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Keywords: Extraction, Adsorption, stripping, vacuum, pervaporation, unconventional, separation, bioethanol

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Review

Overview of Alternative Ethanol Removal Techniques for Enhancing Bioethanol Recovery from Fermentation Broth

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Abstract: This study aims at reviewing the alternative techniques for bioethanol recovery, highlighting its advantages and disadvantages, and to investigate the technical challenges facing these alternatives to be widely used. The findings showed that the integration of these techniques with the fermentation process did not meet a large acceptance in the industrial sector. The majority of conducted studies were mainly focusing on ethanol recovery from aqueous standard solution rather than the investigation of these techniques performance in fermentation-separation coupled system. In this context, pervaporation has received more attention as a promising alternative to distillation. However, some challenges are facing the integration of these techniques in the industrial scale as the fouling problem in pervaporation, the toxicity of solvent in liquid extraction, energy consumption in vacuum fermentation. It was also found that there is a lack of the technical economic analysis for these techniques which may limit the spread of its application in the large scale. Currently, hybrid systems integrating distillation with other alternative techniques are considered as an innovative solution to reduce the high cost of the distillation process and the low separation efficiency of the alternatives techniques.

Keywords: bioethanol; separation; unconventional; pervaporation; vacuum; stripping; extraction; adsorption

1. Introduction

Fossil energy was the key driver of the industrial revolution known at the beginning of the 19th century and the technological, economic development progress that followed it. This revolution was accompanied by a remarkable increase in the global primary energy consumption (TPEC) day by day due to the increase in population and modernization. In 2018, the world's TPEC reached 160,000 TWh as it is depicted in Figure 1, and it is expected to rise by 57% by 2050 [1,2].

Future access to fossil fuels may be severely limited due to the increasing concerns over the consequences of climate change [3]. This will lead to a mandatory choice between the energy and the environment, which could, in turn, result in an environmental crisis, major economic crisis, or both. Preventing such a crisis will not be easy because the climate change is mainly caused by the emission of carbon dioxide emanating from fossil fuel combustion in the atmosphere whereas the fossil fuel is still the main source of energy in the world [4]. Nevertheless, fossil fuels will be substituted partially by new energy sources that can fulfil the energy needs of humanity. Biofuels are considered as a promising alternative to replace fossil oil energy sources, as they can be produced from

abundant natural renewable sources [5]. Despite the difficulties which the biofuel industry faces, like the limitation of feedstocks and the high production costs, promising results have been achieved in the environmental aspect. It was reported that the average carbon dioxide emissions growth during 2014–2016 was the lowest over any three-year period since 1981–1983, and the emissions of carbon dioxide from energy consumption increased by only 0.1% in 2016 compared to the previous year [2]. Bioethanol is considered one of the most promising substitute for fossil fuels, with several advantages over the other alternative fuels as it can be effectively integrated into the current fuel systems where 5–15% bioethanol/gasoline mixture does not require any modification of the current engines [6]. The alcoholic fermentation of biomass feedstocks (e.g., sugar cane, starch crops) is currently used as the main process for bioethanol production [7]. Bioethanol market reached 117×10^9 litres in 2017 and it is expected to rise to 119×10^9 by 2019 [8]. These records reflect the efforts have been devoted to developing bioethanol production in industrial scale. However, the results are still under the expectations due to some technical problems which face the substitution of fossil fuels by bioethanol. The availability of efficient separation and purification technique is one of these major challenges, as it typically represents at least 40% (up to 80%) of bioethanol production cost [9]. Moreover, the product (ethanol) inhibition is another limiting factor for the efficient production of ethanol [10]. It was previously reported that yeast cells do not grow in ethanol concentration above 20 wt% where the ethanol-producing capability of the cells is totally blocked at this concentration [11].

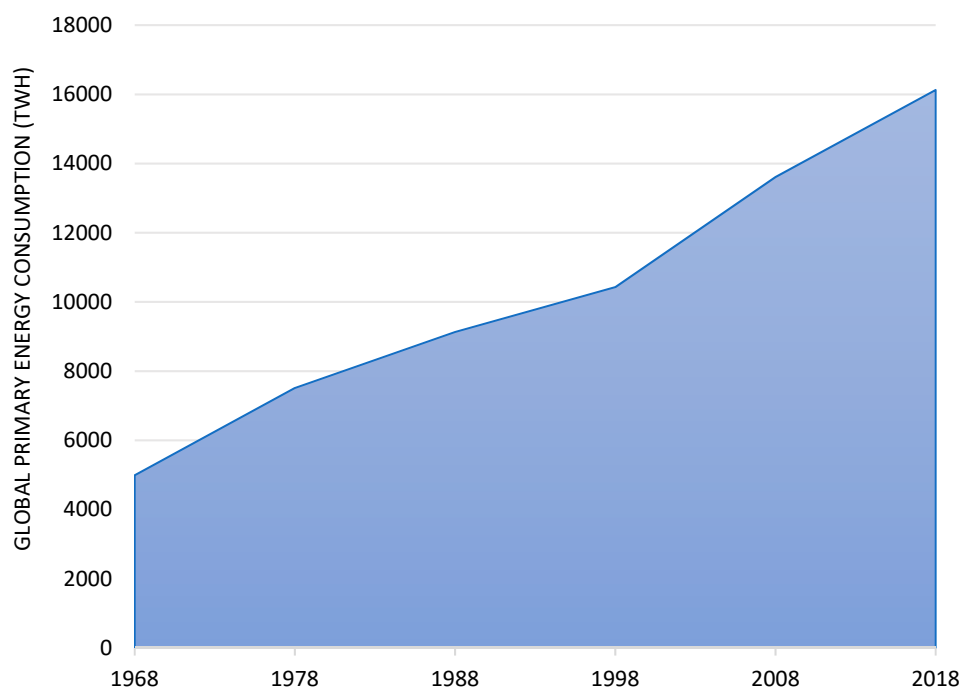


Figure 1. Global fossil fuel consumption between 1968 and 2018 [2,3].

