An Overview on the Bioethanol Production using Membrane Technologies

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Abstract: Membrane process is a novel effective technology that can improve the efficiency of a bio-refinery plant. In this study, an overview of the main subjects dealing with the coupling between bioethanol production plant and membrane process is presented as a new technology. Nowadays, several methods to improve existing processes in industrial environments are studied. For example, methods such as flow back to increase the efficiency and the use of more advanced devices has always been a goal of managers. However, using of membranes and membrane processes can be very efficient and includes a lot of advantages. Indeed, a bio-refinery is one of the suitable choices that can apply membrane technology to improve the conditions for the biofuel production. To achieve these goals and advantages being aware of their useful parts is necessary. Frequently, by helping a bio-refinery, sugar is changed into ethanol in one step using yeast during the fermentation process. Moreover, needed sugars are often provided by Biological sources or starch, cellulose and lignocellulosic materials. Hence, by changing the type of feedstock, the steps to achieve the product can be different in the agenda. Therefore, the improvements by the introduction of membranes in the bioethanol production process are discussed, in terms of efficiency and final product purity.

Keywords: Membrane technolgy, Bioethanol production, Biomass feedstock.

1. INTRODUCTION

In recent decades, the world's present economy is highly dependent on various fossil energy sources such as, oil, coal, natural gas, etc. These sources can be used for the production of fuel, electricity and other goods. As our best knowledge, the primary energy supply differs greatly in the worldwide, and hydrocarbons consider our main means of storing energy, but fossil energy sources are non-renewable. However, most of the renewable energy sources (*e.g.* hydroelectric, solar, wind, tidal, geothermal) aim to the electricity market, while fuels make up a much larger part of the global energy demand (~66%) [1, 2]. Indeed, the term renewable energy describes very diverse energy sectors, grouped in old and new renewable energy technologies,—including hydrothermal and geothermal energy productions techniques, and energy production using wind, solar and biomass, respectively [3]. By the way, biofuels as desirable renewable sources are rapidly being developed. It is clear that, increasing oil prices (in particular in the past few years), environmental awareness, relatively low cost of plant material, and the development of biorefineries cause mankind for a historic transition into a sustainable society in which biological feedstock, processes and products play important roles in–the economy.

Generally, a biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. It stands the variety of possible products from the biorefinery, liquid transportation fuels in the form of ethanol (or what is now referred to as bioethanol) are rapidly gaining significance [4]. As author knowledge, ethanol can be produced chemically (by hydration of ethylene) and by fermentation of sugar-containing feeds (starchy feed materials or lignocellulosic materials = in biorefinery) [5]. However, ethanol as one of the most well-known oxygen-containing organic materials has a wide variety of applications, for example in medical applications, such as sterilization of medical instruments, dressings, directly in the formulation of some drugs and non-medical costs, as additives to fuel motor vehicles, production of vinegar, a variety of solvents, paints and other fields [6].

Additionally, bioethanol is likely a prominent product for future biorefineries; there has been an increasing interest in biomass derived ethanol due to the rapid increase in the crude oil price and the intensity of the global demand for petroleum [6].

Bioethanol has two important advantages; renewable and environmentally friendly [6,7]. It is found that bioethanol can be mixed with gasoline in various

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proportions or used as neat alcohol in dedicated engines, due to the higher octane number and higher heat of vaporization [9]. Also, it is a desirable fuel for future advanced flexi fuel hybrid vehicles. Moreover, the bioethanol is an oxygenated fuel containing 35% oxygen, leading to the reduction of particulate and nitrate oxides (NO_x) emissions from combustion; in addition, it is biodegradable and contributes to sustainability [10]. However, discussions of alternative fuels and advanced technologies for transportation often oversee the essential infrastructure to make them practical and cost effective [11].

Nowadays, one of the main problems to the large scale industrial use of biobased products and biofuels is the lack of cost effective separation methods for the isolation and purification of biobased chemicals and fuels [12]. At present, the separation operations account for 60–80% of the processing costs of most mature chemical processes [13].

Using the crude oil is problematic for biorefinery evolution, since all countries can simply employ the crude oil to produce fuel and oil derivatives. On the other hand, by population growing and subsequently high demand of crude oil sources as non-renewable oil sources, prices are also increased. Therefore, finding an alternative for producing fuel and chemically derived materials is inevitable. It seems that bio-refinery has this potential, but economical design is an important parameter for any industry. As a consequence, using the new cost effective technologies is the most important way to achieve this purpose. According to literatures, membrane technology is one the newest alternative technology which currently is used instead of conventional separation processes. Many countries around the world are seriously considering the implications of a shift toward bioethanol economy helping the membrane technology. The growing interest in bioethanol production is driven mainly by its potential to solve two major challenges confronting with many of the world's economies, how to achieve energy independence, while minimizing the environmental impact of economic activity. In the other hand, according to membrane separation method advantages, it was seen that membranes can be used in biorefinery and improve its performance. Hence, some of the advantages of membrane separation with respect to other methods can be considered as:

- -Simplicity: no need to add chemicals or regenerate a solvent with membranes.
- Low capital costs.
- Compact design.
- Avoidance of operational problems associated with absorption, such as, foaming, flooding, entrainment and channelling.
- Columns with a lower number of separating stages running with lower reflux ratio can be applied in newly constructed bioethanol plants using membrane drying.
- An existing rectification unit can be operated with a higher throughput after retrofitting a membrane drying unit.
- The membrane drying unit can be operated directly coupled with the rectification in vapour permeation
- After the energetic optimization of the whole ethanol production process the energy demand for ethanol drying can be reduced by up to 90 % with compared to conventional techniques [14].

Therefore, the main purpose of this study is the presenting of an overview about membrane technology applications in bioethanol production.

2. FEEDSTOCKS FOR BIOETHANOL PRODUCTION

Based on feedstock type, bioethanol can be produced via two methods,—starch feedstock and cellulosic-lignocellulosic method. Each of these methods has included advantages and challenges that the whole process will affect.

