Production of fuel grade anhydrous ethanol: a review

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Abstract. Alcoholic fermentation of fermentable carbon sources like molasses and table sugar using yeast are typical route in producing alcohol particularly known as bioethanol (C\textsubscript{2}H\textsubscript{5}OH). The key challenge encountered in bioethanol production process is to eliminate the impurity presence within the bioethanol which mainly water. Distillation is an energy extensive process which commonly used to recover ethanol up to 95% purity due to the presence of azeotropic composition. The distillation will no longer appropriate for further purification once the azeotrope composition has reached. Nonetheless, to be able to use as a viable fuel for gasoline engine or for any other utilisations where the purity is a major concern, further dehydration steps are needed producing an absolute ethanol. Few studies have been investigated on various dehydration methods for producing anhydrous ethanol, including azeotropic distillation, extractive distillation, adsorption, membrane pervaporation, and solvent extraction process. This review offers an insight into currently used technology on the ethanol dehydration methods and the future prospect on the continuous improvement particularly on the process energy requirement and efficiency will be discussed.

1. Introduction

Fossil fuels, such as petroleum, coal and natural gas, were introduced to society widely in the 19th century due to the industrial revolution. Hence, the society started to replace woods with coals as a source of heating because the coals produced more energy than woods and easier to be transported than woods [1]. Then at the end of the 19th century, the invention of the internal combustion engine triggered the demand for petroleum increased. Till 2019, the consumption of fossil fuels was exceeded 1.2 million TWh and the energy demand is expected to continue to rise [1,2]. Due to the ever increasing consumption of fossil fuels, several global issues are starting to appear. The issues include the depletion of fossil fuel reserves and climate change that urgently call for the use of renewable energy as alternative fuel that burns much cleaner.

Biofuel is considered as renewable energy that derived from plant materials in the form of solid biomass, liquid fuel and biogas [3]. Among these, bioethanol is one of the most important biofuels which commonly used as fuel, gasoline additive, and can be further used as intermediate feedstock in producing ethyl ester biodiesel. Bioethanol has been produced in the large scale via anaerobic fermentation of carbon sources with the presence of yeast, where it is finally recovered with the designated purification process sequence. Due to the nature fermentation process where ethanol and water are the major
component upon completion, there are always a growing interest on removing water from ethanol in the most economical way.

2. Ethanol Dehydration Method
Anhydrous ethanol is the ethanol without water. It can be produced from the alcoholic fermentation with the presence of carbon sources and microorganisms (e.g. *Saccharomyces cerevisiae*). Since water and ethanol are usually the major component in the broth after the alcoholic fermentation, so the purification method to remove the water is always needed. The purification methods are known as ethanol dehydration method and pervaporation, azeotropic distillation, extractive distillation, adsorption and solvent extraction are the examples of ethanol dehydration method.

2.1. Membrane Pervaporation
Pervaporation is a membrane separation process in which a mixture in the form of a liquid is fed to a membrane to allow the permeation of certain components after the liquid mixture is evaporated into a vapour phase [4]. The principle of pervaporation is illustrated in Figure 1. It includes two basic steps of process, which is permeation and evaporation [5].

![Figure 1](image.png)

*Figure 1.* The schematic diagram for the principal of pervaporation [4].

Generally, the evaporation process will be conducted before the permeation process. In the permeation process, a vacuum pressure is created at the permeate side of the membrane to establish a partial vapor difference, to drive the selective component through the membrane to the permeate side. Besides that, a sweeping gas on the permeate side of the membrane can be used to form a partial vapor difference or by a temperature difference between feed side and permeate side [4].

The surface characteristic of pervaporation membranes can be porous and non-porous structures in morphology classification. Porous membrane is always used in size selection or exclusion, while a non-porous membrane is used for partitioning the molecules and allowing the selected molecules to diffuse through the membrane under a concentration gradient [6]. Some studies were made to investigate the relationship of certain membrane type in different operating conditions. Table 1 summaries the recent studies of pervaporation of ethanol-water mixture that operates with different membrane type and different operating conditions from 2015 to 2020.
Table 1. Summary of the pervaporation of ethanol-water mixture with different membrane type and different operating conditions.