Fermentation and purification are the major steps during bioethanol production. Ethanol and total water are the major components of the broth after alcoholic fermentation. Thus, Separation is needed to purify the bioethanol from the fermentation broth [12]. In this regard, distillation has been used as the main purification method for ethanol recovery for many years [13]. Distillation has a lot of advantages which place it as the preferred choice for industrial application due to: high alcohol recovery (99+%), sufficient energy efficiency at moderate feed concentrations and the ability to simulate the process using process simulation software—which makes the integration of mass and energy in other processes easier to accomplish. On the other hand, distillation has some negative aspects such as Azeotropes—it is not possible to dry effectively the product without coupling in additional separation,

high energy consumption and costs, moreover, the high operating temperatures which lead to the deactivation of microorganisms and proteins [14].

Therefore, developing new separation techniques became a hot issue to improve biofuels production efficiency, and reduce energy consumption during the purification process [15]. Bioethanol recovery techniques from fermentation broth were classified by Serra et al. [16] into conventional or modified conventional systems (distillation system) and nonconventional systems (non-distillation systems).

The nonconventional systems are recently proposed as alternatives for ethanol recovery with energy saving and low investments such as pervaporation separation, vacuum fermentation, adsorption, gas stripping, solvent extraction, and other alternative hybrid processes were mostly developed during the 1970's when there was the interest to produce chemicals using less fossil fuel [17]. Despite that, the application of unconventional techniques for ethanol recovery has been realized in pilot scale a few years ago, the integration of these techniques in the large industrial scale is still limited. Thus, there is an urgent need to review these techniques to be adopted for industrial uses and meet the expectations. In this context, this paper will explore the most alternative techniques currently used for the recovery and separation of ethanol from fermentation broth to investigate the advantages and disadvantages of each technique, and to compare these techniques efficiency in addition to highlighting the future trends in the ethanol recovery field with some recommendations. In this review, only studies that have investigated the ethanol recovery from fermentation broth have been taken into consideration and the studies of ethanol separation from ethanol/water mixture and ethanol dehydration have been excluded.

2. Alternative Ethanol Recovery Techniques

During the biochemical reaction, a wide range of metabolites can be formed by the microorganisms. In several biochemical reactions like the alcoholic fermentation, the accumulation of the end-product in the broth inhibits the fermentation process and stops further production [18–22]. Currently, integrated fermentation/separation coupled systems have received increased attention and have been shown to be successfully used for bioethanol recovery from the fermentation broth as it is formed and to limit end-product inhibition to improve the overall process efficiency. In this context, different separation methods have been developed to be integrated with the fermentation process like pervaporation, adsorption, gas stripping, vacuum fermentation and solvent extraction [7,23–26].

2.1. Pervaporation

Among the different membrane processes, pervaporation is the most promising separation technology which has been widely used for the separation of azeotropic mixtures, organic-organic mixtures, solutions, and for recovering dissolved organics from aqueous solutions as well [27]. Compared to the other membrane processes used in bioreactors, PV is distinctive in term of the possibility of using non-porous membranes. Consequently, the separation using non-porous membrane relies on the membrane characterizations and the chemical properties of the mixture such as the components diffusivity into the membrane and the hydrogen bonding ability. In pervaporation separation, the concentration gradient which is created by vacuum pressure is the driving force for the separation. As the upstream side of the membrane is kept at atmospheric pressure, vacuum pressure is applied on the downstream. Consequently, the selective component which is dissolved on the upstream surface, pass to the downstream side through the membrane [28].

Generally, the pervaporation system may contain a feed tank, feed pump, heater, a membrane module, vacuum pump and condenser cold trap as schematized in Figure 2.

The choice of the membrane material mainly depends on the nature of the selective component. Thus, the hydrophobic membrane will preferentially select organic compounds relative to water and the organic compounds will be recovered in the permeate. Meanwhile, if the membrane is hydrophilic, then the mixture liquid in the feed will be dehydrated and water will be recovered in the permeate [29].

