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DEHYDRATION TO BIOETHANOL (FUEL ETHANOL)

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Abstract. In this artical we describe the technology of degydration of bioethanol (fuel ethanol).

Key words: bioethanol, degydration, adsorption method, molecular sieve, azeotropic method.

Dehydration to Bioethanol (Fuel Ethanol)

1.Introduction

Ethanol leaving the rectification column in the distillation plant is the ethanol-water azeotrope mixture. Azeotropes are also known as constant-boiling mixtures, and this ethanol-water mixture is a minimum-boiling azeotrope at a composition of 89.4 mol% ethanol and 10.6 mol% water. This product is not suitable as a fuel, since it contains a fairly high percentage of water; therefore a special process for removal of the remaining water is required for the production of anhydrous fuel grade ethanol. This step is known as dehydration or drying of ethanol, and will con-centrate hydrous ethanol up to at least 99.5% ethanol required for fuel applications. The distillation and drying to fuel grade ethanol are mature technologies, as corn- and sugarcane-based first generation bioethanol is in wide use as a blend in fuel in the United States, Brazil and a few other countries. These techniques developed for first generation ethanol are generally applicable to cellulosic ethanol as well. The systems of drying or dehydration to fuel grade ethanol will be discussed in this artical. This dehydration step is discussed only in a few review articles [1, 2], but most of the technology is patented.

2. Dehydration Methods

There are a number of dehydration methods that can be used for dehydration of approximately 90% hydrous ethanol leaving the conventional distillation unit to 99.5% bioethanol (fuel ethanol). These methods are basically divided into three groups:

1. Adsorption methods
2. Distillation methods – mainly azeotropic and extrac-tive distillations
3. Membrane-based methods

In azeotropic and extractive distillations a third component is added to the ethanol-water mixture that helps to break the ethanol-water azeotrope, and these methods are mostly used in older ethanol plants. Adsorption-based methods are a more energy efficient alternative to distillation-drying methods. This method is more popular in current corn- and sugarcane-based first generation etha-nol plants. Membrane-based pervaporation is another technique mostly under development as an ethanol dehydration method.

3. Adsorption Method

Adsorption processes employ solid adsorbent material that selec-tively adsorb water molecule leaving ethanol on the basis of the difference in molecular size between water and ethanol. These adsorbent materials are known as molecular sieves as well because the separation depends on the size of molecules. A molecular sieve is a material containing tiny pores of a precise and uniform size. A number of materials with these characteristics are known, which include synthetic zeolites, clays, porous glasses, microporous char-coals, active carbons, as well as a variety of plant-derived adsorbents, including cornmeal, straw, and sawdust. The zeolite-type molecular adsorbents can be made to be both size and sorption-selective for water, thereby achieving a high selectivity for water; therefore, hydrophilic molecular sieves remain an industry standard [3].

Table 1.

Typical concentrations of common impurities in fermenta-tion-produced crude ethanol [4].

Impurity	**Concentration (ppm)**
Acetaldehyde	6.99
Ethyl acetate	12.7
Methanol	17.8
n-Propanol	145.2
n-Butanol	21.7
iso-Amyl alcohol	5.44
Other	20.7
Total	230.5

Impurities in fermentation-produced crude ethanol are mostly higher alcohols, methanol, esters, and aldehydes, but the concentration of these impurities are small. Typical concentrations of common impurities in fermentation-produced crude ethanol are shown in Table 1. As zeolite is highly selective to water, these small amounts of impurities are not removed by molecular adsorbents.

3.1 Dehydration of Ethanol Using Zeolite Molecular Sieves

Ethanol dehydration is accomplished with synthetic zeolite molecu-lar sieves, which are aluminosilicates. These adsorbents have open structures through which small molecules can diffuse, and small enough molecules pass through the pores and are adsorbed or entrapped, while larger molecules pass through without adsorbtion. Zeolite molecular sieves with a pore diameter of 3Å are commonly used in the dehydration of ethanol since they can entrap water mol-ecules which have a diameter of 2.5 Å. Ethanol molecules with a diameter of 4 Å cannot enter the pores and therefore flow around the material. Molecular sieves can absorb water up to 22% of its own weight. The zeolite bed can be regenerated essentially an unlimited number of times by drying it with a blast of hot carbon dioxide.

Al-Asheh *et al*. have studied the breakthrough time and average outlet water content for the adsorption of water vapor on 3, 4, 5 Å types of molecular sieves at different inlet water contents of 5–12 wt% of an ethanol-water system, and their results are summarized in Table 2. These results clearly show that 3 Å molecular sieve has the highest absorption capacity for water [3].

Table 2.

Breakthrough time and average outlet water content for the adsorption of water vapor on different types of molecular sieves at different inlet water contents of an ethanol-water system [3].

