifunction types of equipment (process-intensifying methods), as in the case of reactive distillation [14].

Beyond the definition of process intensification, it is interesting to define how this concept or philosophy matches or differs from the fundamental areas related to process system engineering.

Process system engineering concerns “the improvement of decision-making processes for the creation and operation of the chemical supply chain. It deals with the discovery, design, manufacture, and distribution of chemical products in the context of many conflicting goals.” This means that the action and focus of process system engineering takes place along all the product creation chain, from the molecular scale to particles, compartments, process units, process plants, and enterprise [15]. Process intensification aims to increase the efficiency of single steps in the chain by proposing new mechanisms, materials, and structural building blocks for process synthesis [16]. Process intensification opens up new opportunities for process systems engineering in terms of model development and inclusion of innovative types of equipment [17].

Process system engineering methods and tools such as process integration, process optimization, process synthesis, and design have been somehow combined with
process intensification. Process integration, as reported by Gundersen [18], is defined as “systematic and general methods for designing integrated production systems, ranging from individual processes to total sites, with special emphasis on the efficient use of energy and reducing environmental effects.” Reductions in heat, mass, and power are the most common applications of process integration and, because the final objective is to obtain a more efficient process, it is easy to imagine that the borders between process intensification and process integration are very blurred. Process integration principles are used in process intensification and, as Babi et al. [19] reported, process integration and intensification are considered concurrently. However, in contrast to process intensification, process integration techniques do not include any phenomena addition or enhancement. The term “process integration” is also used to describe the interconnection of equipment by means of recycle streams in an industrial plant. Baldea [20] proved that intensification represents a limit case in tight integration through significant material recycling.

Process optimization is defined as “the use of specific methods to determine the most cost-effective and efficient solution to a problem or design for a process” [21] and it is a core part of process system engineering. Process intensification does not include explicit methods for process optimization, but optimization tools have been successfully applied to the design of complex intensified systems, for example, reactive distillation as reported by Taylor and Krishna [22].

The interaction between process intensification and process synthesis and design is an open challenge where much work remains to be done. A systematic methodology for the development of intensified processes could help the designer to generate all possible alternatives. In the specific case of intensified distillation systems, Rong developed a systematic procedure for generation of divided-wall columns [23], whereas Almeida-Rivera et al. [24] focused their studies on the reactive distillation option.

Nishida et al. [25] defined process system synthesis as “an act of determining the optimal interconnection of processing units as well the optimal type and design of the units within a process system.” Babi et al. [26] specified that the objective of process synthesis is to define “the best process route, from among numerous alternatives, to convert given raw material to specific (desired) products, subject to predefined performance criteria.” Including process intensification into process synthesis requires considering not only the unit operation scale, but also the task and phenomena scales in order to include new intensified alternatives. A possible multiscale approach was discussed by Babi et al. [27] and Lutze et al. [28], who considered a unit operation-based methodology and later introduced a phenomena-based method [29].

Regardless of the definition used to describe process intensification, the ultimate aim is the innovation and improvement of a process through considering contrasting objectives. Process intensification actions can be divided into three main groups or levels. The phase level is the most detailed and considers the molecules that build up a thermodynamic phase. At the process unit level, all phases are embedded in
equipment. At the plant level, the interconnection between equipment units is considered [30].

This chapter explores different process intensification options at the plant level. In particular, it is possible to distinguish between hybrid unit operations following the definition of Babi et al. [19]: “A hybrid/intensified unit operation, is an operation that enhances the function of one or more unit operations performing a task or a set of tasks through a new design of the unit operation or the combination of more than one unit operations.” In these hybrid systems, mass and/or energy exchanges are integrated in the same unit or hybrid flowsheet so that different unit operations are combined to obtain a more efficient process. The latter option is explored in this chapter. However, considering the number of available unit operations and their possible combinations, the analysis is limited to distillation-assisted hybrid flowsheets. In particular, the following hybrid systems are considered:

- pervaporation-assisted distillation
- liquid–liquid extraction-assisted distillation

The possible applications of hybrid systems can also be very different. For this reason, to give a homogeneous view of the different processes, applications based on bioalcohol production have been chosen.

For each process considered, a limited number of references are given. These references were selected as the starting point for further literature research.

### 5.2 Pervaporation-assisted distillation

The term “pervaporation” was introduced by Kober to describe a combination of permeation and evaporation [31]. In this process, a hot fluid contacts one side of a semipermeable membrane, and a vacuum is applied on the other side where permeate vapor is collected. The driving force of the process is the difference in the vapor pressure between the hot fluid and the permeate vapor. Depending on the phase of the hot fluid, it is possible to distinguish between pervaporation and vapor permeation. This difference is depicted in Figure 5.1.

Figure 5.1(a) represents the pervaporation process. In this case, the hot liquid feed is in contact with the membrane that separates the low-pressure permeate vapor. The vapor enriched in one or more components is cooled and condensed. Figure 5.1(b) shows the vapor permeation process. In this case, the membrane is in contact with the vapor stream in equilibrium with the hot liquid feed, while the low-pressure permeate vapor is cooled and condensed. Vapor permeation is thermodynamically equivalent to pervaporation because both processes are subjected to the same driving force [32]. If not specified otherwise, only pervaporation is considered here because most biofuels are produced in the liquid phase as a result of fermentation processes.
Fig. 5.1: Systems for (a) pervaporation and (b) vapor permeation.