Maize seeds and sugar cane stems currently are considered as the main sources of starch and sugars for bioethanol production Other crops used on a large scale, include cassava roots and wheat seeds for starch, and sugar beet roots for sugar. The simplest way for bioethanol production is conversion of glucose to ethanol by adding yeast in a fermenter. The starch can also produce feed of fermented; due to the existing glucose in its structure. Recently, two different concepts for the starch-based bioethanol production are realised on industrial scale: (1) separate hydrolysis and fermentation (SHF) and (2) simultaneous hydrolysis and fermentation (SFF). In SHF, enzymes are added for the hydrolysis step and the yeast in two steps, but in SFF, both enzymes and yeasts are added simultaneously. The main advantage of SHF is that the two steps, hydrolysis and fermentation, can be optimized independently, while SFF overcomes product inhibitions more effectively and hence leads to a higher yield. It should be noted that SFF is the more common concept [15].

Sugars, glucose (C6) or biomasses containing higher levels of glucose are the most common sugars and the easiest to convert to ethanol using fermentation process. Moreover, many microorganisms like fungi, bacteria, and yeast can be used for fermentation of sugars, also Saccharomyces cerevisiae known as Bakers yeast is frequently used to ferment sugar to ethanol (Eq. 1 [16]). Sugar cane is a common example for sugar feedstock [17].

$$C_6H_{12}O_6 \rightarrow C_2H_5OH + 2\,CO_2 \quad (1)$$

Starch is another feedstock which is available abundantly, made up of long chains of glucose molecules, which can be fragmented into simple sugars before fermentation to produce ethanol. The starch biomass feedstocks are including tubers like sweet potato, potato, cassava and cereal grains, etc. Starchy feedstocks undergo hydrolysis to breakdown into fermentable sugars *i.e.*, saccharification. The hydrolysis of starch can be carried out by mixing water with the feedstocks to form slurry, then heated to rupture of cell walls and finally different specific enzymes are added during hydrolysis to break chemical bonds present in the starch materials [17]. The wet milling process also produces high-value co products, such as fiber, germ and gluten via pre-processing before the fermentation to ethanol, thus it is more capital and energy intensive [18]. Moreover, the conventional dry mill consists of grinding, cooking, liquefaction, saccharification of the starch to sugars by enzymes, fermentation of the sugars to ethanol through yeast and in the following by distillation and dehydration processes of ethanol [19].

The hydrolysis process breaks down the cellulosic part of the biomass or corn into sugar solutions that can then be fermented into ethanol. In the process, yeast is added to the solution, and then heated. Thereby, the yeast contains an enzyme called invertase, acts as a catalyst and helps to convert the sucrose sugars into glucose and fructose as the following equation. As a general consequence, it should be noted that 1 kg glucose produces 0.511 kg ethanol [16, 17].

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6 \quad (2)$$

In general, the fermentation process takes around three days to complete and is carried out at a temperature of 250 to 300 °C [17]. By the way, a simplified process flow diagram of combined sugar and ethanol production from sugar beets is shown in Figure **1** [20].

Furthermore, Lignocellulosic biomass consists of three main polymers: cellulose, hemicellulose and lignin. Before fermentation, the biomass should be hydrolysed to release sugars from the polymeric matrix. Different processes have been developed to hydrolyse hemicellulosic sugars from lignocellulosic materials. Therefore, dilute sulphuric acid pre-treatment is frequently used, because it is effective at producing xylose-rich hemicelluloses hydrolysate liquor, while enhancing cellulose enzymatic digestibility [21].

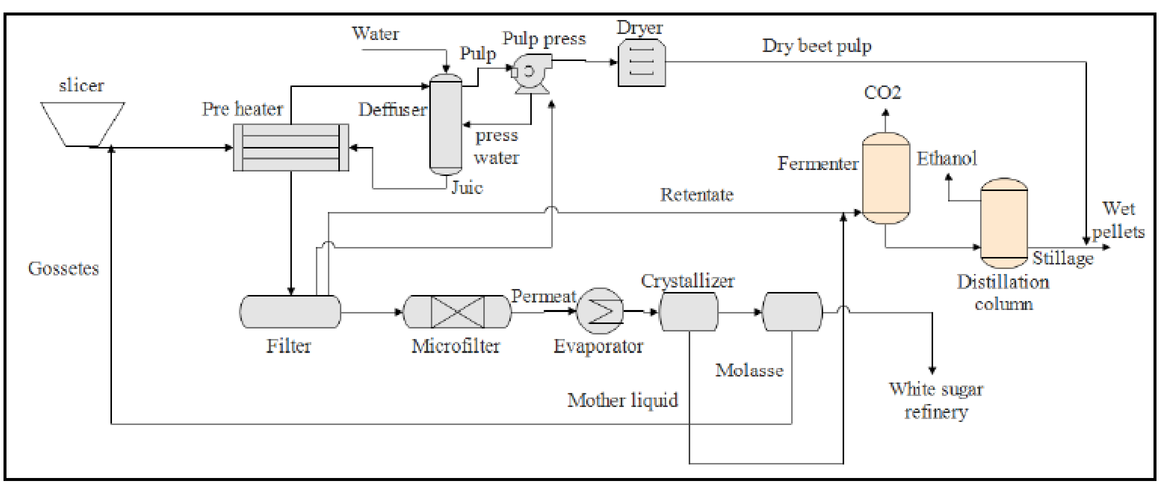

Figure 1: Simplified process flow diagram of combined sugar and ethanol production from sugar beets [20].

Since sugar and starchy materials are expensive and can interfere in human food chain through diverting them to transport fuel production, they are not suggested. Thus, alternative cellulosic materials are better option to solve these problems [22]. Some examples of cellulosic feedstocks are agricultural residues like stalks, leaves and husks of food crops and forestry wastes such as sawdust and chips from timber mills, dead trees, tree branches and etc. [17].

Cellulose molecules consist of long chains of glucose molecules like starch molecules, while have a different structural configurations. In addition to these structural characteristics, the encapsulation by lignin makes cellulosic materials more difficult to hydrolyze than starchy materials [17]. However, technologies for conversion of these feedstocks to ethanol have been developed on two platforms, referred to as the sugar platform and the synthesis gas (or syngas) platform as exposed in Figure **2** [20].