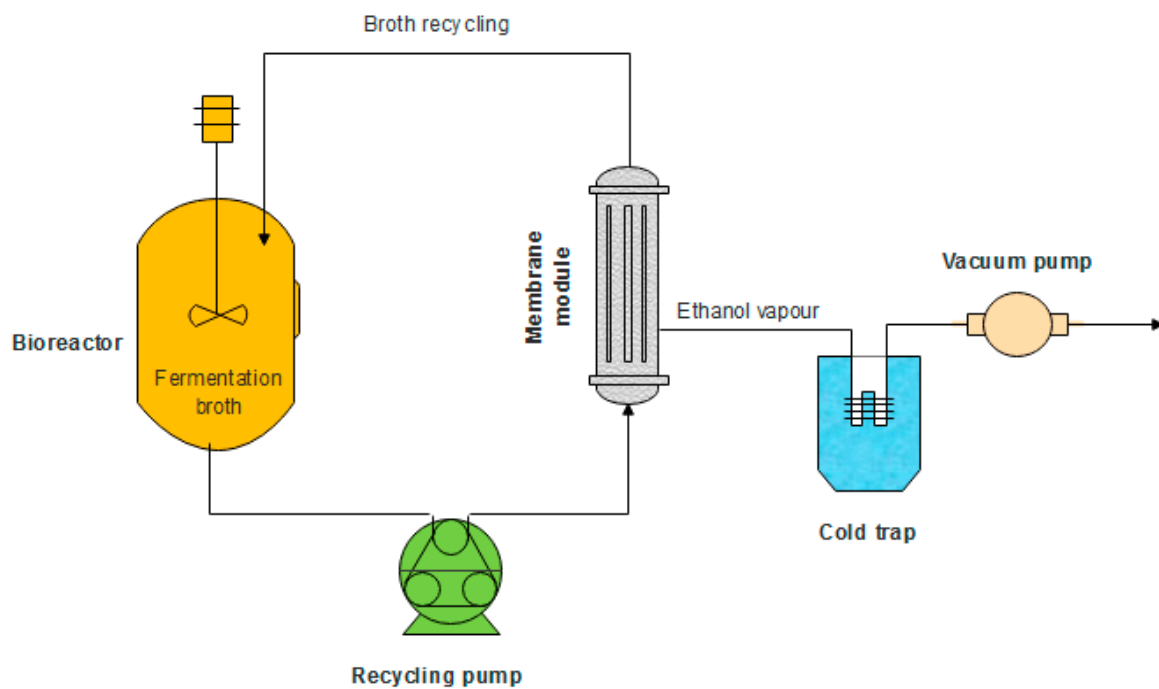


Figure 2. Diagram for fermentation process coupled with pervaporation separation unit.

Pervaporation is the latest membrane separation process to become economically competitive for some industrial applications. The first large-scale industrial pervaporation plant started operation in 1985 in Karlsruhe-Maxau (Germany) and another shortly thereafter in Betheniville (France). Both plants are being used for the dehydration of 94% ethanol [30].

During pervaporation separation, fouling is the biggest challenge leading to the loss of productivity. Fouling may reduce the equipment performance, raise the maintenance costs by repetitive cleaning and cause the contamination problems due to the growth of bacterial cells on the membrane surface [14]. Therefore, extensive studies have been conducted to investigate the nature of fouling problem. Most of these studies have focused on the evolution of permeate flux and total resistance versus time and effect of several factors on membrane fouling, such as module characteristics (shape, size etc.), membrane properties, operating conditions and hydrodynamic forces [31–35]. Moreover, more attention has been turned into the modelling of membrane separation process for the control and optimization purposes [36–39]. Several studies have been reported on the performance of pervaporation using water-selective membranes for ethanol purification or ethanol selective membranes for ethanol recovery, however, the majority of these studies have been devoted to separation process using ethanol/water standard mixture which may lead to some problems during the integration of this process with fermentation process due to the difference in chemical composition and physical properties between fermentation broth and ethanol/water standard mixture. Moreover, some works have been conducted to study the dehydration of ethanol/water mixtures, which would be more suitable for ethanol purification rather than ethanol recovery from the fermentation broth. A large number of papers have been published to study the performance of the pervaporation process to recover ethanol from the fermentation broth. Thus, Table 1 summarizes some recent studies conducted between 2008–2018.

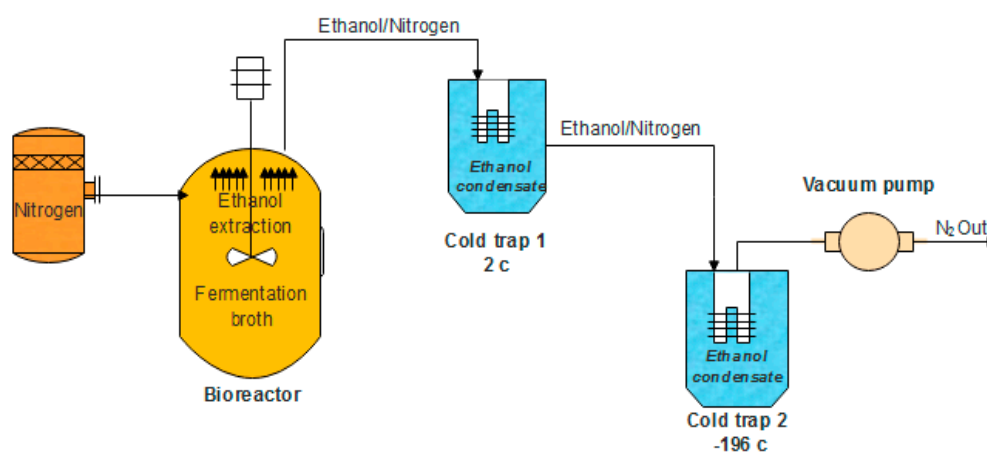
It is clear that limited membrane materials are currently used for bioethanol recovery, looking for new membrane materials may help to optimize the pervaporation process in term of selectivity or total flux. Moreover, further efforts should be devoted to the investigation of fouling problems and design of new membrane bioreactors to meet the needs of the industrial sector.