| Membrane type                          | Feed temperature       | Feed Pressure     | References |
|----------------------------------------|------------------------|-------------------|------------|
| Hybrid silica                          | 60°C, 70°C & 80°C      | 5 & 20 mmHg       | [7]        |
| Graphene oxide                         | 27°C                   | 1 atm             | [8]        |
| Graphene oxide                         | 40°C, 50°C, 60°C &     | vacuum            | [9]        |
| A-type zeolite and amorphous silica    | 70°C                   | Various pressure  | [10]       |

Additionally, the pervaporation can combine with other process to create a hybrid unit, distillation and pervaporation hybrid system to dehydrate ethanol [11,12,13]. The hybrid system can reduces the operation cost and improve the degree of separation as well. For a traditional hybrid system, the pervaporation unit is externally connected to the distillation column, while the new hybrid system that is drafted has a pervaporation membrane that located inside the distillation column as working as a packing bed in a section of the column [11]. The new concept of the hybrid system is proved to function as traditional hybrid system. Besides, the change of the configuration of a hybrid system can affect the energy used. This is proved that the hybrid system with side stream required less energy than the hybrid system without side stream [12]. The Figures 2a and 2b shows the configurations of the hybrid system with or without side stream.

2.2. Distillation
Distillation is a process to separate the components of a mixture through evaporation and condensation. The process can recover ethanol up to 95.6% purity by mass due to the azeotropes behaviour. Azeotropes are the components in the mixtures that boil together at a constant temperature [13]. Ethanol-water mixture is one type of azeotrope, so it is impossible to separate azeotropes completely to obtain anhydrous ethanol by distillation. Thus, a more complex distillation process (e.g. azeotropic distillation and extractive distillation) can be applied to obtain the anhydrous ethanol.

2.2.1. Azeotropic distillation. Azeotropic distillation is an advanced type of distillation that is used to separate the components in azeotropes completely. In azeotropic distillation, a compound or called entrainer is added to the azeotrope to form a new azeotrope. The new azeotrope that combine with the starting azeotrope and entrainer is known as ternary azeotrope and the water in the ternary azeotrope will has a lower boiling point. Hence, the water and entrainer will be recovered as distillate, while the ethanol will be recovered as residue in distillation.

Basically, there are five types of distillation method that required the entrainers. They are homogenous azeotropic distillation, heterogeneous azeotropic distillation, extractive distillation, reactive distillation and salt distillation. The heterogeneous azeotropic distillation is well-known as
azeotropic distillation. For a more accurate principal for a heterogeneous azeotropic distillation, the distillate (water and entrainer) will transfer into decanter and forms two layers, organic and aqueous layers [14]. There are some recent studies that investigate the azeotropic distillation of ethanol-water mixture with different entrainers from 2015 to 2020. All the recent studies are summarized in the Table 2.

In heterogeneous azeotropic distillation, benzene is a commonly used as an entrainer. But the recent studies were carried out using other type of hydrocarbon instead of benzene. This is due to the fact that the benzene is carcinogenic to humans, so the researchers are tried to search for some new materials as a replacement. Moreover, cyclohexane is the most effective entrainers among the entrainers confirmed by the recent studies, as it can achieve a 99.99% mole of purity of ethanol [18]. While the heterogeneous azeotropic distillation that uses n-octane as an entrainer is able to obtain the anhydrous ethanol, although the purity of the recovered ethanol is only 84% mole [17].

Table 2. Summary of azeotropic distillation of ethanol-water mixture with different entrainers.

| Entrainers                                      | Purity of Recovered Ethanol (% mole) | References |
|-------------------------------------------------|--------------------------------------|------------|
| Mixture of hydrocarbon (n-hexane, cyclohexane, toluene and isooctane) and naphtha             | 78.4                                  | [15]       |
| n-octane                                        | 84                                    | [17]       |
| Cyclohexane                                     | 99.9                                  | [18]       |

2.2.2. Extractive distillation. Extractive distillation is one of the most used techniques for dehydrating bioethanol, consisting of the addition of a third substance in the distillation column capable of changing the vapor-liquid equilibrium behavior of the system and modifying the relative volatility of the initial mixture in order to obtain complete separation of the components. The difference between the azeotropic distillation and the extractive distillation is the volatility of the solvent added to the distillation column, where there is the formation of a new azeotrope in the azeotropic distillation system, which does not occur in the extractive process, making extractive distillation is more favorable [26]. In particular, the process has been widely used in the industry as a reliable technology due to its low operating cost in comparison to azeotropic distillation. Furthermore, a sustainable entrainer can be mobilised in the extractive distillation to break down the azeotrope [27].