The purpose of pre-treatment is to remove lignin and hemicellulose, to reduce cellulose crystallinity, and to increase the porosity of the materials. Indeed, pre-treatment must meet the following requirements: (1) improve the formation of sugars or the ability to form sugars by hydrolysis; (2) avoid the degradation or loss of carbohydrate; (3) avoid the formation of by-products inhibitory to the subsequent hydrolysis and fermentation processes; and (4) be cost-effective. In the meanwhile, physical, physico-chemical, chemical, and biological processes have been used for pre-treatment of lignocellulosic materials [23].

2.1. Membrane Performance in Starch Feedstock Bioethanol Production

Frank Lipnizki *et al*. [15] investigated performance of membranes in the bioethanol production with starchy feedstock. The performance of membranes in

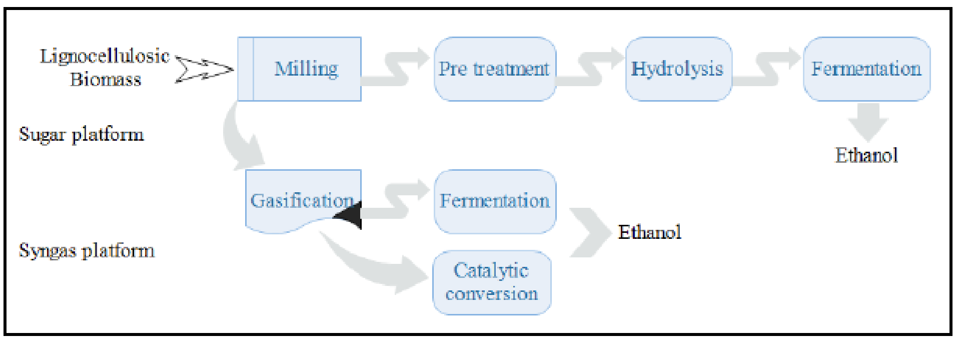

Figure 2: Basic concept of ethanol production from lignocellulosic feedstocks [20].

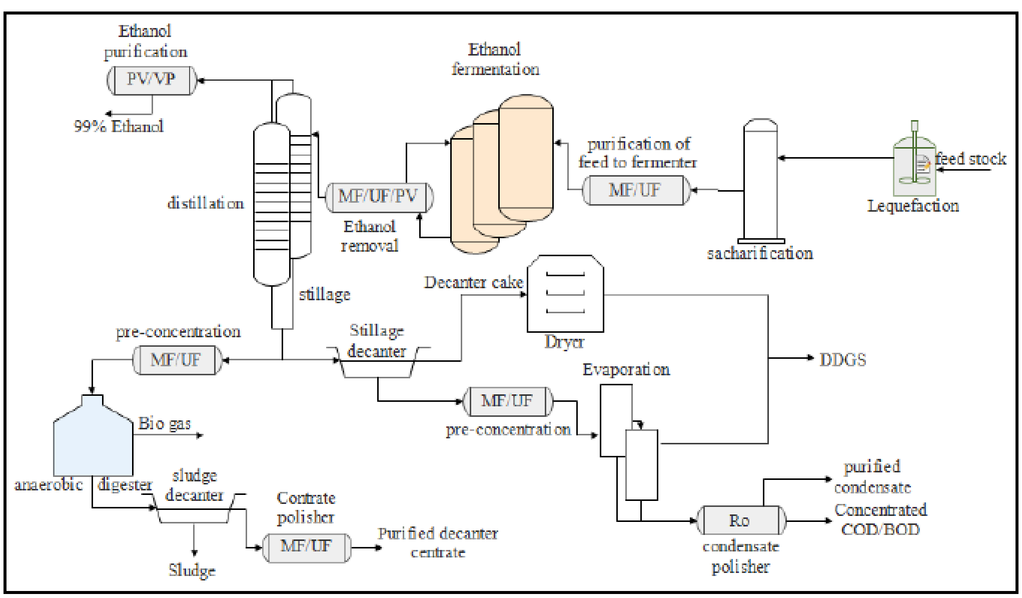

Figure 3: A schematic of SHF process for starch-based bioethanol production with potential membrane applications [15].

bioethanol production is extensive as presented in Figure **3**.

First role of membrane is pre-treatment of fermenter feed and the elimination of product from fermenter to prevent the inhibitory effect of product is another one. It should be noted that, waste water and stillage is a problem, threating the environment. Therefore, membranes play an important role in improving the wastes. Consequently, the purity of final product is one of the most significant parameter that is very difficult to achieve due to the formation of water-alcohol azeotrope, but membranes can be suitable options to improve this problem.

2.2. Membrane Performance in Cellulosic and Lingo-Cellulosic Feedstock

The main limitation of these methods is necessity of harsh conditions for breaking polymeric systems. Unfortunately, this condition can be lead to a batch production of materials named inhibitors, which can decrease the activity of yeast. These inhibitors can be divided into three major groups (Figure **4**): organic acids (acetic, formic and levulinic acids), Furan derivatives [furfural and 5- hydroxymethylfurfural (5-HMF)] and Phenolic compounds, affecting overall cell physiology and often result in decreased viability, ethanol yield, and productivity [24]. Indeed, the depolymerisation of hemicellulose by chemical process yields xylose as the major fraction and arabinose, mannose, galactose, and glucose in smaller fractions in addition to potential microbial inhibitor.

By the way, Frank Lipnizki *et al*. [15] investigated performance of membranes in production of bioethanol with cellulosic and lingo-cellulosic feedstock**.** The performance of membrane for this type of feedstock is similar to starchy sources. The only difference between these two methods is inhibitors that are produced in harsh condition of hydrolysis [15]. Performance of membranes in bioethanol production using cellulosic and lingo-cellulosic feedstock is shown in Figure **5**.

