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RESEARCH ARTICLE

MOLECULAR SIEVE DEHYDRATION: A MAJOR DEVELOPMENT IN THE FIELD OF ETHANOL DEHYDRATION TO PRODUCE FUEL ETHANOL

***[1]Nilesh, P. Patil, [1]Vilas, S. Patil and [2]Shashikant, L. Bhole**

[1]Division of Chemical Engineering University Institute of Chemical Technology, North Maharashtra University, Jalgaon, Umavinagar, P. O. Box No. 80, Jalgaon-425 001 (Maharashtra), India
[2]Division of Chemical Engineering, Shivajirao Jondhale College of Engineering, Dombivli (E)-421 203, Thane (Maharashtra), India

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ABSTRACT

Gasohol, a blend of ethanol and gasoline is a promising alternative to gasoline and has a great potential to come up as an environmentally clean fuel. Though anhydrous ethanol has various advantages, its generation is quite a difficult and costly task. The energy intensive technology ultimately results in an increased per liter production cost of bioethanol. Though the technology is costly, it is not capable of producing purely anhydrous ethanol. To be competitive, and find technical, economic acceptance, the cost for conversion of biomass to bioethanol must be lower than current gasoline prices. In this paper, a detail study of hybrid process that is capable producing an anhydrous ethanol of concentration more that 99.80% (w/w) is presented. It is well known that distillation alone cannot concentrate ethanol beyond its azeotropic point and finds economical acceptance up to 95% (w/w) ethanol only. On contrary, molecular sieves are able to concentrate ethanol to completely anhydrous state but finds economical acceptance for short span of 93–99.80% (w/w) ethanol. Complete dehydration by molecular sieves is never advisable. Therefore a new technology representing combination of simple distillation and molecular sieve dehydration is proposed. Paper also covers the critical review of different separation techniques available for dehydration of ethanol.

INTRODUCTION

In past few years, production of ethanol all over the world is gaining a momentum because of increased demand of ethanol in various sectors of economy. The remarkable applications of ethanol include fuel, beverage and industrial. It was observed that approximately 73% of worlds total ethanol production; corresponds to fuel ethanol, 17% to beverages and 10% for industrial (Sanchez *et al.,* 2008). It focuses on the fact that major share of the world's total ethanol is used as fuel or additive to it thereby extending the life of conventional fuel reserves. In addition to this, properties of ethanol like octane booster further encourage its use as fuel or additive to it. One of the indirect reason behind use of ethanol as additive is its less production cost as compared to its competitor MTBE (Thomas *et al.,* 2001). Addition of bioethanol in diesel results in a decrease in Cetane number, high heating value, aromatics fractions and kinematic viscosity of diesel fuel (He *et al.,* 2003).

****Corresponding author: Nilesh, P. Patil,***
Division of Chemical Engineering University Institute of Chemical Technology, North Maharashtra University, Jalgaon, Umavinagar, P. O. Box No. 80, Jalgaon (Maharashtra), India.