The degree of separation achieved by pervaporation mainly depends on three factors: vapor–liquid equilibria, membrane selectivity, and feed-to-permeate partial vapor pressure ratio [33]. The first parameter is related to the feed composition, and a large amount of data is available from distillation studies. Membrane selectivity is an intrinsic property of the membrane material and is related to the solubility and diffusivity. Solubility selectivity is related to the interactions between feed components and the membrane. For example, hydrophobic membrane materials preferentially sorb hydrophobic compounds. The diffusivity efficiency depends on the size and shapes of permeating components. Because the membrane is the core of the pervaporation process, an essential step for industrial application is development of sorption- or diffusion-controlling materials [34].

The feed-to-permeate partial vapor pressure ratio is related to the separation achievable by pervaporation and can be considered an operational parameter. Usually, the permeate component is very dilute in the feed and its vapor pressure can be increased by increasing the feed temperature. The permeate-side vapor pressure can be reduced by means of a vacuum pump, using a condenser, or with a sweeping fluid. The three alternatives are reported in Figure 5.2.

In Figure 5.2(a), the low pressure on the permeate side is assured by a vacuum pump. This solution is applied for low permeate volumes and low capacities, mainly at laboratory scale. In Figure 5.2(b), the vacuum is spontaneously generated by permeate condensation. This is the most cost-effective solution. Lastly, in Figure 5.2(c), the membrane permeate side is swept with an inert carrier gas that is usually recycled and conditioned.
Pervaporation-assisted distillation

5.2 Pervaporation-assisted distillation

The required feed-to-permeate partial pressure ratio should be higher than 1, but to assure sufficient efficacy in industrial applications, a value between 7 and 10 is recommended [35].

Pervaporation is mainly applied for the separation of volatile organic components, organic/organic separations, organic/water separations, or food-related applications.

In the first category, typical examples are the separation of compounds such as chloroform, benzene, and toluene from aqueous dilute solutions [36]. For organic/organic separations, many different systems have been studied, including methanol/benzene, methanol/toluene, and benzene/cyclohexane, as reviewed by Smitha et al. [37]. The majority of pervaporation systems installed worldwide are for organic/water separations. Most of the mixtures studied are azeotropic solutions of alcohols, due to the need to reduce energy consumption associated with typical separation methods. A review of different aqueous mixtures separated by pervaporation was published by Chapman et al. [38]. Recently, pervaporation has been also applied in food technology, mostly for the separation of aroma compounds [39].

The main reasons to explore the combination of pervaporation and distillation are the widespread use of distillation as a separation method and its efficiency in large-scale production processes. However, a shift of part of the separation work to less energy-intensive methods could bring hybrid solutions that are more efficient. Different possibilities have been proposed for pervaporation-assisted distillation flowsheets. Four alternatives are reported in Figure 5.3.
The configuration in Figure 5.3(a) is usually referred to as a predistillation scheme whereby the column feed is passed through the membrane module. The permeate and retentate are re-introduced in the column in such a way that the operation of the column is not disturbed. For this reason, it is necessary to optimize the permeate temperature and pressure. The configuration of Figure 5.3(b) is called a parallel scheme. When the side stream has the same flow rate and feed withdrawal point, it is mathematically equivalent to the predistillation scheme. The configurations in Figure 5.3(c, d) are called post-distillation schemes, whereby the distillate or the bottom stream are fed to the membrane to reach the desired purity. The energy consumption of different configurations were compared by Alshehri and Lai [40], considering separation of propylene and propane as a case study.

For the same separation case, David et al. [41] proposed a hybrid pilot plant and quantified 20–50% savings in capital costs and up to 50% in operating expenses, compared with the distillation-based processes. Gottschlich and Roberts [42] also examined the separation of propene and propylene, proving the convenience of hybrid pervaporation/distillation systems when high purities are required.

Moreover, different design procedures have been proposed for the design of pervaporation-assisted distillation systems, such as the minimum area method, which is based on the well-known McCabe–Thiele diagram [43, 44].

![Fig. 5.3: Hybrid pervaporation-assisted distillation configurations: (a) predistillation, (b) parallel scheme, (c) distillate post-distillation, and (d) residue post-distillation.](image)
5.2.1 Hybrid distillation/pervaporation processes for bioethanol purification

Bioethanol is produced by fermentation of sugars contained in agriculture residue or energy crops. It has been recognized as a sustainable transport fuel because it has the potential to act partially as a substitute for oil-derived gasoline. It is produced as a dilute aqueous solution, resulting in an energy-demanding concentration step. The presence of the ethanol–water azeotrope makes the separation even more challenging.

For the separation of homogeneous azeotropic mixtures, pervaporation has the advantage of eliminating the need for an external mass-separating agent. Moreover, the energy request is limited only to the latent heat of the permeate components. By contrast, in the case of distillation it is necessary to supply heat to the whole feed. If extractive distillation is considered, the entrainer cost should also be considered [34]. Different works have addressed the synthesis and optimization of distillation alternatives to reduce the energy consumption of separation in order to increase the profitability of bioethanol production [45, 46]. Standalone pervaporation is probably not economically feasible, but it can improve the efficiency of the overall process when combined with other unit operations, such as distillation [47].

The bioethanol production process can be broken down into the five main steps of pretreatment, cellulose hydrolysis, concentration and detoxification, fermentation, and product separation [48]. Pervaporation can be integrated into different parts of the process sequence. One alternative is the integration of pervaporation and the fermentation step. The benefit of this kind of coupling is to reduce inhibition and poisoning of the microorganism by the bioalcohol, with a consequent increase in bioconversion. Usually, a filtration system is placed between the fermentor and the pervaporation unit to remove suspended solids in the broth. The retentate is recycled back to the fermentor, and the permeate is a stream enriched in alcohol. Because distillation hybrid flowsheets are the main focus of this chapter, details on this case can be found in specific references [49–52].