Input water content (wt%)	Molecular sieves	Breakthrough time (min)	Average outlet water content (mol l^{-1})
5	Type 3 Å	88.9	0.81
5	Type 4 Å	78.6	0.97
5	Type 5 Å	49.1	1.51
8	Type 3 Å	81.0	1.04
8	Type 4 Å	65.1	1.31
8	Type 5 Å	23.6	2.56
10	Type 3 Å	67.7	1.57
10	Type 4 Å	50.4	2.41
10	Type 5 Å	19.7	3.33
12	Type 3 Å	61.2	2.07
12	Type 4 Å	43.1	3.05
12	Type 5 Å	12.6	4.13

A number of researchers have studied the adsorption kinetics and pressure swing adsorption methods for dehydration of rectify-ing column ethanol to fuel grade ethanol [5, 6, 4, 7–9].

Generally, two beds of adsorbent are used to make the process continuous, and the dehydration process can be explained as follows. Consider the first column packed with freshly activated molecular sieve. As ethanol-water vapors first enter the bed, water is diffused and adsorbed within the pores of the adsorbent struc-ture in a thin layer. As more ethanol enters the column, it passes through this layer to a slightly lower level where another incre-mental amount of water is absorbed. This continues until a point is reached where all possible water adsorption from ethanol solution is accomplished. Transfer of water from the vapor of ethanol-water solution to the molecular sieve occurs through a zone where water (adsorbate) content is reduced from its inlet to its outlet concentration. This finite length of bed where the adsorbate transfer occurs is known as the mass transfer zone. While the active bed is under pressure carrying dehydration, the regeneration bed is under vacuum. The shift of operation (swing) from one bed to another can be controlled with the help of control valves and automation.

The bed temperature is critical in regeneration. Bed temperatures in the 175–260°C range are usually employed for type 3 Å molecular sieves. This lower range minimizes polymerization of olefins on the molecular sieve surfaces when such materials are present in the gas. Slow heat up is recommended since most olefinic materials will be removed at minimum temperatures; 4 Å and 5 Å molecular sieves require temperatures in the 200–315°C range. After regeneration, a cooling period is necessary to reduce the molecular sieve temperature to within 15–20°C of the temperature of the stream to be processed. This is most conveniently done by using the same gas stream as for heating, but with no heat input. For optimum regeneration, gas flow should be countercurrent to adsorption during the heat-up cycle and concurrent during the cooling.

Jeong and coworkers have studied the production of anhydrous ethanol using various pressure swing adsorption (PSA) processes in a pilot plant [4]. In this research, anhydrous ethanol was pro-duced through different processes such as two-bed, multi-tube bed, two-step, and three-bed for analysis and comparison of each process. A representative sample of their results from two-bed type and multi-tube bed type processes are shown in Table 3. Through this study, two-bed process and multi-tube bed process were both shown to produce 99.5 wt% anhydrous ethanol from 87.0 wt% eth-anol. However, the multi-tube bed process showed lower energy consumption. The two-step bed process has the advantage of being able to produce anhydrous ethanol from input ethanol concentra-tion as low as 83.1 wt%. Lastly, the three-bed process allowed for longer regeneration time, making the process very stable and with higher yield due to less lost time in cycle switching [4].

Table 3.

Results of the two-bed type and the multi-tube bed type processes in a pilot plant using 3 Å molecular sieves: (a) two-bed type process, (b) multi-tube bed type process [4].

(a) two-bed type process

Feed flow rate	**100 L/h**	**130 L/h**	**150 L/h**	**170 L/h**
EtOH purity (wt%)	99.89	99.86	99.78	99.65
EtOH recovery (%)	81.1	73.4	72.9	73.8
Purge flow rate (L/h)	18.9	34.6	40.7	44.5
Daily product (L/day)	1695	1995	2288	2628

(b) multi-tube-bed type process

Feed flow rate	**100 L/h**	**130 L/h**	**150 L/h**	**170 L/h**	**190 L/h**
EtOH purity (wt%)	99.85	99.89		99.67	99.49
EtOH recovery (%)	82.2	71.9	72.4	74.4	73.5
Purge flow rate (L/h)	17.8	36.5	41.4	43.5	50.4
Daily product (L/day)	1718	1953	2271	2649	2930