3. APLICATIONS OF MEMBRANE TECHNOLOGY IN BIOETHANOL PRODUCTION

Different membrane techniques can be used in biorefinery, since they have suitable potential to improve the process. Some of membrane performance methods have been mentioned briefly in Table **1**. According to the application types, different membrane

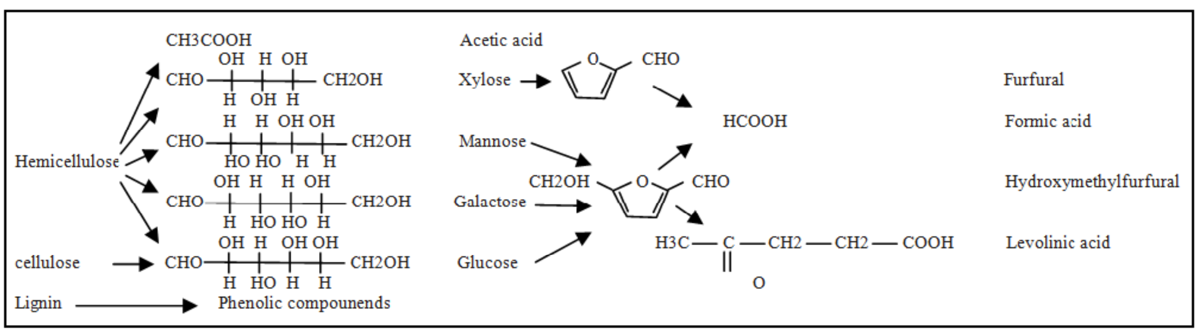

Figure 4: Structural profile of lignocellulose derived fermentation inhibitors [24].

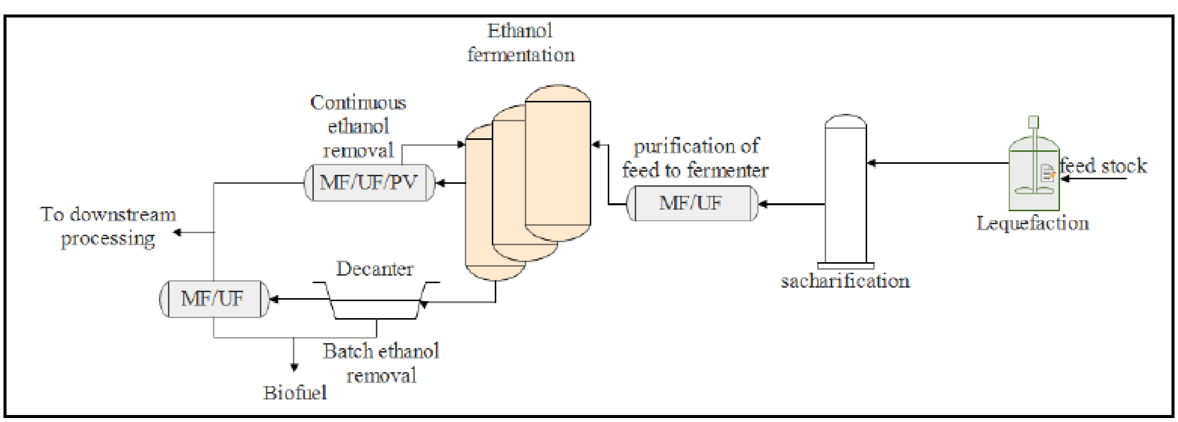

Figure5: Simplified front-end of a cellulosic-based bioethanol production with potential membrane applications [15].

Table 1: Membrane Separation Applications [25]

Application	Membrane Types
Upstream from the fermentation process	
Clarification or fractionation of feed stock material going to the fermenter	Ultrafiltration, Microfiltration
Protein recovery/removal from hydrolyzed prepared biomass	Ultrafiltration
Acid and alkali recovery and reuse Separation of lignin from hydrolyzed biomass	Ultrafiltration, Nanofiltration
Concentration of sugars to enable product yield enhancement in the fermentation process	Nanofiltration
Continuous enzyme reactors retain enzyme and substrate, permitting removal of reaction-inhibiting components	Ultrafiltration, Nanofltration
Downstream from the fermentation process	
Biomass/microbial cell retention that enables continuous recovery of the target product component or removal of fermentation inhibitor molecules	Ultrafiltration, Nanofiltration
Concentration of organic acids with water recovery for reuse	Reverse osmosis
Amino acid concentration and desalting	Nanofiltration
Evaporator condensate treatment for water recovery and reuse enabling environmental compliance	Reverse osmosis
Treatment of downstream from fermentation process	pervaporation

processes can be presented. Therefore, various membranes technology processes applied for bioethanol production is discussed in the following.

3.1. Ion Exchange Membrane

Traditionally, ion exchange membranes are classified into anion exchange membranes and cation exchange membranes depending on the type of ionic groups attached to the membrane matrix. Cation exchange membranes contains negative charged groups, such as $–SO^{-}$, $–COO^{-}$, $–PO_3{}^{2-}$, $–PO_3H^{-}$, $–C_6H_4O^{-}$, etc., fixed to the membrane backbone allowing the passage of cations, and rejecting anions. While anion exchange membranes contains positive charged groups, such as $–NH_3{}^{+}$, $–NRH_2{}^{+}$, $–NR_2H^{+}$, $–NR_3{}^{+}$, $–PR_3{}^{+}$, $–SR_2{}^{+}$, etc., fixed to the membrane backbone which allow the passage of anions and reject cations [23,24].

Polymers can be used for fabrication of ion exchange membrane, therefore, an ion exchange membrane can also be prepared from inorganic material, such as zeolites, betonite or phosphate salts [25-27]. Till now, various ion exchange membranes including bipolar membranes (ion exchange composite membranes), inorganic–organic (hybrid), amphoteric, and mosaic ion exchange membranes–are available [12].

Ion exchange membranes are beneficial for improving the bio ethanol processes. One of the disadvantages of cellulosic and lingo-cellulosic bioethanol production is formation of the acid compounds. S. Ranil *et al* [31] carried out an experimental study to compare adsorptive membranes and resins for acetic acid removal from biomass hydrolysates. An ion exchange membrane, Sartobind Q, was used to remove acetic acid from two hydrolysate solutions. An ion exchange resin, Amberlyst A21, was also investigated, and compared its performance to that of the Q membrane. The Q membrane module consisted of 25 mm diameter discs, surface area of 75 cm^2, thickness of 4 mm and nominal pore size larger than 3 mm. First, the membrane was equilibrated with water at pH 7.0. Next, the membrane was loaded with acetic acid solution at pH 7.0 and followed by washing with water at pH 7.0. A 0.1 mol L^{-1} HCl solution was used to elute the acetic acid from the membrane. Finally, the membrane was regenerated with water at pH 7.0. Flow rates of 0.375–5.0 mL min^{-1} were investigated. The results showed that the membrane exhibits a better performance in terms of dimensionless throughput and product loss [32].