Different integrations between pervaporation and distillation are possible in the product separation section of the general bioethanol production line. The aim is to obtain fuel-grade quality bioethanol, with a purity grade equal to or higher than 99.5 wt%. With ordinary distillation, it is impossible to reach this purity because of the presence of the ethanol–water azeotrope. Different alternatives are available for overcoming this limitation (pressure swing distillation, extractive distillation, etc.), resulting in different integration possibilities.

A hybrid distillation/pervaporation system was patented by Tusel and Ballweg in 1983 [53]. It consists of a distillation column followed by two pervaporation units, as schematically represented in Figure 5.4. The distillation column is fed by a 8.8 wt% solution of ethanol and water preheated to its boiling point. The distillation column separates a distillate stream with a purity of 80 wt% ethanol, which is condensed and brought to a pressure of 3 bar to be fed to the first pervaporation module. The vapor
side of the module is kept at a pressure of 70 mbar. This module is constituted of a lower selective membrane so the water separates quickly. The permeate from the first module contains 10 wt% ethanol and is recycled back to the distillation column. The retentate has an ethanol content of 95 wt% and, using a heat exchanger circuit, is sent to the upper part of the distillation column to recover part of the column’s vapor condensation heat, which is necessary for the second pervaporation module. Part of the retentate is recycled to the first pervaporation module and the remaining part is fed to the second module. This module is equipped with a higher selectivity membrane to give a final ethanol concentration of 99.8 wt%. As for the first module, after condensation, the permeate is recycled to the distillation column feed.

The scheme proposed has the advantage of increasing the ethanol concentration in the feed of the first pervaporation module from 80 to 92.5 wt%. Moreover, recovery of the condensation heat by the retentate allows reduction of the reflux ratio required by the distillation column. The authors quantified a reduction in steam consumption of between 5 and 1.6 kg/L alcohol produced.

Other post-distillation arrangements have been reported by several authors. Examples include the Lurgi pervaporator, where a plate-type membrane module and the permeate condenser are combined into a compact unit [54], and two heat-integrated distillation columns coupled with a pervaporation module [55]. The control properties of pervaporation modules integrated into the distillate side of an ordinary distillation column were also examined, proving their applicability on an industrial scale [56].

A different configuration was also proposed, whereby the pervaporation module was included between two distillation columns [57, 58]. This system is reported in Figure 5.5 and fits well with the separation of minimum temperature azeotropic mixtures such as ethanol–water. In the first column of the hybrid flowsheet, pure water is recovered as the bottom stream, while the distillate approaches the azeotropic composition. The distillate of the first column is fed to the pervaporation module where, by means of hydrophilic membranes, a water-rich permeate is separated and recycled back to the first column after being condensed. The retentate phase, rich in ethanol, is fed to the second distillation column. In this column, ethanol is the heaviest component and is obtained pure as the bottom stream. The distillate stream, with a composition
close to the azeotrope, is recycled to the feed for the pervaporation module. Gooding and Bahouth [57] reported a case study based on this configuration, considering a 5 mol% ethanol feed, distillate compositions of 81 and 95 mol% for the first and second columns, respectively, a retentate stream with 97 mol% ethanol, and a final product of 99.5 mol% purity. Unfortunately, no economic data were reported for comparison with azeotropic or extractive distillation.

Brüschke and Tusel [59] considered the same system for concentration of a mass flow rate of 2000 kg/h containing 94 wt% ethanol to produce a stream of 1867 kg/h with a purity of 99.85 wt% ethanol. The authors claimed a 28% saving in the capital cost and a 40% reduction in the operative cost compared with separation by distillation using an entrainer.

Note that integrated systems using vapor permeation are also possible. For example, Huang et al. [60] discussed mechanical vapor-recompression distillation combined with membrane vapor permeation. In mechanical vapor compression, the overhead vapor is compressed and used as auxiliary fluid in the column reboiler where it exchanges its latent heat of condensation. Part of the condensed vapor is used as liquid reflux and the other part is the final product. This technology alone is not able to reach fuel-grade purity, so other separation units are normally required. In this case, coupling of distillation with membrane vapor permeation has the double benefit of increasing the achievable purity at the same time as reducing the energy consumption. The membrane module is placed as shown in Figure 5.6 and the main issue is related to the resistance of the membrane at a temperature of 130 °C, which is required to keep the water–ethanol mixture above the dew point.

Composite membranes were successfully applied by the authors. The membrane preferably permeates water that is reintroduced in the column. The energy saving in the integrated system was quantified as half of the requirement when only distillation was considered. Even higher savings were reported by Vane et al. [61] when the vapor permeation was coupled with a stripping column.
5.2.2 Hybrid distillation/pervaporation processes for biobutanol purification

Butanol produced through fermentation processes is usually referred as biobutanol. Before 1950, almost two-thirds of global butanol supplies were produced in this way. Development of the petrochemical industry made synthetic butanol cheaper and biological processes were abandoned. Recently, the discovery of new strains able to tolerate higher concentrations of butanol, development of new separation options, and the possible use of biobutanol as biofuel are attracting the interest of academia and industry and stimulating reconsideration of the fermentation production route. In particular, biobutanol as biofuel has some advantages over bioethanol. It has lower vapor pressure, is not hygroscopic, is less corrosive, can be used pure or blended in any concentration with gasoline, and has a higher energy content [62]. The anaerobic fermentation of starchy substrates using different strains of *Clostridium acetobutylicum* or *Clostridium beijerinckii* produces a fermentation broth that is typically a mixture of acetone, butanol, and ethanol (ABE mixture) with a component ratio of 3:6:1 [63]. However, separation is challenging and energy intensive because of the diluted feed and presence of the ethanol–water homogeneous azeotrope and the butanol–water heterogeneous azeotrope.