In a recent study Yamamoto and coworkers compared adsorp-tion characteristics of five zeolites for dehydration of ethanol by evaluating diffusivity of water in porous structure [10]. For this study they used five species of commercial zeolites from Tosoh Corp. (LTA-Na, LTA-K, LTACa, FAU-Na and MOR-Na) with different frameworks, and different exchanged cation species. In their experiments equilibrium adsorption was measured using zeolite powder with a grain size of 75–100 µm after out gassing at 573 K. On the other hand, a packed bed breakthrough curve (BTC) was obtained using particles (containing 20 wt% of binder prepared from natural clay) with a grain size of 150–250 µm packed in a bed. Adsorption isotherm of water vapor on zeolites, differential heat of the adsorption of water vapor, the liquid-phase adsorption isotherm of water in ethanol and packed bed breakthrough curves (BTC) for the adsorption of water in ethanol were studied in this comprehensive investigation. As a result, they confirmed that an LTA or FAU zeolite exchanged with a monovalent cation species, such as a sodium cation or a potassium cation, showed a strong affinity to water in ethanol. They also found that the Langmuir model explained the liquid-phase adsorption of water in ethanol on the zeolite more accurately than the Freundlich model. Using the constants determined from the Langmuir isotherm, they calculated the BTC for a zeolite packed bed as regards to the dehydration of ethanol. The intraparticle diffusion coefficient of water in the zeolite particles was also estimated by fitting the calculated BTC to the experimental result. Dehydration performance of the zeolites examined by Yamamoto and coworkers are shown in Table 4.

Table 4.

Dehydration performance of zeolites with different exchanged cations: Na, K, and Ca [10].

Zeolite	**dp [nm]**[a]	**$q_{H_2O,eq}$ [kg kg−1]**[b]	**$q_{H_2O,BTC}$ [kg kg−1]**[c]
LTA-K	0.3	0.130	0.105
LTA-Na	0.4	0.150	0.135
LTA-Ca	0.5	0.094	0.082
FAU-Na	1.0	0.166	0.149

[a] *Average pore diameter*

[b] *Adsorbed amount of water estimated from adsorption isotherm at the equilib-rium concentration of* 1.97×10^{-3} *mol* m^{-3}.

[c] *Adsorbed amount of water determined from a packed bed BTC; in estimation of* qH_2O, *BTC, the weight of the binder is excluded (not included in the net weight of the zeolite).*

3.2 Dehydration of Ethanol Using other Adsorbents

A number of researchers have studied the use of other adsorbents for dehydration of ethanol. Some examples from recent literature are natural materials such as corncobs, activated palm stone, oak [3], starch (corn and potato), xylan, pure cellulose, corn residue [11, 12], bleached wood pulp, sawdust, kenaf core [13], cassava starch, cassava pulp [14], corn (*Zea mays*), upright elephant ear (*Alocasia macrorrhiza*), cassava (*Manihot esculenta*), sugarcane bagasse [15], rice flour and maize flour [16].

In a comparison study Benson and George used three lignocel-lulosic material-based adsorbents, bleached wood pulp, oak saw-dust and kenaf core, where a thermal swing adsorption column was used to evaluate the effectiveness on the removal of water from ethanol-water mixtures of 90, 95 and 97 wt% ethanol. They gener-ated breakthrough curves to determine the effectiveness of these adsorbents and to compare them. These researchers observed that water is preferentially adsorbed allowing for complete dehydration of ethanol and also presented the mass transport properties for the diffusion of water molecules into porous matrices of the adsorbents as well as the length and velocity of mass transfer zone.

The adsorption capabilities of rice flour and maize flour for gaseous-phase selective water adsorption for ethanol dehydration was investigated by Chang and coworkers via a bench-test fixed-bed absorber at constant temperature [16]. In this experiment, ethanol concentration in the feed was 93.4% (mass) and each of the dried biomass was used as adsorbent; breakthrough curves and temperature distribution in adsorptive bed were obtained for different bed depths, superficial velocities, granularities of adsor-bent and temperatures. Bed pressure drop curves for different bed depths and superficial velocities were also measured. Additionally, they found that ethanol product purity of 99.5% (mass) could be achieved through both kinds of biomass adsorbents. When 99.5% (mass) of ethanol purity is defined as the breakthrough point, the capacity for adsorbent was within 0.0915–0.2256 gram water/gram adsorbent [16].

The application of corn (*Zea mays*), upright elephant ear (*Alocasia macrorrhiza*), cassava (*Manihot esculenta*), and sugarcane bagasse (*Saccharum*) for dehydration of ethanol was evaluated by Quentero and coworkers [15]. In this study enzymes (R-amylase and cellulase for starch and cellulose, respectively) were evaluated as modify-ing agents with the aim of increasing water adsorption capacity of these cellulosic materials as well. Water adsorption capacity ranges from 4 to 19g/100g adsorbent were found for evaluated materials. Cornstarch had the highest water adsorption capacity (19g/100g ads), while upright elephant ear starch presented the lowest (4.2g/100g ads). Tested materials showed affinity with water for both native and enzyme-treated cases.