Table 1. Summary of studies about the effect of different operating conditions on pervaporation separation membrane using different membrane materials.

| Membrane Materials | Feedstock | Operating Conditions | Separation Factor | Total Flux (Kg/m ² h) | Ref |
|------------------------|--------------------|--------------------------------------|-------------------|----------------------------------|------|
| Cellulose acetate/PVA | Sorghum juice | 50 °C, 50.8 mm Hg, 14.8 wt%, NA | 6.6 | 2.7 | [40] |
| PDMS | Barley straw | 30 °C, 15 mm Hg, 15 wt%, 950 g/min | 4.2 | 0.567 | [41] |
| PDMS | Willow wood chips | 30 °C, 15 mm Hg, 15 wt%, 950 g/min | 4.8 | 0.498 | [41] |
| PDMS | Banana waste | 25 °C, 19.5 mm Hg, 3.8 wt%, 19.8 L/h | 10.36 | 0.001 | [42] |
| PDMS/silicalite | Lignocellulosic | 40 °C, 1.05 mm Hg, 5 wt%, 1.5 L/min | 11.6 | 0.291 | [43] |
| PDMS | Glucose | 40 °C, 5 mm Hg, 4.7 wt%, 1.8 L/min | 9.0 | 0.049 | [44] |
| PDMS | Newspaper waste | 40 °C, 5 mm Hg, 4 wt%, 1.8 L/min | 7.9 | 0.050 | [44] |
| Silicalite /PDMS /PVDF | Sweet sorghum stem | 30 °C, 0.75 mm Hg, 11%, 1.5 L/min | 9.8 | 0.395 | [45] |

2.2. Gas Stripping

Gas stripping is one among the separation techniques to remove components by the dissolution of the mixture into a gas passing through the fermentation broth. In this process, anaerobic gas such as the carbon dioxide or nitrogen is recycled through the bioreactor and evaporates the bioethanol which will be recovered from the gas stream via a condenser (Figure 3).

**Figure 3.** Schematic of integrated in situ extraction-gas stripping process.

As it does not require complex equipment and does not need any plant modifications, gas stripping can be considered a simple process [46], requiring minimal investment costs and providing no harm to the culture [47]. During the integration of gas stripping process and fermentation process, the increase in stripping factor leads to an increase in cell concentration, substrate consumption, an improvement in ethanol productivity, and limitation of ethanol inhibitory effect [48].

Air, CO₂, technical N₂ and pure N₂ are the most commonly used stripping gases. Zhang et al. [49] reported that different stripping gases had different effects on cell growth as well as ethanol and glycerol production in Gas Stripping Ethanol Fermentation (GSEF). Aeration stimulated cell growth and glycerol production, and maintained cell count and viability, but decreased ethanol productivity. CO₂ appeared to be inhibitory to yeast growth and decreased overall glycerol production. 99.5%~99.8% N₂ was verified to be the preferable type of gas in gas stripping ethanol fermentation (GSEF) where the ethanol and glycerol productivity increased by about two times than that of the control. Besides the nature of the gas, other operating conditions have been reported to affect gas stripping performance, such as feed temperature, stripping gas temperature, specific stripping gas flow rate, and liquid height-to-column diameter ratio (h/D) [50]. Despite its advantages, gas stripping technology has not received significant interest and has only been reported in a limited number of studies summarized in Table 2.

Table 2. Summary of studies about the fermentation-gas stripping coupled system.

| Stripping Gas | Aim of the Study | Findings | Ref |
|--------------------------|---|---|------|
| Carbon dioxide | Integration of continuous fermentation and stripping of ethanol | Biomass yield was lower than in a simple continuous fermentor 150 days of operation without contamination. | [51] |
| Carbon dioxide | Effects of ethanol concentration and stripping temperature on continuous fermentation rate. | Fermentation rate was linearly related to the ethanol concentration and stripping temperature. | [52] |
| Carbon dioxide | Optimization of Fed-Batch fermentation coupled with gas stripping | Integration of gas stripping increased ethanol production by 65%. Fermentation using high sucrose concentration (up to 428.6 g L ⁻¹) was usefully achieved with ethanol removal. | [53] |
| Nitrogen | Continuous ethanol fermentation of pretreated lignocellulosic biomasses with gas stripping | The yield was 0.47–0.49 g/g close to maximum theoretical yield with 1.2–2.7 g/L/h volumetric ethanol productivity and 90–99% sugar conversion. | [54] |
| Carbon dioxide | Extractive batch fermentation with CO ₂ stripping for ethanol production | Optimal conditions for ethanol stripping was 2.0 vvm of CO ₂ flow rate and 34 °C of feed temperature. 25% higher productivity was obtained after 3 hours of stripping. | [55] |
| Carbon dioxide | Enhancing sweet sorghum state fermentation by gas stripping | Optimal conditions were 10 h of gas stripping time, 35 °C gas stripping temperature, 28 h of fermentation, and 0.15 cm particle thickness of GS-SSF. 6% to 10% increase of ethanol yield with gas stripping. | [56] |
| Carbon dioxide | Sugarcane molasses fermentation with in situ gas stripping | Ethanol concentration was kept below the threshold of toxicity (<60 g/L). A mathematical model was developed to describe the system. | [57] |
| Nitrogen, Carbon dioxide | Optimization of alcohol recovery from fermentation broth with gas stripping | 60 L·min ⁻¹ flow rate and 10 wt% ethanol concentration were the optimal conditions for efficient recovery Carbon dioxide stripping did not show recovery potential at low ethanol concentrations. | [58] |

2.3. Vacuum Fermentation

This technique was first developed by Cysewski and Wilke [59] to limit ethanol inhibitory effect during the fermentation process. They proved that quick and complete fermentation was achieved using concentrated sugar mediums by maintaining the bioreactor under vacuum conditions. During the vacuum fermentation process, the bioethanol is continuously recovered from the fermentation broth by application of vacuum pressure under the fermenter, so that ethanol may evaporate at the fermentation temperature and is subsequently condensed using condensation cooling system or chilling water. During the vacuum fermentation system (Figure 4), ethanol concentration can be controlled at low levels which limits or minimizes the inhibition effect of ethanol on the yeast metabolism and the fermentation process [60].