When only distillation is considered as separation method, different alternatives have been reported in the literature, as reviewed by Liu et al. [64]. In general, the main possibility for decreasing the energy demand of the process is increasing the butanol concentration in the distillation feed. In contrast to bioethanol purification, where the pervaporation step is used to enhance product purity, in this case the optimal pervaporation position is before the separation train. Figure 5.7(a) shows a distillation-based sequence for the purification of ABE mixture similar to that proposed by Marlatt and Datta [65]. Figure 5.7(b) reports the hybrid process studied by Rom et al. [66]. For both configurations, it was assumed that acetone and ethanol had already been removed from the feed.

The main difference between the configurations is that, in Figure 5.7(a), the first column is fed with a diluted stream, then a decanter is used to separate an aqueous...
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Fig. 5.7: Configurations for (a) distillation and (b) hybrid pervaporation-assisted distillation alternative.

phase and a butanol-rich phase. The second column is used to reach the required purity for the butanol. In the configuration of Figure 5.7(b), the pervaporation unit increases the concentration of butanol in the permeate to the immiscibility region. In this way, it is possible to directly connect the feed to the decanter. Rom et al. [66] compared the two alternatives, considering a feed stream with 0.5 wt% butanol at 35 °C, using a poli(dimethylsiloxane) organophilic membrane and a permeate side pressure of 0.004 bar. The energy consumption for the separation by distillation was quantified at 72 MJ/kg butanol. When the butanol concentration was increased to 9 wt% by means of the pervaporation unit, the energy demand was reduced by 50%. If it were possible to bring the concentration to 50%, the energy demand could be 90% less than in the distillation-based design. It is necessary to investigate membranes able to
reach this high concentration. For the hybrid flowsheet, a butanol concentration of 5 wt% was identified as the lower limit for economic advantage.

Most of the possibilities explored in the literature on the use of pervaporation modules in biobutanol production focus on pervaporation-assisted fermentation. The objective of this coupling is to remove butanol from the fermentor to alleviate product inhibition, increase the butanol final concentration, and allow the use of more concentrated feedstocks. It is evident that a higher concentration of butanol corresponds to lower energy consumption in the final separation step. Similar results to the case discussed were reported, among others, by Cai et al. [67], Sethhaku et al. [68], and Van Hecke et al. [69].

### 5.2.3 Hybrid distillation/pervaporation processes: final remarks

Distillation and pervaporation are two distinct unit operations that can be interlinked in a more efficient hybrid process. The main benefits derive from the partial shift of some separation duties from distillation to pervaporation. In particular, this shift concerns cases of difficult separations such as azeotropic mixtures or compounds with a low relative volatility. The shift allows distillation to operate in its optimal region, avoiding the use of a high number of stages, high reflux, or external mass-separation agents. Pervaporation, not being limited by the vapor–liquid equilibria, can efficiently improve the overall separation economy. Bioalcohols, as produced by fermentation processes, are dilute aqueous solutions containing one or more azeotropes. Pervaporation is able to reduce the energy consumption, limiting the heat duty to that needed for the pervaporate. Moreover, no external mass-separating agents are required to overcome the azeotropic composition. In this way, the product has a higher market appeal; furthermore, the process is safer and has a low environmental impact. Some challenges remain in developing industrial hybrid pervaporation/distillation processes and are mainly related to membranes that are able to keep high selectivity at high flux.

Intensified hybrid pervaporation/distillation systems, where the two separations are combined into a single unit, have also been described in the literature [70]. An intensified system is shown in Figure 5.8.

Some of the column stages are replaced by a pervaporation module. The module can be a ceramic hollow fiber membrane such that the permeate is recovered from the inside lumen. The main advantages of this kind of integration are as follows:

- Energy required for pervaporation is provided by the distillation column vapor, removing the need for interstage heating.
- Mass and energy transfer between liquid and membrane is enhanced by turbulence induced by the vapor.
- The driving force is maximized because the liquid is close to its saturation point.
5.3 Liquid–liquid extraction-assisted distillation

Liquid–liquid extraction is the separation of one or more components included in a liquid mixture by contact with another immiscible or partly miscible liquid. The separation is achieved when the components in the feed distribute preferably in the second liquid. As for distillation or absorption, it is possible to repeat the separation in stages to reach the required purity.

In the process description, the following definitions apply [71]:

**Feed**: inlet stream in which the substance to be extracted is initially dissolved  
**Solute**: substance transferred from the feed  
**Solvent**: second liquid phase added to the process, in which the solute is dissolved  
**Extract**: outlet stream containing solute-enriched solvent extracted from the feed  
**Raffinate**: outlet stream containing solute-depleted feed

In general, extraction is favored over distillation for the following [72]:

- dissolved or complexed inorganic substances in organic or aqueous solutions  
- removal of diluted contaminants  
- removal of diluted high-boiling components  
- recovery of heat-sensitive components  
- separation of mixtures according to chemical type (e.g., removal of aliphatics from aromatics)  
- separation of close-boiling liquids where solubility differences can be exploited  
- separation of azeotropic mixtures

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The membrane area necessary for separation is less than that needed for external pervaporation.