Binbing Han *et al* [33] also compared the performance of ion exchange membrane and ion exchange resin. Additionally, the efficiency of an anion exchange membrane was compared to that of an anion exchange resin, for acetic acid removal from a DI water solution and an acidic hemicellulose hydrolysate. It is found that the membrane has exhibits a better performance in terms of dimensionless output and product loss.

3.2. Reactive Extraction Membrane

Membrane extraction is non-dispersive and it can overcome the disadvantages of conventional extraction [34]. Typically, a hollow fiber module is applied comprising a bundle of hydrophobic membranes. Spiral-wound modules could be applied as well, but no commercial products are available up to now. Due to their abundant availability organic solvents such as n-heptane are first choice, but alternative solvents such as ionic liquids can be utilized as well. Indeed, in comparison to a conventional extraction, which is carried out by simply mixing the two immiscible fluids, membrane extraction offers the following advantages:

- The micro or ultrafiltration membrane provides a large surface area to bring the aqueous phase in contact with the extractant. Each pore allows for the diffusive transfer of product from the feed solution into the extractant.
- The modularity of the membrane elements allows for a continuous operation while being scalable through parallelization of the modules.
- The permeate stream, expressed in terms of a mass transport coefficient, can be optimized by adjusting the volume flow ratio. The mass transport coefficient identifies the velocity of the transferred solute through the membrane and depends on the membrane, the hydrodynamic conditions of concentration polarization at the membrane surfaces, the substance system and the solute concentration differ between feed solution and extractant [22].

Grzenia *et al* [33] studied detoxification of biomass hydrolysates by reactive membrane extraction. Moreover, extraction of sulphuric, acetic, formic and levulinic acid as well as 5-hydroxymethylfurfural and furfural have been investigated. Octanol and oleyl alcohol were used as organic phase solvents. Alamine 336 was used as the aliphatic amine extractant. As a consequence, a reactive extraction of sulphuric, acetic, formic and levulinc acid was observed, while 5-hydroxy-
methylfurfural and furfural were extracted due to their distribution in the organic solvent. Significant removal of all toxic compounds was also obtained and an enhancement in pH from 1.0 to 5.0 was observed. When small quantities of the organic phase transferred into the hydrolysate during extraction, the toxicity of the organic phase must be considered. On the other hand, since detoxification will require the use of another unit operation in combination with membrane extraction, thus the economic viability of the combined process should be considered [33].

3.3. Microfiltration Membranes

He *et al*. [34] proposed performance of Microfiltration membranes in biorefinery. In addition, Lignin and hemicelluloses recovery, Enzyme recovery, Biogas and Biodiesel production, beside Acetic acid production, all processes are correlate to bioethanol production. It should be noted that, pressure is driving force of Microfiltration membranes, sieving mechanism is separation principle, symmetric porous is structure, polymeric and ceramic are materials, thickness is around ~10–150(μm), pore size is around ~50–10,000(nm) and configuration can be Flat sheet/plate and frame, tubular, hollow fiber [34].

Lignin is one of the primary constituents of lignocellulosic biomass, comprised of a complex phenolic polymeric structure mainly derived from three major monolignols: p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) [35]. Besides being used as a simple biofuel, lignin offers several other applications due to its diverse functional groups. It can be used as a dispersant in cement and gypsum blends, as an emulsifier or chelating agent for the removal of heavy metals from industrial wastewater, or as a replacement for part of the phenol in phenol-formaldehyde resins [36]. Lignin can also be utilized as a precursor for carbon fibers or as a wet strength additive for kraft liners [37].

Also, hemicelluloses are in abundance in lignocellulosic materials and are hetero-polysaccharides consisting of various sugar units with different proportions and substituents [38]. The most common hemicelluloses are glucuronoxylan, xylan, xyloglucan, glucomannan, arabinoxylan, glucurono-arabinoxylan and galactoglucomannan [39]. Hemicelluloses may be used for hydrogels and barrier films production, converted to ethanol by hydrolysis and fermentation, and used as a feedstock for xylitol production. The flow sheet for bioprocessing of biomass to bioethanol production from cellulosic and ligenocellulosic sourcess is presented in Figure **6**.

3.4. Ultrafiltration Membranes

Ultrafiltration membranes can be employed in biorefinery for Lignin and hemicelluloses recovery,

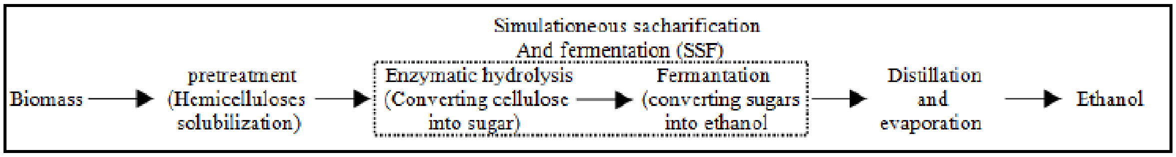

Figure 6: Schematic flow sheet for the bioprocessing of biomass to ethanol.

Enzyme recovery, Biogas and Biodiesel production, Algae harvesting, and Acetic acid production. Additionally, Lignin and hemicelluloses recovery, Enzyme recovery and Acetic acid production are performances that can be considered in bioethanol production. For Ultrafiltration membranes driving force is pressure. Also separation principle is sieving mechanism, structure is asymmetric porous, Materials are polymeric and ceramic, thickness (Top/sub layer) is ~150(μm), pore size is ~1–100(nm) and configurations are flat sheet/plate frame, tubular, spiral wound, hollow fiber and capillary [34].