Several studies have highlighted the potential of vacuum fermentation as an efficient alternative technique for continuous ethanol recovery. Generally, the theory of vacuum fermentation process mainly depends on the physical properties of the broth and biochemical properties of fermentation reaction and the nature of the used yeast strain. The alcoholic fermentation of sugars using the yeast is commonly carried out at a temperature of 30 to 35 °C and the mixture of ethanol-water boils at 78.3 to 100 °C [61]. During the vacuum fermentation process, the boiling point temperature of this mixture decreases to a point in the range of fermentation temperature. However, this integration approach implies some practical limitations such as the requirements of high energy to maintain the vacuum and the need to high working volumes of bioreactors. Over the past 40 years, the number of studies highlighting the vacuum fermentation is still scarce; further efforts are needed for the optimization of this process to upgrade this technique. The following table (Table 3) reviews these works.

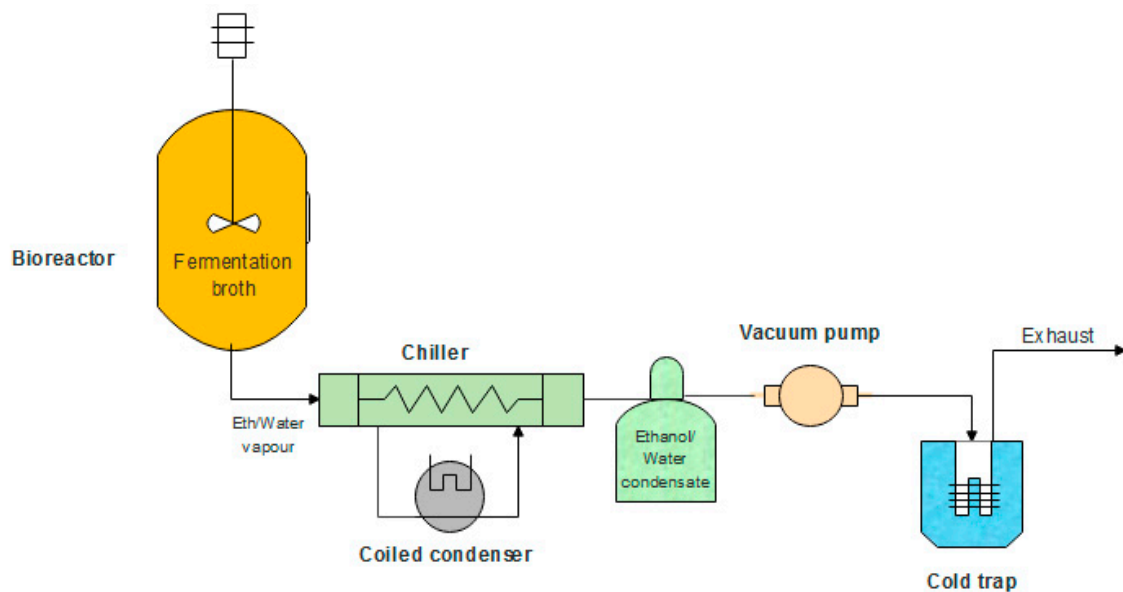


Figure 4. Setup of fermentation process coupled with the vacuum stripping system for ethanol recovery.

Table 3. Review of studies about ethanol removal using vacuum fermentation (C: Substrate concentration, P: vacuum pressure, T: temperature).

| Parameters | Aim of the Study | Findings | Ref |
|--|---|--|------|
| Glucose C = 250 g/L P = 47–760 mm Hg, T = 33 °C | Effect of vacuum pressure on ethanol fermentation | 33.2 wt% ethanol condensate was collected at the outlet. A model to predict the kinetic parameters for the fermentation under the vacuum was developed. | [61] |
| Glucose C = 100 g/L P = 65–700 mm Hg, T = 30 °C | Effect of pressure and glucose concentration in ethanol fermentation | Vacuum condition can increase yeast growth and ethanol productivity. The optimal pressure was 36.6 mmHg. | [62] |
| Glucose C = 25 g/L P = 48.75 mm Hg T = 35 °C | Investigation of extractive fermentation by using a vacuum fractionation technique | High substrate utilization rate was obtained at 26.6 g/L h. Ethanol production increased more than 8-fold higher compared to batch fermentation. | [63] |
| Corn C = 450 g/L P = 711.2 mm Hg T = 32 °C | Effects of vacuum application on improving ethanol yield during high solids fermentation | 30% increase in ethanol yield after vacuum application. | [64] |
| Rice straw C = 100 g/L P = 80 mm Hg T = 40 °C | Effect vacuum cycling on simultaneous saccharification and fermentation (SSF) for ethanol production | Increase with 4 folds in the ethanol productivity in SSF after using vacuum cycling. | [65] |
| Cassava root C = 100 g/L P = 80 mm Hg T = 40 °C | Integration of vacuum fractionation technique in extractive fermentation from ethanol production from fresh cassava roots | The recovered ethanol concentration was around 86 wt%. The concentration of ethanol in the broth was kept below 2 wt%. | [66] |
| Sweet sorghum C = 0–600 g/L P = 48.75 mm Hg T = 35 °C | Optimization of vacuum fermentation and techno-economic assessment | 80 wt% ethanol concentration was continuously removed. Low production cost with time saving compared to the conventional fermentation. | [67] |