This single-unit intensified system is in its early stages of development and more experimental work is required to promote its application on an industrial level.
The choice of solvent is a crucial point and affects the economy and feasibility of the whole process. Different authors have reported selective criteria, some of which are listed as follows [73, 74]:

- **Selectivity**: expresses how the solute is distributed between the solvent and feed
- **Partition ratio**: related to the amount of solvent required for the separation
- **Density**: large density difference between the feed and solvent is usually required to make separation easier
- **Miscibility**: feed and solvent ideally should be immiscible
- **Safety**: nontoxic and noninflammable solvents are preferred
- **Cost**: cost of the solvent is part of the overall economic evaluation

The equipment used to bring the two liquid phases in contact and permit material transfer is normally classified into four types [75]: mixer-settlers, continuous countercurrent extractors, continuous counterflow extractors with mechanical agitation, and centrifugal extractors.

The first type is the simplest technology. In mixer-settlers, the two liquids are mixed in a vessel using different types of impellers; then, the two phases are separated in a gravity decanter. Usually, to reach the required purity target, different mixers and settlers are connected in countercurrent flow. Continuous counterflow extractors are generally spray, packed, or tray columns. Continuous counterflow extractors with mechanical agitation are required for a low density difference between the liquid phases or for high viscosity liquids. In this case, the column is equipped with rotating agitators driven by an axial shaft.

The extractor design includes identification of the number of stages and the amount of solvent required to perform the target separation. Details on the design procedure for the different extractor types can be found in Henley et al. [72].

Liquid–liquid extraction could be considered intrinsically hybrid, because the solvent is usually recovered by distillation. An example of extraction followed by distillation solvent recovery is showed in Figure 5.9.

The extract obtained from the extraction column is fed to a distillation column and the solvent is recovered and recycled to the extractor. This configuration is not considered a liquid–liquid extraction-assisted distillation scheme because the solvent re-
covery section is a necessary step for a reasonable and sustainable design. Integrated liquid–liquid extraction/distillation flowsheets are here intended as combined operations where extraction is used to perform part of the whole separation process in more efficient way.

5.3.1 Hybrid liquid–liquid extraction/distillation processes for bioethanol purification

As discussed in the Section 5.2.1, different distillation-based configurations are used to concentrate the bioethanol produced by fermentation processes. One of the most commonly used alternative includes a preconcentration column to approach the azeotropic composition, followed by an extractive distillation column to overcome the azeotropic composition, as reported in Figure 5.10. The overall configuration is composed of three columns. Because the extractive column uses an external entrainer, an additional column is required for its recovery. Several studies have used this configuration as a base case for comparison with different alternatives [76, 77].

Aviles Martinez et al. [78] proposed two hybrid flowsheets where liquid–liquid extraction was used to reduce the energy demand of distillation-based alternatives. The hybrid flowsheets are reported in Figure 5.11.

The authors compared the hybrid alternatives shown in Figure 5.11 with the reference case of Figure 5.10, considering the energy consumption, total annual cost (TAC), and carbon dioxide emission as performance criteria. The ethanol feed composition was set at 10 mol%, according to the typical yield obtainable from the fermentation of sugar cane bagasse. The purity targets were 99.99 mol% for water and ethanol and 99 mol% for the solvents to be recycled. For the extractive distillation, ethanol purity in the distillate stream of the prefractionator was set to 83.76 mol% and glycerol was used as solvent. In the liquid–liquid extractor, n-dodecane was selected for its ability

Fig. 5.10: Base case extractive distillation configuration for dehydration of diluted ethanol feeds.
to separate light alcohols from water. For the configuration shown in Figure 5.11(a), an almost pure water stream was obtained as raffinate in the liquid–liquid extractor. The flow rate of this stream was very similar to that of water separated as bottom stream in the prefractionator column of the base configuration in Figure 5.10. The extract stream containing \( n \)-dodecane, ethanol, and some water was fed to the extractive distillation column where, by adding glycerol, ethanol at the required purity was recovered as distillate. The bottom stream proceeds for the recovery of both solvents. The second hybrid configuration proposed, as reported in Figure 5.11(b), differs from the first in the separation order after the extractor. Although the authors did not report any synthesis procedure for generating alternatives, it is possible to suppose that this second hybrid alternative was generated by following the general rule to remove the mass-separation agent right after its introduction. It is possible to see from Figure 5.11(b) that \( n \)-dodecane is separated as bottom stream in the first distillation column; then, the distillate is sent to the extractive distillation column for ethanol purification. The last column performs glycerol recovery.

In all configurations, the wastewater stream is composed mainly of water (85 mol%), traces of solvents, and ethanol. Comparing the performances of the hybrid alternatives with the base case, for the configuration of Figure 5.11(a) the energy con-
assumption and the carbon dioxide emissions were 37% higher than for the distillation-based alternative, while the TAC was almost 19% higher. These performances were expected because the solvent used in the extractor is recovered in the last distillation column, flowing through all the intermediate separation units. On the other hand, the configuration reported in Figure 5.11(b) exhibited excellent performance, demonstrating 30% reduction in energy consumption, 47% TAC reduction, and 30% reduction in carbon dioxide emissions. Although this hybrid alternative includes a higher number of units than the pure distillation case, the liquid–liquid extraction can save the amount of energy required by the prefractionator for separation of the water stream. The cost corresponding to the amount of energy saved is higher than the expected increase in annualized capital costs. Liquid–liquid extraction-assisted distillation processes are a valid alternative for reducing energy consumption in bioethanol separation plants.