It is concluded that ethanol blended diesel (E-15) causes the 41% reduction in particulate matter whereas 5% in NO_X emissions (Subramanian *et al.,* 2005). Moreover high oxygen content (35%) of ethanol helps in complete combustion of fuel thereby reducing particulate emission in the environment. As far environmental aspects are concerned, the problem of green house gas (GHG) emissions arising through the burning of conventional fossil fuel is satisfactorily addressed by use of bioethanol. The negative impact of fossil fuels on the environment are rigorously studied (Hahn-Hagerdal *et al.,* 2006). It is reported that; bioethanol is an only transportation fuel that does not contribute to the green house gas (GHG) emissions (Foody, 1988). Additionally, GHG like carbon dioxide, released through the combustion of fossil fuels are captured and utilized by plants to synthesize cellulose during photosynthesis thereby aiding in the sequestration of carbon dioxide. Also the toxicity of the pollutants emitted through the burning of ethanol is lower than that of gasoline (Wyman *et al.,* 1990). Bioethanol significantly reduces the harmful GHG emissions causing potential reductions in ozone precursors by 20 - 30%. It is suggested that reduction in GHG emissions is the main motive for the application of bioethanol as a fuel (Demirbas, 2007). (Puppan, 2002) enlisted the different advantages of biofuels in his article. Besides its advantages, production of bioethanol is associated with few but influential limitations. The most important limitation in the production of biofuel is its economical incompetativeness with gasoline. On analyzing the production cost of corn based bioethanol, it is observed that approximately 29% more energy is required to produce a gallon of ethanol than the energy obtained from a gallon of ethanol (Pimentel, 2003). It is reported that early studies by the U.S. Department of Energy (USDOE) concerning bioethanol production from biomass reported a negative energy return (Pimentel *et al.,* 2007). He further quoted that these are the government subsidies that makes the bioethanol competitive. But providing subsidies for encouraging the production of bioethanol is neither a practical nor ethical way since the amount of these subsidies are recovered by imparting a heavy taxes on tax payers. Ultimately these subsidies are responsible for inflation in various sectors of economy. Additionally, it is observed that though anhydrous ethanol can be readily blended with gasoline; hydrated ethanol with more than 2% (v/v) of water is not completely miscible with gasoline. It demands complete dehydration of ethanol, which is impossible by distillation. Distillation can concentrate ethanol up to 95.63% (w/w) only. Further dehydration to remove remaining 4.37% (w/w) water requires special treatments. This further treatment adds costs to bioethanol production. The production cost of bioethanol is somewhat offset by by-products, such as bio-methane, bio-fertilizers in case of molasses and dry distillers grains (DDG) in case of corn. However, production cost analysis of ethanol from cane molasses without subsidies; is entirely opposite to that of corn. Production of bioethanol from cane molasses is somewhat competitive to conventional fossil fuels. The rigorous comparison can be made on the basis of use of feedstock as human food, cropland required, various treatments required in its conversion to bioethanol, types of energies required in its conversion, environmental pollutions caused and past production treatment processes.

The conclusions regarding economical benefits of bioethanol production are incomplete or misleading since only some of the factors that contributes to total energy calculation in the ethanol system are considered for the assessment. It put a more emphasis on the fact that the rigorous assessment of the bioethanol production cost including earlier mentioned parameters be done. Therefore to be competitive, and find economic acceptance, the cost for conversion of biomass to bioethanol must be lower than current gasoline prices. Therefore more attention must be given towards improvement in energy efficiency of biomass conversion technologies. The paper after rigorous review of available bioethanol production technologies; proposes a hybrid technology combining distillation with dehydration by molecular sieves. The paper explains the possible energy saving by hybrid technology.

Multi-Pressure Distillation (MPRD) Technology

In last few years, MPRD is a widely accepted technique for separation of ethanol from fermented wash in distillery. It consists of seven distillation columns, in which two columns are operated at pressure, three at vacuum and the remaining two are at atmospheric pressure. Only two columns operating at pressure are supplied with saturated steam to meet their heat requirement. The vapors from the top of these two columns are used as a source of heat for the three columns which are under vacuum and one column operating at atmospheric pressure. The remaining one column operating at atmospheric pressure is supplied by flash steam generated from the steam condensate. The operating parameters for MPRD are as shown in table.1. (Patil *et al.,* 2016a) analyzed the energy consumption in MPRD in terms of steam consumption and found to be reduced to 3.2 kg/liter of produced ethanol as compared to that of 5.8 kg/liter in atmospheric distillation. Mere application of heat integration in a process brings about 55% reductions in steam consumption. Obviously it will contribute some cost to process as a whole. This cost will be in terms of increased pressure of steam supply; the same is explained in table.2. (Cardona *et al.,* 2007) also signifies the importance of process integration in reducing the energy consumption in distillation.