2.4. Adsorption

It is an innovative ethanol recovery technique from fermentation broth using a porous adsorbent. The pore size of such adsorbent is similar to the molecular size of ethanol. In this separation technique, the fermentation broth passes through a bed packed with the adsorbent, and the effluent is recycled again to the fermentation broth. This technique usually involves two steps: adsorption followed by desorption to recover a concentrated ethanol solution and regenerate the adsorbent (Figure 5) [68].

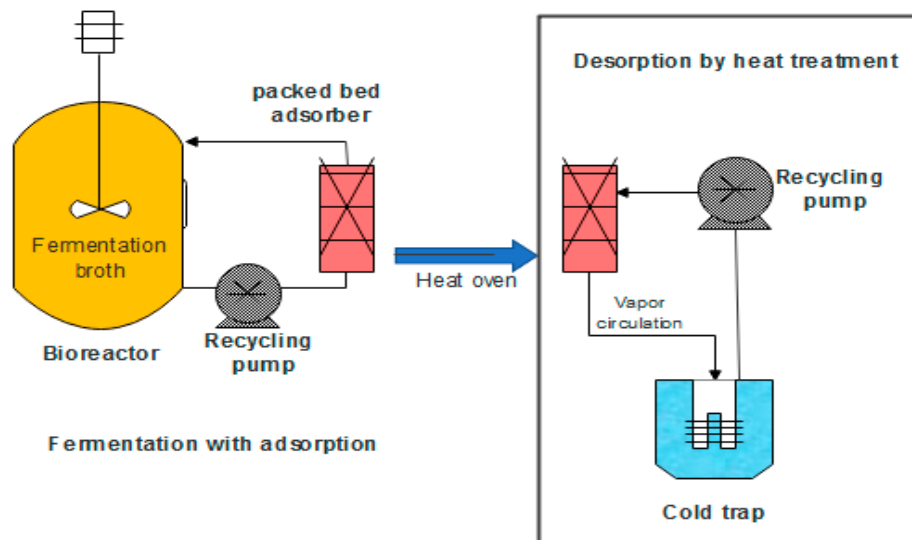


Figure 5. Diagram of the continuous fermentation with adsorption unit for ethanol separation.

Some criteria must be taken into consideration to select the suitable adsorbent material for this process: (a) Selectivity: The sorbent has very high adsorption selectivity of ethanol compared to the water and glucose adsorption. (b) Desorption: the ethanol desorption must take place at low temperatures or, otherwise, the adsorption would be weak. (c) The adsorption/desorption: the equilibrium between adsorption and desorption must be reached fairly quickly so as to minimise the contact time requirements with the desorption gas or with the fermentation broth [69]. In 1983, Walsh et al. [70] tested one type of activated carbon (Filtrisorb F-200) as adsorbent and showed a good performance to separate ethanol from the 6 mol% ethanol-water solution. Motivated by this work, several adsorbent materials have been investigated whereas the activated carbon (AC), zeolites ($\text{SiO}_2/\text{Al}_2\text{O}_3$) and ion-exchange resins have been the widely studied types of adsorbents for bioethanol adsorption.

Activated carbon is the most commonly used ethanol adsorbent. Hashi et al. [71] compared four activated carbon adsorbents (Sorbonorit B4, Filtrisorb 200, WV-B 1500 and Nuchar RGC 40) and two hydrophobic ZSM-5-type zeolites (HiSiv 3000 and CBV 8014), it was found that activated WV-B 1500 has the highest ability to adsorb ethanol, and activated carbons showed higher ethanol adsorption ability than the two zeolites. Despite different types of adsorbents has been reported as a potential adsorbent for ethanol recovery, the majority of the reported works used ethanol/water, ethanol/glucose or ABE mixture models during the investigation [72–79]. These studies could prove the ethanol adsorption had great potential; however, it did not show the selectivity to ethanol among other byproducts or carbon sources. Adsorption affinity of any molecule does not confirm its suitability to be integrated into the fermentation process unless it showed good ethanol selectivity among the other components of fermentation broth. Among the limited studies investigated the integration of adsorption and fermentation process, a study conducted by Jones et al. [80] which has reported that the addition of F-600 activated carbon during the alcoholic fermentation for in-situ ethanol adsorption showed an increase in ethanol production achieving 45 g/L compared to 28 g/L in the control. After

3 cycles, 80% increase in ethanol production was observed when compared to the control over a period of 180 h.

Seo et al. [81] have investigated the adsorption capacity of molecular-sieving carbon (MSC) in pilot scale for bioethanol production, the ethanol adsorption was (0.163 g g^{-1}). It was clear that both initial ethanol concentration and adsorption temperature have a significant effect during the adsorption stage.