In the extractive distillation column, the entrainer or solvent is fed continuously at a different point than the ethanol-water mixture. This will convey an additional extractive section in the column, between the stripping and the rectifying sections. The basic principle of the extractive distillation is that the entrainer interacts differently with the components of the original mixture and thereby the relative volatility of ethanol will be increased. Ethanol is recovered at the top of the extractive distillation column, while the water with entrainer mixture are removed at the bottom which is then transported to the regeneration column. At the bottom of the regeneration column, when the solvent is recovered with a satisfactory purity, it is recycled back to the extractive distillation column [23]. The extractive distillation process flowchart for ethanol dehydration is shown in Figure 4. Majority works of extractive distillation processes in the literature were carried out at the range of 20 to 50 stages. From the extractive distillation, the ethanol stream may indicate a product of anhydrous ethanol with a high purity nearly 99.49% [20].
Figure 4. Extractive distillation process flowsheet for ethanol dehydration [22].

In recent times, ionic liquids (ILs) have been suggested as a potential replacement for the organic solvents. This is due to the ability of ILs to yield high separation, easy recovery, non-detectable vapor pressure, relatively low melting point [23], and high thermal and chemical stability [22]. Based on several ILs chemical structures, it composes of the anion e.g. Cl\(^{-}\) with different frame lengths in the organic cation, which are 1-methylimidazolium chloride ([mim]Cl), and 1-butyl-3-methylimidazolium chloride ([bmim]Cl). There is also an effect of the cation length on the vapor-liquid equilibrium particularly the smaller the ionic liquid chain, the stronger ionic liquid-water interactions. Therefore, this effect will lowered down the ethanol concentrations. However, ionic liquids containing the anion [Cl\(^{-}\)] have a high viscosity which may affect the operation of the distillation column [21]. Therefore, the selection of low viscosity IL is generally desirable. It was found that certain IL improves mass transfer in the extractive and recovery units as well as reduces the energy necessary in the process [22].

To promote saving of energy, a renewed attention given for salt extractive distillation, which has the advantages of energy-saving, reduced equipment size and initial costs, yielding high purity products with a single column. There is also a possibility of production at different scales as compared with other dehydration processes [28]. When a salt is dissolved in an ethanol-water mixture, which consisting of two volatile miscible liquid components, the activity of the two volatile components will affect by salt through the formation of liquid phase associations. In ethanol-water mixture, more polar water molecules interact strongly with anions and cations of the salt forming hydration spheres in their vicinity. A comparatively small concentration of salt is capable of increasing the relative volatility of the more volatile component (ethanol) and this behavior is called the salt effect [25]. Calcium chloride (CaCl\(_2\)) has been widely used as a separating agent in the salt extractive distillation of mixtures composed of ethanol and water because this electrolyte effectively has been demonstrated salting-out effect on the phase equilibrium of the ethanol-water system. A number of positive aspects of extractive distillation with soluble salts, when compared to the extractive distillation with liquid solvents include a high level of energy savings, the lower toxicity level of certain salts, and production of distillate that is free from the salt [25].

2.3. Adsorption
Adsorption-based methods are of interest to dehydrate the bioethanol due to a more energy-efficient in comparison to its counterpart as it offer lower cost [32] without detectable solvent residue in the final product [31]. Adsorption processes utilize adsorbent material in a porous solid form known as molecular sieves that selectively adsorb water molecules whilst ethanol remain non-diffusing component. This is due to the fact that the molecular size of ethanol is greater than water. A molecular sieve characterises as tiny and uniform size of pores. There are many types of adsorbents, which include synthetic zeolites, microporous charcoals, active carbons, as well as natural adsorbents, including cornmeal, straw, and
sawdust. The zeolite-type molecular adsorbents can achieve a high selectivity for water that can be made to be both size and sorption-selective for water [29]. The adsorption method usually conducted by pressure swing and thermal swing adsorption processes [30].