4. Azeotropic Distillation Method

Azeotropic distillation is another method that can be used for con-centration of ethanol to 99.5%, and this is the method used in many early fuel ethanol plants. In this technique a third component is added to the water-ethanol mixture. This third component is called the entrainer, and this compound selectively interacts with one of the components in the azeotrope mixture, allowing the azeotrope to be broken and the components separated. Several compounds such as benzene [17], cyclohexane [18], hexane [19, 20], normal heptane [20], isooctane [21, 22], normal pentane [17, 23], acetone [21], diethyl ether [23], and polymers [24] can be used as an entrainer to produce anhydrous ethanol from water-ethanol azeotrope mixture. However, cyclohexane and benzene are the most commonly used entrainers. Presently, benzene is very rarely used due to its carcinogenic nature, although it is still being employed in some countries. The process using *n*-pentane is to be operated under high-pressure conditions due to the relatively low boiling point of pentane. The added component, or entrainer, being present in the liquid phase can alter the activity coefficient of various components, and unless the components already present are identical in the physical and chemical properties, the change in activity coefficient will be different for each component, thereby altering their relative volatility. This technique of adding an entrainer to alter the volatility is effective only when the component in the original mixture does not obey Raoult's law. In general, deviation from Raoult's law makes it easier to significantly alter the relative volatility by the addition of the entrainer component. The added entrainer is recovered after the azeotropic distillation dehydration of fuel ethanol, and the recovered entrainer must be recycled or reused for a practical process. The recovery of entrainer is usually carried out by decantation, or separation of the phases, and then the entrainer is returned back to the azeotropic distillation column [2].

A schematic diagram for the dehydration of ethanol using azeotropic distillation using an entrainer like benzene or cyclohexane is shown in Figure 1. Ethanol is first concentrated in a conventional distilla-tion column to near the binary azeotropic composition as described in Chapter 14 to approximately 90% ethanol, with 10% water. This 90% concentrated ethanol is fed into the azeotropic column shown in Figure 15.1. A secondary feed, which is rich in entrainer, is introduced on the top tray. The bottom product from this tower is at least 99.5% or nearly pure ethanol. The vapor at the top of the azeotropic distillation column approaches ternary azeotrope composition and is fed into a decanter [2]. This decanter works similar to large liquid-liquid separatory funnel, which separates the heavier water phase from lighter organic phase rich in entrainer. The entrainerrich organic phase of the decanter and a small entrainer make-up stream comprise the secondary feed and are recycled to the azeotropic column. The aqueous phase from the decanter is sent to a second column called the strip-ping column as shown in Figure 1, where it is processed further to recover ethanol and entrainer. This recovered ethanol and entrainer is retuned back to the azeotropic distillation column and the water removed is drained from the bottom of the stripper [2].

This process requires quite a large amount of energy because it is necessary to maintain and recirculate large quantities of entrainer throughout the column to achieve the desired effect. In addition, pure ethanol must be adequately stored to prevent water from the atmosphere being absorbed by it. It is interesting to note that now it is possible to directly attain a "dry" mixture of ethanol plus hydrocarbon, utilizing less energy, instead of obtaining anhydrous ethanol. In this case, high concentrations of entrainer necessary to circulate throughout the column are achieved by a new input stream of the hydrocarbon and not by its vaporization–condensation. The ethanol plus hydrocarbon mixture thus obtained may be employed as an additive to gasoline without the need of subsequent distillation. This technique is possible because many of the constituents in gasoline may be used as entrainers in the dehydration of eth-anol by azeotropic distillation. In one experiment usin gasoline

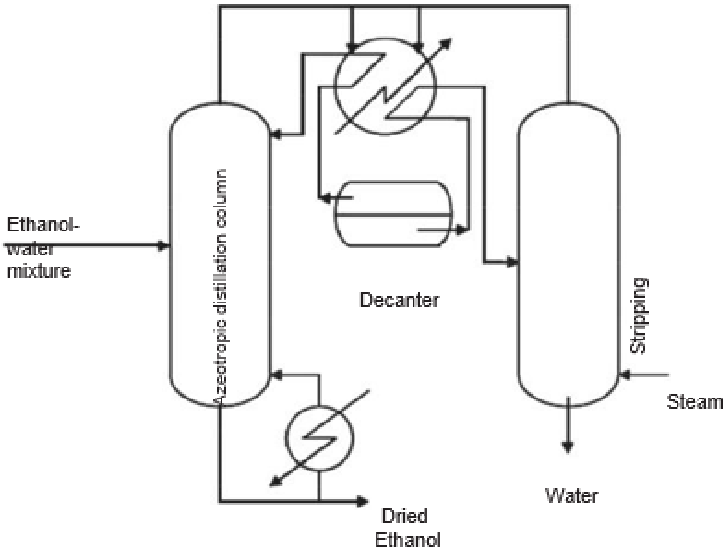

Figure 1. Heterogeneous azeotropic distillation of ethanol-water mixtures. (Reprinted with permission from reference [2]).