The optimal sequence of Figure 5.11(b) was also considered by Vazquez-Ojeda et al. [79] and compared with the typical extractive distillation configuration. Their work focused on process optimization by means of a differential evolution algorithm with restrictions. Octanoic acid, octanol, and iso-octanol were considered as possible solvents for the extraction, while ethylene glycol was used in the extractive column. Different feed compositions were explored, ranging from 2 to 15 mol% of ethanol. The results obtained for a feed composition of 10 mol%, even if different solvents were employed, were in agreement with the results obtained by Aviles Martinez et al. [78].

When the ethanol content in the feed was reduced to 5 or 2 mol%, the hybrid configuration lost its convenience, mainly due to the need for a high number of stages in the liquid–liquid extractor.

### 5.3.2 Hybrid liquid–liquid extraction/distillation processes for biobutanol purification

As discussed in Section 5.2.2, the separation of butanol obtained by fermentation represents a bottleneck in the overall process economy. Because it is coproduced together with acetone and ethanol, the complexity of the mixture and the dilute fermentation broth make separation by distillation an energy-intensive process. One of the most competitive ways to produce pure biobutanol is by liquid–liquid extraction-assisted distillation. One of the first attempts to define liquid–liquid hybrid flowsheets for biobutanol production was carried out by Dadgar and Foutch [80] with the aim of promoting the fermentative over the synthetic process. Their example was then followed by other researchers. For example, Kraemer et al. [81] gathered the properties of 44 different solvents proposed for the ABE extraction and identified mesitylene as a novel extracting solvent, taking advantage of progress in solvent screening by computer-aided molecular design. The general hybrid configuration is reported in Figure 5.12.
The authors demonstrated how the downstream separation sequence depends on the composition of the distillate stream obtained from the recovery column, which, in turn, depends on the solvent selected in the extraction column. The purification section, indicated as a box in Figure 5.12, was defined considering mesitylene and oleyl alcohol as solvents. The results were compared with those obtained using separation by distillation. The specific energy demand for the mesitylene process was 4.8 MJ/kg butanol produced versus 13.3 MJ/kg for the oleyl alcohol and 18.4 MJ/kg for the distillation. Although the main objective of the work was to prove the convenience of hybrid operations, another issue was unconsciously introduced. When multicomponent separations are considered, the combination of two different unit operation is not univocal. This means that, for the same separation, different hybrid configurations are possible. Therefore, it is necessity to define the synthesis procedure for the generation of a research space including all the alternatives. If the generation method is able to predict all the possible alternatives, then the optimal configuration can be identified. For the ABE separation, this issue was explored by Liu et al. [64], who used the following four-step approach:

1. The unit operations used for the separations were defined.
2. A P-graph representation of the operating units was performed.
3. The network was constructed including all the combinatorially feasible flowsheets.
4. A finite number of optimal and near-optimal flowsheets was generated.

The fermentation broth was fed to either a gas stripper or a liquid–liquid extractor. After these units, different combinations of distillation, gas stripping, and extraction were considered. Using the TAC as objective function, the first ten optimal flowsheets obtained were all composed of liquid–liquid extraction followed by different distillation column sequences. The optimal configuration selected is reported in Figure 5.13.

**Fig. 5.12:** Hybrid liquid–liquid extraction/distillation flowsheet for purification of acetone, butanol, and ethanol.
5.3 Liquid–liquid extraction-assisted distillation

Fig. 5.13: Optimal hybrid configuration defined by Liu et al. [64].

The hybrid configuration is composed of a liquid–liquid extractor followed by three distillation columns. The first column performs solvent recovery, the second is used for acetone separation, and the third for butanol purification from ethanol. The distinctness of this configuration is represented by the acetone/ethanol butanol column. This column has a side stream and, therefore, classifies as a complex column. For the separation of ternary mixtures, this kind of sequence was also reported by Doherty and Malone [82] and classified as a “complex direct configuration.”

Defining a hybrid configuration is not a simple combination of two or more unit operations. The combination can be realized in different ways and, for multicomponent separations, various alternatives are usually possible. In this case, process synthesis strengthens process intensification by generating a set of alternatives to be explored in order to define the optimal solution for the separation problem.

5.3.3 Hybrid liquid–liquid extraction/distillation processes: final remarks

The combination of liquid–liquid extraction and distillation is usually considered a natural consequence of the need to recover solvent from the extract stream. In the context of the definition of hybrid configurations, liquid–liquid extraction is considered a unit operation able to improve the separation economy of pure distillation alternatives. In particular, extraction is considered efficient in separating components that exhibit a strongly nonideal behavior, such as azeotropic mixtures. Both separation methods are mature, with well-defined design procedures, and are extensively applied on an industrial scale. In hybrid flowsheets, it is very common that liquid–liquid extraction is used first; then, the components separated in the extract are recovered by distillation. Feed composition and distillate-to-feed ratio are the main parameters that liquid–liquid extraction alters to make distillation more efficient. A fundamen-
tal point in developing such hybrid configurations is development of highly selective solvents with a low environmental impact. As shown by the two separation cases considered, for binary mixtures such as bioethanol–water, the process structure can be easily predicted. More alternatives are possible for a multicomponent feed such as biobutanol fermentation broth. The dimension of the problem can grow even more when complex configurations are included in the search space. For multicomponent distillation, process synthesis is a fundamental tool for generation of all possible alternatives. This aspect is considered in the following case study.