It is also claimed that application of heat integrated distillation column (HIDiC) (Nakaiwa *et al.,* 2000) will significantly contribute to reduction in steam consumption to 3.0 kg/liter of produced ethanol; however the same was not proved experimentally. Besides its low energy consumption, MPRD is useful in concentrating the ethanol to azeotropic composition (95.63% ethanol and 4.37% water (w/w) at 78.15^{0}C) only. However, It is reported that distillation is effective for concentration of ethanol from 10–85% (w/w); further concentration from 85–96.63% (w/w) requires high reflux ratios and additional equipment which makes operation more expensive (Crawshaw *et al.,* 1990) Therefore efforts must be channelize to reduce further energy consumption in a process. Few researchers suggested direct vapor recompression to be one of the influential techniques in reducing the energy consumption in a process (Pribic *et al.,* 2006). But this system appears to be capital intensive and economically justifiable only in some large capacity plants operating above atmospheric pressure where low boiling temperature difference exists. Additionally application of newly designed trays brings significant contribution to the reduction in energy consumption. On studying the comparative performance of various types of trays it is concluded that movable valve trays (valve tray with movable flapper) offer better operating characteristics over conventional trays (Patil *et al.,* 2016b). As far as the domain of efficiency, capacity, turndown and maintenance is considered; movable valve tray performs great at slightly higher cost. For energy conservation in conventional distillation system, (Bhole *et al.,* 2016) further developed a new single stage distillation technique with artificial irrigation by external re-circulation pump. After successful testing of technique for methanol-water system, he concluded that irrigation in stage by external re-circulation pump offers significant enhancement in rectification and is clearly observed in terms of increased MVC (Methanol) concentration in distillate. Considering all the facts about distillation, it is observed that high energy consumption is perhaps the only weakness in distillation and can be eliminated to greater extent by the application of MPRD.

Molecular Sieve Dehydration (MSDH) Technology

MSDH Technology works on the principle of pressure swing adsorption. Electrostatic interactions and polarity between adsorbent and ethanol-water mixture are the basis for operation.