components in the direct dehydration of ethanol, Gomis *et al*. studied the viability of an azeotropic distillation process using isooctane as an entrainer to dehydrate ethanol and obtain a dry mixture of ethanol plus isooctane [21]. The experimental results indicate that azeotropic distillation allows obtaining mixtures of isooctane plus ethanol with water concentrations lower than 50 ppm. The results point out that the most critical parameter for this process is the reboiler heat duty. Low values of this parameter (< 2.2 kJ/g of feed ethanol) produce mixtures of ethanol plus isooctane with excessive water contents. At high-heat duty values (> 3.6 kJ/g of feed ethanol) the azeotropic distillation column does not function properly, as the top stream condenses, giving only one liquid phase. High capital cost, high energy consumption, reliance on toxic chemicals like benzene and sensitivity to feedstock impurities are some disad-vantages of the azeotropic distillation process range [2].

5. Extractive Distillation Methods

Extractive distillation is another method for concentration of water-ethanol mixture to nearly anhydrous fuel grade ethanol. This type of dehydration can be carried out using either a high boiling sol-vent or an inorganic salt.

5.1 Extractive Distillation Using High Boiling Solvents

This extractive distillation method uses a relatively non-volatile liq-uid solvent which is fed into a distillation column some trays above the ethanol feed tray. The presence of the high boiling new compo-nent at relatively high concentration in the liquid on the trays alters the volatility of one of the feed components more than the other, so a separation of the feed components can be made in the column. Such a solvent is referred to as an extractive distillation solvent. A number of readily available relatively stable organic liquids have been used to produce dry ethanol by this method. Lee and Phal screened a series of solvents for extractive distillation and reported that promising solvents are glycerin, ethylene glycol, tetraethylene glycol, and triethylene glycol [25]. Furthermore, they reported that with a suitable solvent, such as ethylene glycol, anhydrous ethanol could be produced with only 18 theoretical trays. A low reflux ratio of 1.5 and a low solvent-to-feed ratio of 0.27 would be needed for the separation [25]. In addition to this, toluene, and furfural have also been used in this technique [2].

In the extractive distillation, added solvent might be the one which enhances the volatility of ethanol more than that of water. In this case, the ethanol would appear in the overhead product. Conversely, the solvent selected might enhance the volatility of water more than that of ethanol. In this situation, water would appear in the overhead product. Figure 2 shows a flow diagram of extractive distillation process for separating water from ethanol using ethylene glycol as the solvent [2].

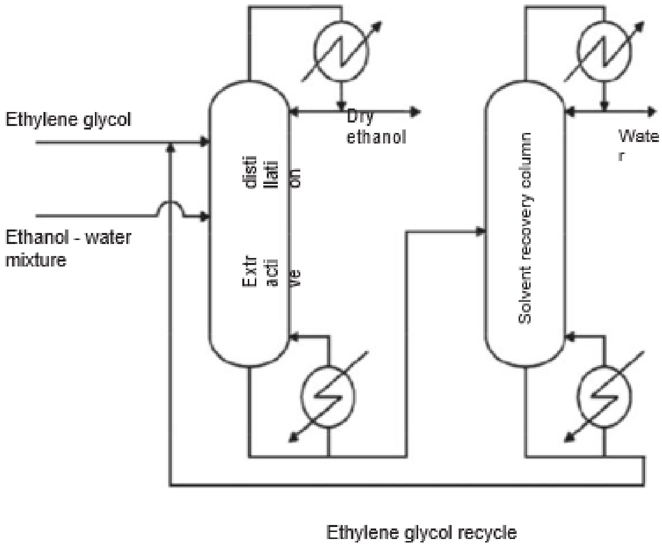

Figure 2. Dehydration of ethanol water mixture by extractive distillation using ethylene glycol. (Reprinted with permission from reference [2]).

In this type of extractive distillation process, a water-rich mixture from the bottom of the extractive distillation column is fed into a sol-vent recovery column, where high boiling ethylene glycol and water are separated. Water is removed from the bottom of this column, and ethylene glycol with some ethanol is fed back to the extractive distillation column. Extractive distillation with ethylene glycol as solvent has features of high quality of product and suitability for large-scale production, relatively less volatilization amount and lower consumption of solvent. However, there are a few weaknesses in high boiling solvent extraction technology such as the need to recycle a large amount of the high boiling solvent, which requires a large amount of energy. Brito and coworkers have used process sim-ulation methods for optimization of extractive distillation using eth-ylene glycol as the added solvent [26, 27]. As expected, the increase in the number of stages causes a reduction in energy consumption, even though it is a minor decrease. However, unlike the conven-tional distillation column, this is not always in line with the reduced reflux ratio, which shows once again the strong influence of solvent flow rate on the separation in extractive distillation [26].