5.4 Synthesis, design, and optimization of alternative hybrid configurations for biobutanol separation

The hybrid flowsheet identified by Liu et al. [64], and reported in Figure 5.13, is here considered as a reference for generating alternative configurations. The synthesis procedure includes the following three main steps:

Introduction of thermal couplings: A thermal coupling is a bidirectional vapor–liquid stream used to replace one or more condensers and/or reboilers associated with nonproduct streams. Referring to Figure 5.13, there are two auxiliary exchangers that satisfy the conditions for substitution, the condenser of the first column and the reboiler of the second column. The exchangers can be eliminated individually or in a combinatorial way. Figure 5.14 reports the possible thermally coupled alternatives.

Section recombination: The introduction of one or more thermal couplings creates a structural degree of freedom to move the column section, providing the common reflux ratio and/or vapor boil-up between columns connected by thermal coupling. The configurations obtained are called thermodynamically equivalent. For the case con-

![Fig. 5.14: Three possible thermally coupled configurations derived from Figure 5.13.](image)
sidered, five configurations are possible. As an example, the possible configurations obtained from the thermally coupled alternative reported in Figure 5.14(c) are shown in Figure 5.15. The complete set of alternatives was reported by Errico et al. [83].

**Intensification:** The objective of intensification is a reduction in the number of columns compared with the reference case. The reduction is performed, starting from the thermodynamically equivalent configurations, by elimination of single column sections. For example, the second column of the configuration in Figure 5.15(a) is used mainly for transportation of the ethanol–butanol mixture, its elimination leading to the intensified configuration of Figure 5.16(a). Proceeding in the same way, the third column of the configuration in Figure 5.15(b) can be eliminated and the ethanol directly withdrawn from the second column, as depicted in Figure 5.16(b). Five possible intensified configurations are possible. Here, for the sake of brevity only three are reported in Figure 5.16. All the alternatives were reported by Errico et al. [83].

The synthesis procedure described here allows the designer to define different classes of alternatives, varying from thermally coupled to thermodynamically equivalent to intensified structures. All the configurations are structurally related to the reference used to initialize the procedure. This point proved to be very useful during design and optimization [84, 85].

To prove the potential of the configurations proposed, they were modeled by means of the process simulator Aspen Plus. The feed composition, as defined by Wu et al. [86], is reported in Table 5.1 together with its physical characterization.

The nonrandom two-liquid (NRTL) Hayden–O’Connell thermodynamic model was used and hexyl acetate was selected as solvent for the liquid–liquid extraction. The purity requirements were fixed as 99.5 wt% for butanol and acetone and 95 wt% for ethanol. The column pressure was optimized to use cooling water in the overhead condensers. Two different objective functions were chosen to compare the perfor-

![Fig. 5.15: Three thermodynamically equivalent configurations obtained from Figure 5.14(c).](image-url)
Fig. 5.16: Three intensified alternatives derived from Figure 5.15.

Tab. 5.1: Feed characterization.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature [K]</td>
<td>322.04</td>
</tr>
<tr>
<td>Vapor fraction</td>
<td>0</td>
</tr>
<tr>
<td>Flow rate [kg/h]</td>
<td>45.36</td>
</tr>
<tr>
<td>Butanol [wt%]</td>
<td>0.3018</td>
</tr>
<tr>
<td>Acetone [wt%]</td>
<td>0.1695</td>
</tr>
<tr>
<td>Ethanol [wt%]</td>
<td>0.0073</td>
</tr>
</tbody>
</table>

The design and the objective function values for the reference configuration of Figure 5.13 are reported in Table 5.2.

The design of the thermally coupled configurations of Figure 5.14 was obtained by considering the correspondence of the column sections in the reference case and
5.4 Synthesis, design, and optimization of alternative hybrid configurations

Tab. 5.2: Design, operative parameters, and comparison criteria for the reference configuration (Figure 5.13). C₁, C₂, C₃ indicate the column number in Figure 5.13.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Extractor</th>
<th>C₁</th>
<th>C₂</th>
<th>C₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of theoretical stages</td>
<td>5</td>
<td>26</td>
<td>46</td>
<td>20</td>
</tr>
<tr>
<td>Overall efficiency</td>
<td>0.654</td>
<td>0.766</td>
<td>0.721</td>
<td>0.834</td>
</tr>
<tr>
<td>Reflux ratio</td>
<td>–</td>
<td>0.905</td>
<td>6.034</td>
<td>14.836</td>
</tr>
<tr>
<td>Feed stage</td>
<td>1</td>
<td>13</td>
<td>32</td>
<td>5/15</td>
</tr>
<tr>
<td>Solvent feed stage</td>
<td>5</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Side stream stage</td>
<td>–</td>
<td>–</td>
<td>44</td>
<td>–</td>
</tr>
<tr>
<td>Column diameter [m]</td>
<td>0.335</td>
<td>0.322</td>
<td>0.325</td>
<td>0.292</td>
</tr>
<tr>
<td>Distillate flow rate [kg/h]</td>
<td>–</td>
<td>21.687</td>
<td>7.694</td>
<td>0.333</td>
</tr>
<tr>
<td>Side stream flow rate [kg/h]</td>
<td>–</td>
<td>–</td>
<td>1.901</td>
<td>–</td>
</tr>
<tr>
<td>Solvent flow rate [kg/h]</td>
<td>708.549</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Solvent makeup [kg/h]</td>
<td>0.709</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Condenser duty [kW]</td>
<td>–</td>
<td>7.284</td>
<td>7.736</td>
<td>1.239</td>
</tr>
<tr>
<td>Reboiler duty [kW]</td>
<td>–</td>
<td>65.919</td>
<td>8.428</td>
<td>0.907</td>
</tr>
<tr>
<td>TAC [k$/year]</td>
<td>234.172</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eco-indicator [points/year]</td>
<td></td>
<td>13,017</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From the values obtained, it is clear that of all the thermally coupled alternatives the one shown in Figure 5.14(c) has the best performance criteria. Figure 5.17 shows the Pareto-optimal solutions, where the chosen solution is marked with a circle. It is evident how the two objective functions compete.