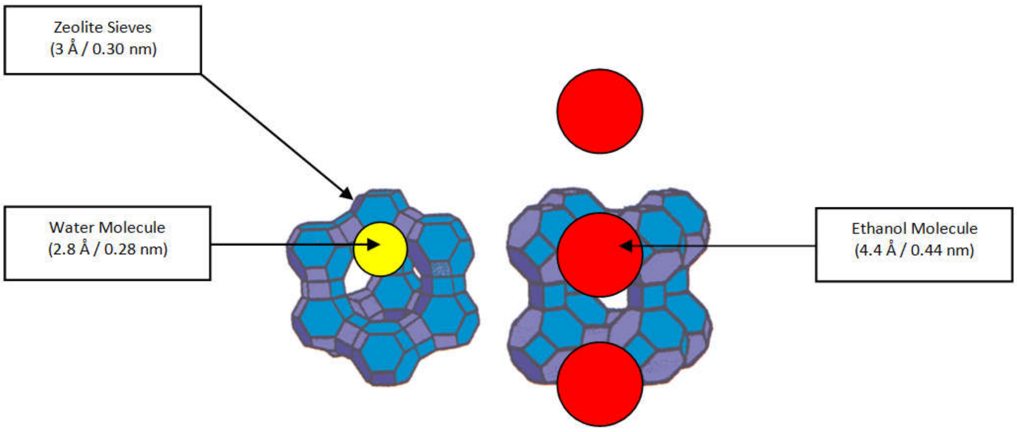

Figure 1. Schematic Diagram of the Pressure Swing Adsorption

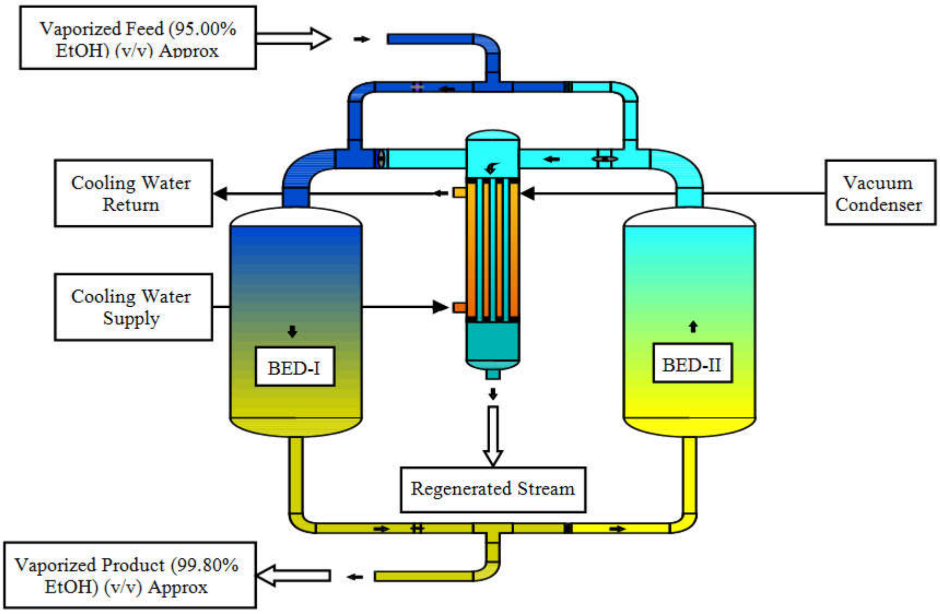

Figure 2. Schematic diagram for beds used in ethanol dehydration by molecular sieves

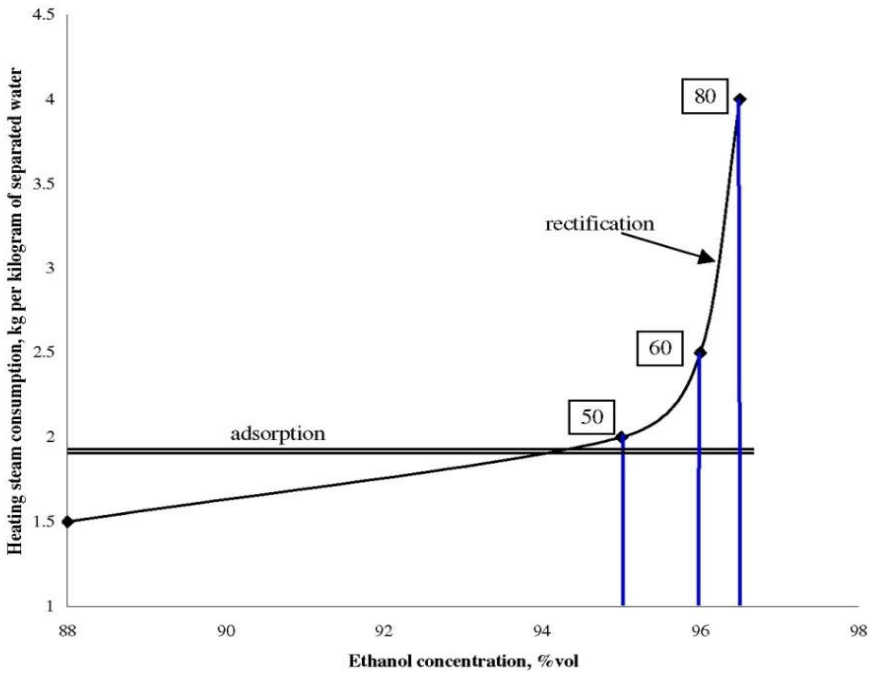

Figure 3. Graph representing the competitiveness of multi-pressure distillation and molecular sieve dehydration (adsorption) over operational range