2.5. Solvent Extraction

An alternative system is proposed by Minier & Coma [82] which combines alcoholic fermentation and a separation unit operating via solvent extraction process. This technique involves both plug flow reactor and liquid-liquid extraction to extract continuously the ethanol from the fermentation broth. During the liquid-liquid extraction process, the fermentation broth is recycled through an extraction unit to be in mass-transfer contact with the extraction solvent, the concentrated product will be recovered and both fermentation broth and solvent are transferred to the fermenter, as presented schematically in Figure 6.

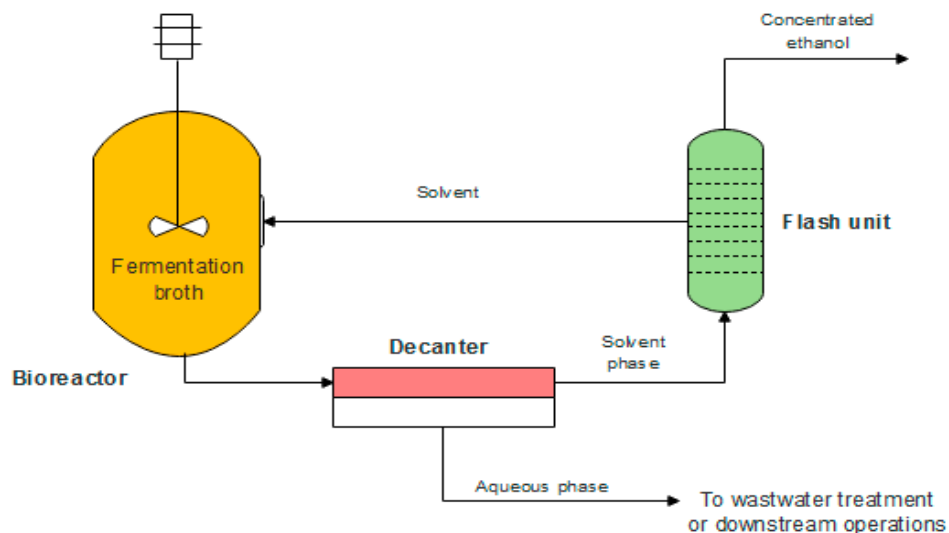


Figure 6. Simplified schema of the alcoholic fermentation process coupled with ethanol recovery system using solvent extraction.

The contact between the fermentation broth and the extractant solvent can be direct, assured by a mixing device or alternatively using a packed-column contactor, or can be indirect, commonly via a non-wetted porous membrane for the separation of the two liquids. To reuse the extractant solvent, the absorbed components must be collected in a regeneration unit [14]. Ethanol removal in situ by the integration of solvent extraction process offers numerous advantages such as increasing the fermentation rate, possibility of fermentation at high substrate concentration, saving water consumption, etc. [83].

It was reported by Offeman et al. [17] that the conditions for a successful liquid-extraction of ethanol from fermentation broth are as follows: (1) a great separation factor of ethanol (2) a high ability of ethanol absorption to reduce the extractant solvent use, (3) a low solvent solubility in the water to avoid the solvent losses, (4) existence difference in density between the aqueous phase and organic phase to ease fast separation, (5) chemical stability, and (6) an effective technique for ethanol recovery and recycle the extractant solvent, (7) the solvent should not have a toxic or inhibitory effect on the yeast growth and metabolism. Kollerup and Daugulis [84] have systematically screened around 1500 solvents to test for their extraction ability to be used for ethanol extraction from the aqueous phase. Sixty-two solvents which have shown extraction ability, have been experimentally tested with yeast cultures to assess their biocompatibility, phase stability, and distribution coefficients. Fifteen of the tested solvents have been found to be fully biocompatible, meanwhile, 26 solvents have shown

complete toxicity, the remaining solvents have different degrees of inhibition. Solvent extractive fermentation has been studied however there is a clear lack of recent studies indicating a low interest in this method. Only a few studies investigated this technique between 1980–1990, and the summary is shown in Table 4.

Table 4. Summary of studies about ethanol recovery from the fermentation broth using solvent extraction (C: substrate concentration, P: vacuum pressure, T: temperature).

| Parameters | Solvents | Findings | Ref |
|---|---|--|------|
| <i>S.cerevisiae</i> Glucose C = 100 g/L T = 30 °C | 25 solvents (alcohols and esters) | Most of these solvents were toxic to the ethanol-producing microorganism. Immobilizing the cells using Porapak Q showed effective protection against solvent toxicity. | [85] |
| <i>S.cerevisiae</i> Glucose C = 407 g/L T = 35 °C | Dodecanol | Ethanol productivity was 5 fold higher than the productivity achieved in conventional fermentation. | [82] |
| <i>C.thermohydrosulfuricum</i> NA C = NA T = 65 °C | Hexadecane, isooctane, kerosene, oleyl alcohol, Shellsol TD | With excepting the kerosene, all solvents showed high ethanol separation from the aqueous phase. Oleyl alcohol showed the maximum partition coefficient for ethanol ($K_D = 0.34$). Both solvents have shown high partition coefficients for ethanol but they have heavy toxicity. | [86] |
| <i>S.cerevisiae</i> Glucose C = 100 g/L T = 30 °C | O-isopropylphenol (OIPP) O-tert-butylphenol (OTBP) | Immobilizing of the yeast cells using alginate gel together limit the toxicity of both solvents. | [87] |
| <i>S. bayanus</i> Glucose C = 300 g/L T = 35 °C | Valeric, Hexanoic, Octanoic, Oleic | Oleic was the best selective solvent. Immobilizing the cells using k-carrageenan essentially was protective against solvent toxicity. The highest productivity was 1.39 g/L/h at 5:1 oleic acid fermentation medium ratio. | [88] |