Pressure swing adsorption (PSA) is one of the most frequently used technologies for a large scale for ethanol dehydration. The main advantages of the pressure swing adsorption for ethanol dehydration are a high-quality alcohol production without solvent contamination can be obtained [31]. In addition it has lower energy consumption when compared to distillation-based separation. The key reason that the pressure swing adsorption is more favored than its counterpart, i.e. temperature swing adsorption (TSA), is that it is simpler and quick to switch from low to high pressure or high to low pressure as compared to temperature, leading to a shorter cycles and thus increasing the servicing period of adsorbent [33]. Both pressure swing adsorption and temperature swing adsorption consist of the two main steps which are adsorption and desorption. Temperature swing adsorption is where the adsorption or desorption is carried out by increase or decrease the temperature [34].

Biosorbers have advantages for dehydration of alcohol as they can be developed from cost-effective feedstocks such as waste agricultural biomass and have adsorption capacities. Biosorbers have the potential for selective water adsorption by the polar interaction of hydroxyl, carboxyl, carbonyl, and amine groups with water molecules. Water adsorption with biosorbents may consume less energy than adsorption using other adsorbents. In addition to this, biosorbents require less energy as compared to synthetic adsorbents for regeneration. Even if regeneration is not possible with biosorbent, the spent biosorber can be utilized as a raw material for the production of biofuels. On the other hand, liquid phase adsorption is generally less energy requirement as the sorption can be carried out at room temperature and ambient pressure but has a disadvantage of leaching of biomass components into the solution which may be undesirable for product purity, while the vapor phase adsorption is favored as the continuous operation is feasible with high product purity [33].

2.4. Solvent extraction
Solvent extraction utilizes two homogeneous liquid phase with different thermodynamic properties. Use to separate chemicals and pharmaceuticals like penicillin and extraction of ethanol for bioethanol purification. There are few recent studies of solvent extraction for ethanol dehydration. However, solvent extraction is feasible for ethanol dehydration with the appropriate solvent. The advantage of liquid-liquid extraction is the low energy requirement, but the recovery of the products from the solvent is usually carried-out by means of distillation, that is high energy intensive. The successful liquid-liquid extraction of ethanol has the following characteristics including great extraction performance, high ability of ethanol absorption to minimize the extractant solvent use, low solvent solubility in the water to avoid the solvent losses, the density difference between the aqueous phase and organic phase to ease rapid separation, chemical stability, efficient technique for ethanol recovery and recycle the extractant solvent, using of non-toxic solvent, and the solvent is sustainable for the process as well as economic and performance aspect.

Furthermore, the separation selectivity of ethanol relative to water against the distribution coefficient of ethanol was reported in the study. The separation selectivity of ethanol relative to water with m-xylene is the highest among other solvents, followed by benzaldehyde and furfural. The distribution coefficient of ethanol was larger with furfural or benzaldehyde compared to m-xylene, and those with furfural and benzaldehyde were in identical level. This shows that the separation selectivity of ethanol relative to water with m-xylene was the largest, but the distribution coefficient of ethanol was the smallest. For the solvent mixture, the solvent mixture of furfural and m-xylene indicated the higher distribution parameter thus high selectivity to ethanol relative to water than the solvent combination of benzaldehyde and m-xylene. In case of larger mass fraction of m-xylene in the solvent phase, the solvent mixture of furfural and m-xylene still exhibiting a relatively high distribution coefficient, selectivity towards ethanol. Therefore, the mixture solvent of furfural with a larger mass fraction of m-xylene is considered as a best solvent mix to concentrate ethanol.
3. Conclusion
There are four ethanol purification techniques were reviewed herein: Membrane pervaporation, distillation, adsorption and solvent extraction. Among these, the exploitation of adsorption and membrane pervaporation is the right choice to produce anhydrous ethanol with ultimate requisites of alternative fuels. In this respect, both process technologies have many benefits as it offers a simple, low cost and compact alternatives and can be made as modular configuration. In particular, the growing demand for efficient use of energy makes the society to contemplate on devising sustainable and green processes. However, there will always a trade off between the efficiency and the capital cost in which the process selection is highly dependent on the available technology as well as supporting resources. Therefore, getting the right balance are the key factors that determine the process viability.

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