5.2 Extractive Distillation Using Salts

Extractive distillation with soluble salt is another method for dehydration of ~90% ethanol. When a salt is dissolved in a liquid mixture like ethanol and water consisting of two volatile miscible liquid components, the salt may affect the activity of the two vola-tile components through the formation of liquid phase associations or complexes. If the dissolved salt associates preferentially with the molecules of one component of the liquid solution compared to those of the other, the solubility relationship between the two volatile components is altered such that one component is “salted out” in respect to the other. In the case of water ethanol mixture, more polar water molecules interact strongly with anions and cations of the salt making hydration spheres around cations and anions of the salt. In such a case, the activities of the two volatile components of the liquid solution are altered relative to each other in a man-ner which results in a modification of composition of the equilibrium vapor phase, regardless of the fact that no salt is present in the vapor phase. Therefore, extractive distillation by the use of a dissolved salt as the separating agent can be applied to systems of low relative volatility or systems exhibiting azeotropic behavior in com-position regions critical to separation. Most importantly, a comparatively small concentration of salt is capable of increasing the relative volatility of the more volatile component of the liquid solution to be distilled. This behavior is known as the salt effect, and is probably due to the preferential solvation of the ions by water molecules.

A number of common salts have been tested and shown effec-tive for extractive distillation of the ethanol-water system. These include calcium chloride [28], calcium nitrate, sodium iodide, potassium iodide, cupric chloride, cobalt (II) chloride [29], nickel (II) chloride, strontium bromide [30], sodium and potassium acetates as well as glucose [31]. Even though glucose is not a salt, it may work similarly by interaction with water via hydrogen bonding. The distillation set-up for the extractive distillation with soluble salts is basically similar to the extractive distillation arrangement with high boiling liquid solvents. The salt, a non-volatile compo-nent, is introduced at the top or near the top tray of the distilla-tion column, flows downward along the column, and is completely removed with the bottom product. There are a number of positive aspects of extractive distillation with soluble salts when compared to the extractive distillation with liquid solvents such as [2]:

1. High level of energy savings due to the absence of the vaporization–condensation cycle of the volatile liquid solvent (high boiling liquid separation agent) inside the column.
2. Production of a distillate totally free from the separa-tion agent – salt.
3. Lower toxicity level of certain salts in comparison to previously cited liquids such as benzene used in the production of dry ethanol.

The technique of using inorganic salts to break the ethanol-water azeotrope for industrial production of anhydrous ethanol from dilute solutions dates back to patents registered in the period of 1932–1934 [32]. Salt-assisted extractive distillation has been used in industry as far back as the 1930s, and it is reported that over 100 plants based on the process with production capacities of up to 43,000 tonnes/year were built between 1930 and 1950 in Europe and elsewhere. The anhy-drous ethanol produced was blended with gasoline to make gasohol containing 10% ethanol [33]. The last of these plants ceased operation in Brazil in 1965. Another example of salt-assisted extractive distilla-tion is the HIAG process, which was developed in Germany in the 1930s and used a mixture of sodium and potassium acetates as the extractant. The users of the HIAG process claimed lower capital and operating costs in comparison with conventional azeotropic distillation using benzene or extractive distillation using ethylene glycol [33].

6. Membrane-Based Pervaporation Methods

Pervaporation is another technique that can be used in the dehydra-tion of ethanol-water azeotropic mixture to fuel grade ethanol. In the pervaporation process, the membrane acts as a selective barrier between the two phases, the liquid phase feed and the vapor phase. It allows the desired component(s) of the liquid feed to transfer through it by vaporization. Separation of components is based on a difference in transport rate of individual components through the membrane. This process is used by a number of industries for several different processes, including purification and analysis, due to its simplicity and in-line nature. Typically, the upstream side of the membrane is at ambient pressure and the downstream side is under vacuum to allow the evaporation of the selective component after permeation through the membrane. The driving force for the separation is the difference in the partial pressure of the components on the two sides and not the volatility difference of the components in the feed.

The driving force for transport of different components is provided by a chemical potential difference between the liquid feed/retentate and vapor permeates at each side of the membrane. The retentate is the remainder of the feed leaving the membrane feed chamber, which is not permeated through the membrane. Separation of components in water-ethanol mixture is based on the differences in transport rate of individual components through the membrane. This transport mechanism can be explained using the solution-diffusion model based on the rate/ degree of dissolution of a component into the membrane and its velocity of transport (expressed in terms of diffusivity) through the membrane, which will be different for each component and membrane type leading to separation. A schematic diagram of a membrane pervaporation system is shown in Figure 3.