3. Economic Comparison Between the Different Ethanol Recovery Techniques

Efficient recovery technique of ethanol from the fermentation broth is commonly a tradeoff between the recovery rate, costs and system longevity [58]. In terms of costs, an alternative technique for ethanol recovery should be economically competitive to be integrated in the industrial scale. Vane [14] have carried a technical economic analysis for different ethanol recovery techniques based on energy consumption. During ethanol production, operating costs are dependent on the assumptions made about the feedstock costs, enzyme costs, and the kind of pretreatment to be employed. Therefore, it is not sufficient to simply conduct a comparison in term of energy consumption only. Thus, more factors as the capital and the operating costs must also be included for reliable comparison.

Moreover, the difference in feedstock nature and operating conditions (ethanol concentration, temperature, pressure, etc.) lead to complexity of comparison between the economic costs per product unit in the same technique itself and between the other techniques. Figure 7 represents an average production cost of ethanol in pilot scale from previous studies for pervaporation [40], vacuum fermentation [67], and distillation [89], however, no data is available for the other techniques. For efficient techno-economic analysis to compare these techniques, it is recommended to conduct a study taking all the costs into account and under similar operating conditions.

It is clear that the alternative techniques including pervaporation and vacuum fermentation seem more economically viable with 0.9 USD/litre and 0.7 USD/Liter respectively compared to 1.41 USD/Liter. On the other hand, these costs still appear to be too high with regard to the price of ethanol on the

market. These high costs are mainly a result of the application of these techniques only in the small scale. It is expected that the application of these techniques at a large scale may reduce the costs of bioethanol production and can, therefore, promote the ethanol industry as an alternative to fossil fuel.

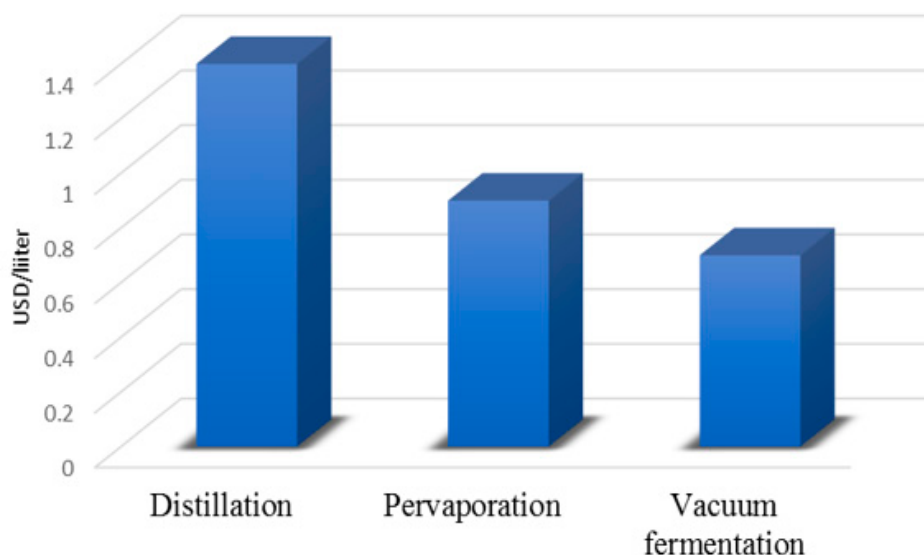


Figure 7. Evaluation of ethanol production costs using different recovery techniques.

4. Conclusions and Future Trends

Ethanol purification is a critical process during bioethanol production. In the industry, purification is mainly done by distillation. Distillation is still an effective and favourable separation technique for the bioethanol industry due to several advantages such as the high separation capacity of ethanol and the simplicity of application. However, other alternative techniques have been optimized for ethanol recovery which are with more energy- and cost-efficient, such as pervaporation, adsorption, and gas stripping, vacuum fermentation. Thus far, the alternative methods have been successfully used for ethanol recovery in laboratory scale but have not yet met the same acceptance in the industrial scale. Despite that these alternative techniques are less energy consuming but the integration of these techniques large may imply some technical problems such as maintenance requirements, high sensitivity, and the need for qualified labour which is not really needed for distillation. For the pervaporation technique, the fouling is the most challenging problem hindering the wide application of this method. However, some innovative solutions as rotary membrane module and preparation of new antifouling membranes and reduction of membrane fouling by injection of the air jet are under development to overcome these issues [90,91]. The integration of fully unconventional techniques in bioethanol as an alternative to distillation seems too far but hybrid systems combining distillation with unconventional techniques have currently received more attention. A hybrid integrated system termed Membrane Assisted Vapor Stripping (MAVS), coupling the vapour stripping, vapour compression, and vapour permeation membrane separation was evaluated by Vane [92] for the recovery and dehydration of ethanol from ethanol/water mixture as an alternative to the conventional distillation processes. The results showed that MAVS system had the ability to save more than 50% of the energy consumed during the conventional distillation. In another work, Kunnakorn et al. [93] conducted a techno-economic comparison between hybrid system (distillation followed by pervaporation process) and azeotropic distillation which showed that the hybrid system was more efficient in term of purification ability with 99.4 wt% of ethanol recovered and it was low energy consuming with 52.4% less energy compared to the azeotropic distillation.

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