Biological conversion of lignocellulosic biomass for producing fuel-grade ethanol presents an attractive opportunity for the development of renewable and environmentally friendly biofuels. As indicated in Figure **6**, the biorefinery process consists of three major steps including pre-treatment, hydrolysis and fermentation. The enzymes (cellulases) used to hydrolyze cellulose to fermentable sugars are considered one of the most significant production expenses, constituting approximately 50% of the total cost of hydrolysis process and 20% of the total cost of ethanol production [40]. Therefore, recovery of enzymes is an important step in bioethanol production process and membrane separation is one the effective method to recover and recycle cellulases from the hydrolyzed solution.

Mores *et al*. [41] and Nguyen *et al*. [42] reported the performance of MF for enzyme recovery, but majority of the reports show the performance of UF membranes for enzyme recovery. Steele *et al* was also used UF membranes for Cellulase in addition to cellobiase (Novo 188). Here, membrane manufacturer was Millipore, MWCO (kDa): 10, material was polyethersulfone, configuration was flat sheet/plate-and-frame, scale was laboratory/bench scale, and Cycle index was 3. Also, the retentate is recycled to the feed tank while permeate is withdrawn. The result was showed that Initial enzyme loading (% w/v) was 15 (Unit is FPU/g glucan)/40(Unit is CBU/g biomass.) [34].

3.5. Nanofiltration Membranes

Nonofiltration membranes have many performances like Lignin and hemicelluloses recovery, fermentation inhibitor removal and Biodiesel production in a biorefinery. Pressure is considered as driving force of Nanofiltration (NF). Separation principle is solution diffusion, structure is composite, material is polymeric, thickness (Top/sub layer) is ~1/150(μm), Pore size is <2 (nm) and configurations are flat sheet/plate frame, tubular and spiral wound [34].

There are many applications for NF membranes in biorefinery technology. Lignin and hemicelluloses recovery [37], Fermentation inhibitor removal [43] and Biodiesel production [44] are some usages of this method. Weng *et al*. [45] was experimented the separation of acetic acid from xylose by Nanofiltration method. They noted that Acid hydrolyzation of lignocellulose releases sugars (mainly d-xylose) and several derivatives. The sugars in the hydrolyzate are then converted into ethanol by fermentation. Since acetic acid is considered to be one of the inhibitors limiting the yield of ethanol, it is beneficial to remove acetic acid from the hydrolyzates before fermentation. In this study, a Desal-5 DK Nanofiltration (NF) membrane was used to separate acetic acid from xylose, using a synthetic acetic acid–xylose solution as the model. The Desal-5 DK membrane had an isoelectric point of 3.7 and a pore size of 0.83nm based on streaming potential measurement and model calculation. It was found that both the solution pH and the applied pressure affected the separation performance. The observed retention of xylose and acetic acid varied from 28% to 81% and −6.8% to 90%, respectively, depending on the solution pH and the applied pressure. The maximum separation factor was 5.4 when the system was operated at pH 2.9 and 24.5 bar. In addition, negative retention of acetic acid was detected only in the presence of xylose. The results suggested that intermolecular interactions play an important role in the separation of xylose and acetic acid [45]. Pinto *et al* [46] experimented the NF membrane for separation of Ethanol/water mixture. Moreover, Gautam *et al* [47] denoted the performance of NF membranes. NF membranes were evaluated for their ability to separate inhibitors (organic and mineral acids, furans and phemolic compounds) from sugar.

3.6. Pervaporation Membranes

He *et al*. [34] studied the performance of pervaporation (PV) in a biorefinery. Bioethanol production and dehydration of bioethanol are the most important performances of PV and are regarded very important for bioethanol production. Sushil *et al* [48] investigated the application of pervaporation in ethanol production process from lignocellulosic biomass. They presented the performances as shown in Figure **7**.

Therefore, it can be suggested that pervaporation is an influential method which can help to the bioethanol unit and improves it. The driving force of PV is partial vapor pressure, separation principle is solution diffusion, structure is homogeneous or composite, materials are polymeric, ceramic, and organic–inorganic, membrane thickness is ~0.1 (μm), pore size is Nonporous (dense) and configurations are flat sheet/plate frame, tubular and hollow fiber [34].

In pervaporation method, an additional phase change occurs as the fluid feed is transferred into the vapour phase at the permeate side of the membrane. Even though a vacuum pump is applied in such a system and the mass transport increases while reducing the permeate side vacuum pressure[22]. The production of ethanol from lignocellulosic biomass has been widely investigated to replace non-renewable fossil fuels. However, the ethanol productivity in the conventional batch fermentation process is low (2–2.5 g ethanol/L/h) due to the low concentration of microorganisms, end product inhibition, and substrate consumption [49]. One of the approaches to enhance the productivity of ethanol fermentation is to conduct continuous fermentation at a high cell concentration. Unfortunately, the impact of end product inhibition in continuous fermentation is more severe than in batch processes, because the fermentative microorganisms are constantly exposed to the high ethanol concentrations [50]. Thus, continuous fermentation coupled with simultaneous ethanol removal can be an attractive alternative to relieve ethanol inhibition [51]. In this meanwhile, Zhang *et al*. [52] show an increase in producing of product to 2.75/3.25.

As a consequence, purity of final product is an important factor that can be improved with pervaporation membrane for bioethanol dehydration. Indeed, membrane pervaporation processes can be categorized into three major groups based on the membrane used: polymeric, inorganic and organic–inorganic hybrid [34].

The most of pervaporation membranes used at an industrial scale are of the polymeric type due to their low cost of fabrication [49]. Furthermore, several polymers, such as cuprammonium regenerated cellulose (CRC) [53], polyamidesulfonamide (PASA) [54], sodium alginate (SA) [55], polyphenylene oxide (PPO) [56], and chitosan (CS) [57], have been investigated. The diverse materials were also used for homogeneous membrane fabrications.