Membrane-based pervaporation is an emerging technology for the bioethanol industry and has the potential to reduce energy usage and operating costs [35–40]. In pervaporation, a fraction of the liquid feed is selectively evaporated, significantly reducing the amount of energy required relative to technologies in which the entire stream is evaporated. The ideal pervaporation membrane would achieve high permeability, high water selectivity, be easy to fabricate, and assemble into module forms. A number of research groups around the world have developed polymeric [41–52], inorganic [53–56], and composite membranes [57–59,48,60] for ethanol-water separations.

Polymeric membranes are attractive because they are relatively easy and economical to fabricate. However, polymeric membranes typically display a permeability–selectivity tradeoff. This is because permeability normally varies inversely with selectivity. Thus, membranes with desirable permeabilities often do not meet selectivity criteria. In addition, the performance of most polymeric water-selective membranes is a strong function of the water concentration. High water concentrations cause membrane swelling, resulting in higher permeabilities and lower selectivities. At low water concentrations, the benchmark dehydration membrane material, poly(vinyl alcohol) (PVA), becomes glassy and exhibits a very low water permeability. In addition, at low water concentrations, the driving force for transport across the membrane can be quite low, resulting in extremely low observed water fluxes. For example, the partial vapor pressure of water at 70°C in equilibrium with liquid ethanol containing 0.5 wt% water is only 7.5 Torr (1k Pa). Under these conditions, pervapo-ration experiments are challenging to perform. Also, most literature studies on ethanol dehydration by pervaporation focus on water concentrations at or above the standard azeotropic composition. Several research groups have studied the PVA membranes for dehydration of wet ethanol. Pervaporation data reported in the literature for selected PVA-based membranes evaluated at 10 wt% water and at similar temperatures are shown in Table 5.

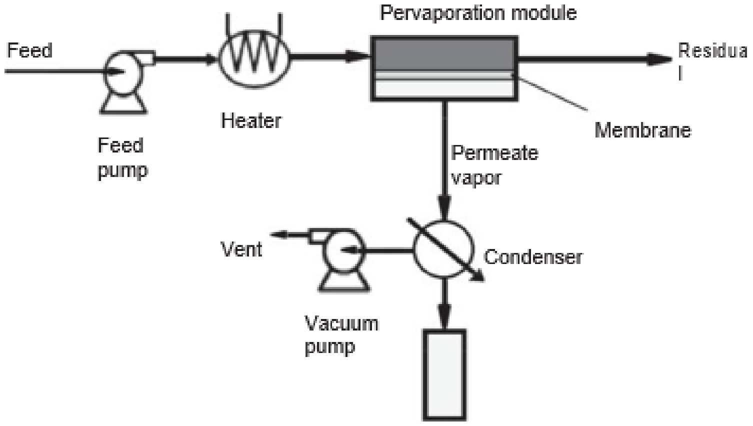

Figure 3. Schematic diagram of a membrane pervaporation system. (Reprinted with permission from reference [34]).

6.1 Direct Pervaporation of Ethanol from Fermentation Broth

In 2013 Gaykawad and coworker reported their studies on a novel approach for using pervaporation in dehydration of wet ethanol. In these experiments direct pervaporation of ethanol from lignocellulosic fermentation broth was investigated without using the traditional dis-tillation step. They postulated that this type of single-step operation can save energy and lower the production cost in the whole cellulosic eth-anol process. In these experiments, pervaporation experiments were performed using a commercially available PDMS (polydimethylsilox-ane) membrane obtained from Pervatech BV (Enter, the Netherlands) using fermented barley straw and willow wood hydrolyzates [67]. Pervaporation was carried out with three different lignocellulosic fermentation broths. The researchers noted that fermentation broths reduced the membrane performance by 17–20% as compared to a base case containing only 3 wt% ethanol in water. The membrane fouling caused by these fermentation broths was irreversible. Solutions con-taining model lignocellulosic components were also tested during pervaporation at the same conditions. A total flux decrease of 12–15% compared to the base case was observed for each component except for furfural. Catechol was found to be the most fouling component, whereas furfural permeated through the membrane and increased the total flux. Furthermore, Gaykawad and coworkers reported that membrane selectivity increased in the presence of fermentation broth but remained unchanged for all selected components [67].

Table 5

Performance of PVA-based membranes reported in the literature at 10 wt% water in feed (the values of some parameters were estimated by interpolation and/or calculated from other reported parameters).