It has been extensively proven that there is a correspondence between alternatives included in the different subspaces [89, 90]. This means that, once the best configuration is identified in a specific subspace of alternatives, only the configurations derived from that one are expected to be promising. For this reason, because the best thermally

Tab. 5.3: Objective function values for all the alternatives of Figures 5.14–5.16.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>TAC [k$/year]</th>
<th>Eco-indicator 99 [points/year]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.14a</td>
<td>214.280</td>
<td>12,462</td>
</tr>
<tr>
<td>5.14b</td>
<td>212.428</td>
<td>13,350</td>
</tr>
<tr>
<td>5.14c</td>
<td>188.143</td>
<td>11,642</td>
</tr>
<tr>
<td>5.15a</td>
<td>189.102</td>
<td>12,017</td>
</tr>
<tr>
<td>5.15b</td>
<td>188.471</td>
<td>11,571</td>
</tr>
<tr>
<td>5.15c</td>
<td>184.930</td>
<td>11,894</td>
</tr>
<tr>
<td>5.16a</td>
<td>198.160</td>
<td>19,684</td>
</tr>
<tr>
<td>5.16b</td>
<td>168.490</td>
<td>16,681</td>
</tr>
<tr>
<td>5.16c</td>
<td>163.631</td>
<td>15,595</td>
</tr>
</tbody>
</table>
coupled configuration has been identified, only the alternatives derived for that configuration are considered. Their performances are reported in Table 5.3. All the thermodynamically equivalent configurations have a better TAC than the reference case. The configuration in Figure 5.15(c) achieved the best economic performance, although the eco-indicator value was not as good as for the best thermally coupled configuration. Considering the intensified alternatives, the improvement in TAC value is evident. For the best case, the alternative shown in Figure 5.16(c), the TAC was reduced to 43% of the reference configuration. The corresponding design parameters are reported in Ta-

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Extractor</th>
<th>$C_1$</th>
<th>$C_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of theoretical stages</td>
<td>5</td>
<td>58</td>
<td>20</td>
</tr>
<tr>
<td>Overall efficiency</td>
<td>0.654</td>
<td>0.783</td>
<td>0.718</td>
</tr>
<tr>
<td>Reflux ratio</td>
<td>–</td>
<td>27.182</td>
<td>–</td>
</tr>
<tr>
<td>Feed stage</td>
<td>1</td>
<td>45</td>
<td>–</td>
</tr>
<tr>
<td>Solvent feed stage</td>
<td>5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Side stream stage</td>
<td>–</td>
<td>–</td>
<td>12</td>
</tr>
<tr>
<td>Column diameter [m]</td>
<td>0.335</td>
<td>0.323</td>
<td>0.324</td>
</tr>
<tr>
<td>Distillate flow rate [kg/h]</td>
<td>–</td>
<td>7.711</td>
<td>–</td>
</tr>
<tr>
<td>Thermal coupling flow rate [kg/h]</td>
<td>–</td>
<td>118.621</td>
<td>–</td>
</tr>
<tr>
<td>Side stream flow rate [kg/h]</td>
<td>–</td>
<td>–</td>
<td>0.336</td>
</tr>
<tr>
<td>Solvent flow rate [kg/h]</td>
<td>708.289</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Solvent makeup [kg/h]</td>
<td>0.684</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Condenser duty [kW]</td>
<td>–</td>
<td>31.094</td>
<td>0.000</td>
</tr>
<tr>
<td>Reboiler duty [kW]</td>
<td>–</td>
<td>65.642</td>
<td>24.517</td>
</tr>
</tbody>
</table>

Fig. 5.17: Pareto-optimal solution for the best thermally coupled configuration, as shown in Figure 5.14(c).
Although the best intensified alternative realized a significant reduction in TAC, the opposite was observed for the eco-indicator. In this case, a 16.5% increase was observed compared with the reference case. This increase is a result of the higher reboiler duty of the intensified alternative and the consequent increase in carbon dioxide emission, corresponding to the production of the auxiliary fluid.

Recently, the study of alternative configurations was completed by including the possibility of waste heat recovery [91] and proving their controllability [92].

### 5.5 Conclusions

Bioethanol and biobutanol produced by fermentation processes are the frontrunner bioalcohols for the substitution of petro-derived gasoline. Compared with chemical and petrochemical processes, bioprocessing is characterized by lower capacity, dilution of the streams, and (normally) by the presence of azeotropes. For all these reasons, unit operations typically applied to final product purification result in high energy demand, reducing the overall competitiveness of the process.

The definition of alternative separation schemes remains an active research field and distillation one of the most studied processes. Different distillation-based processes have been proposed over the years, including complex configurations and divided-wall columns. Hybrid solutions are also emerging as viable alternatives for finally bringing biofuel production to an industrially competitive level. Hybrid flow-sheets can be obtained by the combination of different unit operations to overcome their individual limitations. From the cases examined, it is clear that pervaporation and liquid–liquid-assisted distillation are valid alternatives for bioalcohol separation,
but there are issues to be resolved. For the case of multicomponent separations, hybrid flowsheets are generated by intuition and there is seldom systematic prediction of all the possible alternatives. Moreover, the search space for the best alternative should include complex distillation columns such as thermally coupled or divided columns, because their convenience has been proven in many separation cases.

5.6 Bibliography


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