Liu *et al*. [58] experimented the performance of PV membrane for removal of furfural which is an inhibitor for fermentation process. The furfural deliberately being produced as a platform chemical too, and have an ability to come in contact with water in many other situations, like acting as an inhibitor in biomass fermentations (at concentration of 41 g/ L) and as a major component of industrial wastewater (at concentration of 4100 ppm). In this work, a homogeneous ZIF-8-silicone rubber Nanocomposite membrane with high particle loading was successfully fabricated on a hierarchically ordered stainless-steel-mesh (HOSSM) employing a novel ''Plugging–Filling'' method. The membrane exhibits the highest pervaporation separation index (separation factor 53.3 and total flux 0.90kgm^{-2} h^{-1}) reported so far and

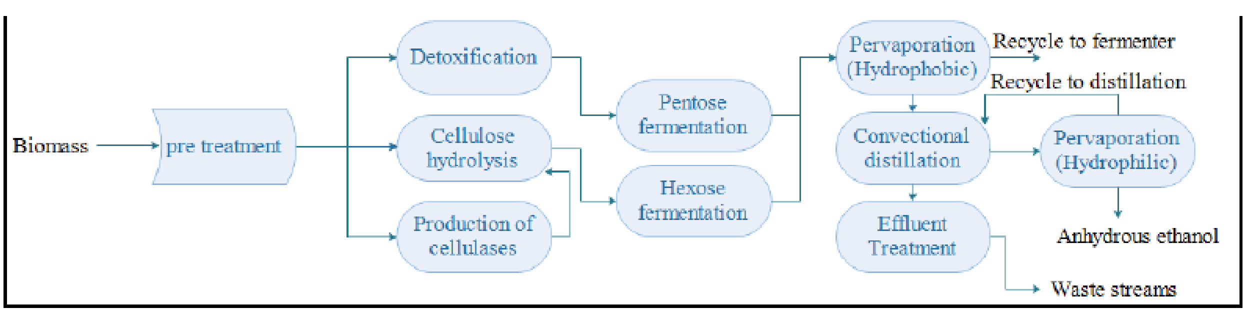

Figure 7: Potential application of pervaporation in ethanol production process from lignocellulosic biomass; C-cellulose; H-hemi-cellulose; L-lignin; P-pentose; I-inhibitors; G-Glucose; EtOH-ethanol; Cel-cellulases; CF-co-fermentation; SSF-simultaneous saccharification and fermentation; SSCF-simultaneous saccharification and co-fermentation; CBP-consolidated bioprocessing [48].

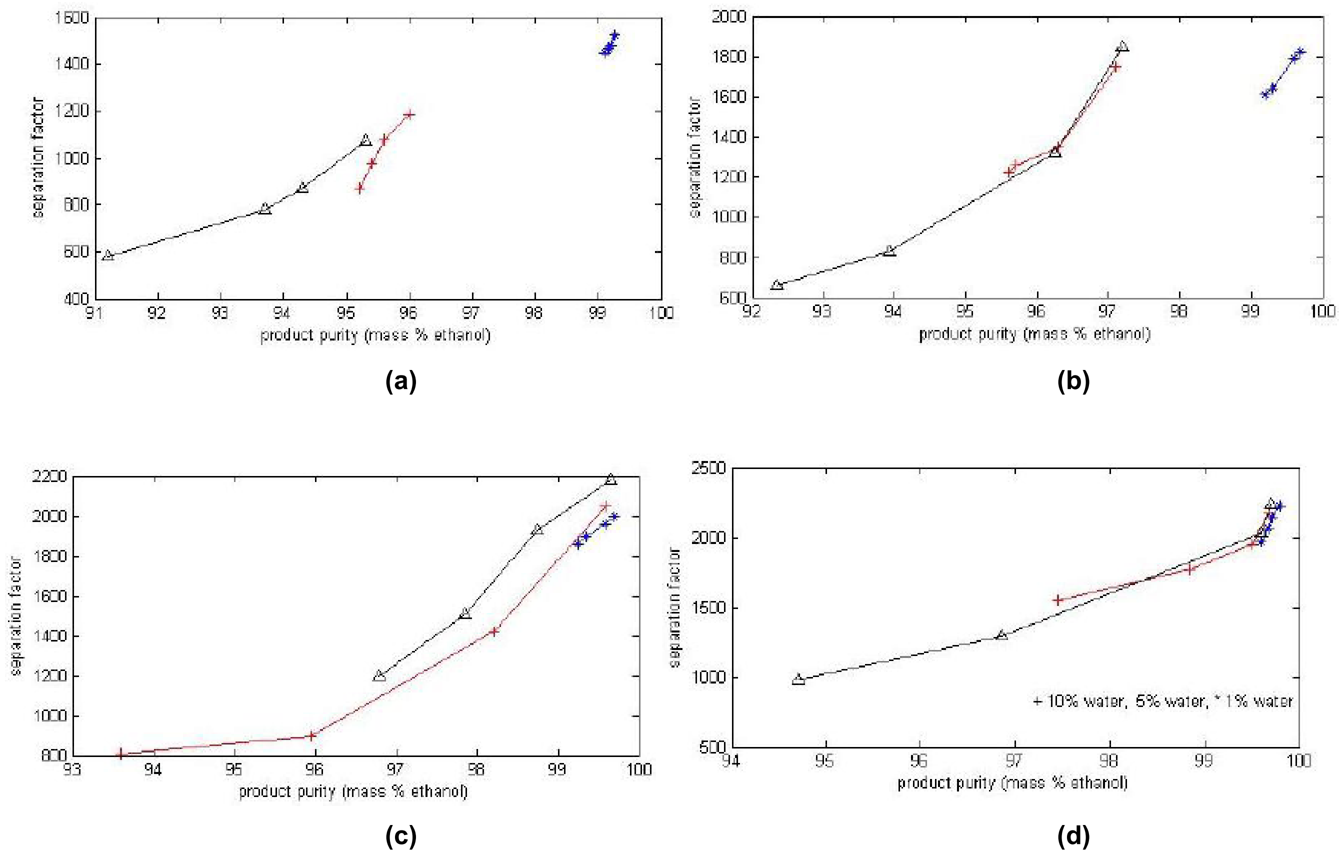

Figure 8: a: Separation factor achieved for ethanol-water at feed composition of 1%, 5% and 10% water at 313.15 K [59].
b: Separation factor achieved for ethanol-water at feed composition of 1%, 5% and 10% water at 323.15 K [59].
c: Separation factor achieved for ethanol-water at feed composition of 1%, 5% and 10% water at 333.15 K [59].
d: Separation factor achieved for ethanol-water at feed composition of 1%, 5% and 10% water at 343.15 K [59].

excellent stability in at test of more than 120 h at 80 °C for recovery of furfural (1.0wt%) from water [58].