Membrane	**Temperature (C)**	**Total flux (kgm^{-2} h^{-1})**	**Separation factor**	**Selective layer thickness used in permeability calculation (mm)**	**Water per-meability (kmolmm^{-2} s^{-1} kPa^{-1})**	**Reference**
PVA composite membrane (Deutsche Carbone AG/GFTa)	60	0.14	170	_	_	[61]
PVA composite membrane (Deutsche Carbone AG/GFTa)	80	0.68	100	_	_	[61]
PVA composite membrane (PERVAP 2201, Sulzer Chemtech)	60	0.1	100	_	_	[62]
PVA on ceramic support	70	1.25	35	0.5	0.58E−12	[63]
PVA, 95% hydrolyzed	70	0.086	88	30	2.6E−12	[64]
PVA, 99% hydrolyzed	50	0.20	50	20	9.2E−12	[65]
PVA blended with sodium alginate on ultrafiltration support	45	0.40	250	1.8	2.5E−12	[66]

7. Other Dehydration Methods

Distillation and dehydration of ethanol to the fuel grade product is an energy intensive process that requires significant improve-ments in the realization of large-scale economical cellulosic ethanol plants. A number of research groups around the world have stud-ed various alternative techniques, in addition to widely applied absorption methods and pervaporation methods currently under development. Some of these include:

1. Chemical dehydration process
2. Dehydration by vacuum distillation process
3. Diffusion distillation process

8. Comparisons of Common Dehydration Methods

There are several methods available for dehydration of wet ethanol to fuel grade nearly anhydrous ethanol. The choice of the method depends on the energy requirements and the capital cost of the technology. Dilute ethanol-water mixture is usually first concen-trated by fractional distillation to approximately 90% ethanol and then is dehydrated by one of the several processes discussed ear-lier to produce fuel grade ethanol. The energy requirements of ethanol purification by fractional distillation remain essentially constant for feeds containing more than 15–20 wt% ethanol and less than 92–94 wt% ethanol. As ethanol concentration in the feed decreases, the reflux ratio required must increase dramatically, and this results in increased energy requirements. The fractional distillation requires a disproportionate raise in energy at prod-uct concentrations above 92–94 wt% ethanol due to the shape of the vapor-liquid equilibrium curve for the ethanol-water system. Table 6 shows a number of common dehydration methods and also shows the amount of energy necessary to accomplish the water removal from aqueous ethanol as a fraction of energy in a kilogram of anhydrous ethanol.

The combustion energy of anhydrous ethanol is about 29.5 MJ/ kg, and the amount of energy required for drying ethanol as a per-centage of energy in ethanol is shown in the last column. Extractive distillation with ethylene glycol requires the highest amount of energy of 18.84 MJ/kg, and extractive distillations with salts require less energy compared to other distillation methods. Extractive distillations with calcium chloride require the least amount of energy of 5.02 MJ/kg.

Table 6. Energy consumption of various processes for dehydration of wet ethanol to fuel grade ethanol [2].

Type of process	**Energy consumption (MJ/kg ethanol)**	**Fraction of ethanol heating value (%)**
Azeotropic distillation		
Pentane	10.05	34
Benzene	15.49	38
Diethyl ether	12.56	43
Extractive distillation		
Gasoline	9.21	31
Ethylene glycol	18.84	64
Extractive distillation with salt		
Calcium chloride	5.02	17
Potassium acetate	9.27	31
Non-distillation processes		
Pervaporation	4.61	16
Adsorption on molecular sieve	0.528	0.89

The non-distillation processes for the production of anhydrous ethanol includes adsorption and membrane pervaporation. In comparison to all other methods, adsorption on molecular sieves requires only a distinctly small amount of energy of 0.528 MJ/kg, which is only 0.89% of the energy in processing equal weight of ethanol. This includes the energy required to regenerate the molecular sieve after adsorption of water from ethanol vapor containing 7.4% water, heat required to vaporize the feed, the energy needed to heat the regenerating air from ambient to an inlet temperature of 95°C and heat losses from the overall system. The heat of adsorption is retained in the bed if adsorption is stopped when the concentra-tion wave begins to leave the adsorption column. Hence, it is desir-able to adsorb up flow and regenerate by passing gas down flow, thus making use of some of the heat of adsorption stored at the upper part of the bed to drive off adsorbed water from the bottom of the bed. In 2008, Kaminski *et al*. reported a comparison of vapor permeation, pervaporation, azeotropic distillation and adsorption on molecular sieve processes on the basis of cost of production of anhydrous ethanol [68]. For small installations (100 dm^3/day) they showed the cost of ethanol dehydration by azeotropic distillation is twice as high in the case of adsorption, and 1.5 times higher than that in pervaporation.

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