The separation factor is the ratio of the components in the permeate vapour to the ratio of the components in the feed vapour, as shown in Eq. 5:

$$B_{mem} = (P_{il} / P_{jl}) / (P_{iO} / P_{jO}) \quad (5)$$

Peterson *et al* [59] showed that separation factor and percent of pollutant in feed are effective parameters on purity of final product in permeate side of membrane and the temperature has little effect that these effects are shown in Figure **8**.

According to Figures (**8-a**) to (**8-d**), it seems that the achieving a pure product with poor feed is difficult and also varies by temperature. John *et al* [60] carried out an modelling study for bioethanol separation of fermentation process. Given to the obtained results, it was observed that for the PDMS (Polydimethylsiloxane) membrane and the set of conditions used in this research project for the recovery of ethanol, a higher permeate ethanol concentration is achieved even when the ethanol concentration is low in the feed. Additionally, this membrane provided good ethanol separation, as was verified in the ethanol concentration in the permeate side.

It should be noted that, ideal condition for a membrane is high separation factor and flux. Hence, the novel organic-inorganic hybrid membranes can be used for bioethanol production. Uragami *et al* [61] investigated the effect of different parameters on this membrane performance in mentioned process. Moreover, Zhang *et al* [37] used this kind of membrane for ethanol dehydration process.

Furthermore, the pervaporation process is already an established process for the recovery of alcohols from fermentation broths and has extensively been studied over the last three decades for alcohol dehydration. The bioreactor concepts were also studied, in which fermentable sugar cane or corn was processed. These processes benefit from a simple pretreatment which is mechanical crushing in the case of corn [22]. In addition, Gagne *et al* [62] were applied a bioreactor for separation of ethanol, where the bioreactor was coupled with a pervaporation membrane module consists of silicone-rubber hollow fibres operated in the inside-out mode.

Moreover, the batch fermentations were carried out with and without membrane separation of ethanol. It should be noted that starting with a feed solution containing around 30 vol% of ethanol the batch fermentation without coupled pervaporation required about 27 h, while with membrane separation of ethanol only 16.5 h were needed. In particular, without membrane separation, a fructose yield of 99% and an ethanol yield of 78% were reached, while with membrane separation, the values of 96.5% for fructose and 79.5% for ethanol were obtained.

In the other hand, Kang *et al* [63] compared the pervaporation processes with molecular sieve methods. Their results showed that molecular sieves are commonly used to produce pure ethanol (>99.5%). The investments dedicated that the high capacity of molecular sieve are required and the steam consumption are considered as major drawbacks of this method. Therefore, the hydrophilic membranes and pervaporation method can be regarded as suitable alternative.

3.7. Membrane Distillation

Membrane distillation (MD) can be divided into four types according to the condensation methods: direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), gas membrane distillation (SGMD), and vacuum membrane distillation (VMD). DCMD is often used in desalination, crystallization, concentrating fruit juices and treatment of waste water; SGMD has been applied at laboratory scale for the treatment of aqueous solutions containing non-volatile solutes such as salts (NaCl) as well as volatile solutes such as ammonia, alcohols (ethanol, isopropanol) and acetone; and AGMD is used in desalination, solar units, food processing, treatment of aqueous alcohol solutions, breaking of azeotropic mixtures and extraction of volatile organic compounds [64].

He *et al*. [34] suggested the application of MD process in biorefinery for bioethanol production. It should be noted that driving force of MD process is vapour pressure difference. In the meanwhile, separation principle is vapour–liquid equilibrium, structure is symmetric or asymmetric porous, material is hydrophobic polymer, thickness is around 20–100 (μm), pore size is ~200–1000 (nm), and configurations are flat sheet/plate frame, tubular and capillary.

4. CHALLENGES AND OPPORTUNITIES

It should be noted that many challenges are associated in exploiting the advantages of membrane application for bioethanol production. However, most of these challenges are related to applying the membrane technologies. Thereby, the main steps are presented as follow:

- -Need for defect-free membranes with high selectivity and flux.
- -Difficulty in reproducing laboratory- scale results on a larger scale suitable for commercialization of membrane process for biorefinery.
- -Need to decrease fouling phenomena in membrane. (Membrane fouling is the reversible or irreversible adsorption/deposition of solidified solutes on or in the membrane which results in a significant increase in hydraulic resistance.)

Furthermore, Flux decline[37,65], Toxicity [33, 66], Enzyme denature/inactive [40], Deterioration of pervaporation performance [67], Selectivity decrease [68], Concentration and temperature Polarization [69], Inhibition of ethanol production, Higher permeability with lower water selectivity [70] and Shock [71] are some of other challenges that presented in the using of membrane separation methods in biorefinery. However, using of membrane technologies have many advantages in compared with the convectional technologies [34].

As an opportunity, the development of membrane processes in future can increase tendency of their application for biofuels production.

5. CONCLUSION

In this study, the major issues dealing with the coupling between membrane technology and a bioethanol production process have been overviewed, considering different membrane processes and feed source types in the bioethanol production. In particular, bioethanol is a noticeable product for future bio-refineries, and there has been an increasing interest in biomass derived ethanol due to the rapid increase in the crude oil price and the intensity of the global demand for petroleum.

The membrane separation process can be applied as an efficient method for separation or purification via ~~in~~ different configurations and in various stages of the bioethanol production. The separation processes have many advantages that can improve the total efficiency of bioethanol production refineries. In addition, these methods are sustainable for environment due to the production of less waste water. Moreover, high purity of final product, especially bioethanol, is an important constraint that can be achieved with membrane separation processes.

Hence, by comparing the different available process options, it is highlighted that major benefits can be obtained when the biochemical plant such as bioethanol production plant is coupled with membrane systems. Therefore, applying different configurations of membrane technology according to mentioned advantages can show more potential in different applications especially for bioethanol production.

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