Process consists of two adsorber columns (beds) filled with 3Å Zeolite molecular sieves; however sieves of any size ranging from 2.9 Å to 4.3 Å can be used. The continuous flow of ethanol-water vapor (approximately 95.63% (w/w) ethanol) is allowed to pass through sieve bed. These sieves, based on their specific pore size (3Å), retain the water molecules (2.8Å) from vapors of ethanol-water mixture thereby preventing ethanol molecules (4.4Å) from entering through it. Thus the water molecules enter through the pores and are trapped in the cages of the Zeolite as shown in Figure.1.

conventional dehydration processes and a good attempt in reducing the energy consumption over them (Jeong *et al.,* 2009) suggested that. The energy consumption of the process measured in terms of its steam consumption can still be lowered by applying liquid phase adsorption, since both liquid and vapor-phase adsorption are technically possible. However, vapor-phase adsorption which involves evaporation and superheating of the ethanol water mixture prior its exposure to the molecular sieve bed is usually preferred (Vane, 2008).

Table 1. Operating pressures and temperatures in MPRD (Patil *et al.*, 2016a)

Columns	Operating Pressure		Operating Temperature	
	Top	Bottom	Top	Bottom
Analyzer Column	0.47	0.55	73.0	82.0
Degassifying Column	0.45	0.47	72.0	73.0
Pre-Rectifier Column	2.20	2.42	98.0	125.0
ED Column	0.50	0.68	81.0	82.0
Rectifier Column	2.20	2.49	98.0	127.0
Recovery Column	1.013	1.213	78.0	105.0
Simmering Column	1.013	1.213	78.0	83.0

Table 2. Comparison of operating parameters for different separation techniques

Parameter	Atmospheric Distillation	Multi-Pressure Distillation	Molecular Sieve Dehydration	Hybrid MPRD + MSD
Product	Extra Neutral Alcohol	Extra Neutral Alcohol	Anhydrous Ethanol (Fuel Grade)	Anhydrous Ethanol (Fuel Grade)
Distillation Column	7	7	0	3
No. of Distillation Column Required Steam	7	2	0	1
Adsorption Column	0	0	2	2
No. of Adsorption Column Required Steam	0	0	2	2
Enrichment of Ethanol (From – To) %	10 – 96.5	10 – 96.5	96.5 – 99.5	10 – 99.5
Steam Requirement kg/liter Ethanol	5.8 kg	3.20 kg	0.6 kg	2.0 kg
Steam Properties Requirement	1.5 +/- 0.05 kg/cm2(g) at 128^0C	3.5 +/- 0.05 kg/cm2(g) at 148^0C	3.5 +/- 0.05 kg/cm2(g) at 148^0C	3.5 +/- 0.05 kg/cm2(g) at 148^0C
Flash Steam Generation	NO	YES	NO	YES
Heat Integration	NO	YES	YES	YES
Cooling Water Requirement	X* m^3/hr	0.55X* m^3/hr	0.1X* m^3/hr	0.5X* m^3/hr
*- X depends on case to case basis i.e. on plant capacity				

During pressurized adsorption step, water molecules from ethanol-water vapor, get adsorbed in the pores of molecular sieves whereas an unadsorbed ethanol vapor, free from water molecules leaves the column. These ethanol vapors, after leaving the adsorption column, get condensed and the condensed purely anhydrous ethanol is then collected in a tank. After certain interval of time, the column under adsorption gets saturated with water molecules. This saturated column is then subjected to desorption for regeneration of sieves. During regeneration of the column water is removed by depressurizing the column (by applying vacuum) and purging the bed with a portion of purified ethanol vapor. These sieves in the columns are alternately subjected to adsorption and desorption of water. MSDH is a promising alternative to

It will cause a considerable increase in its steam consumption, but still the energy consumption of the process is low as compared to other dehydration techniques. The basic difference in membrane processes and molecular sieves used for ethanol dehydration is that, the productivity of a membrane system increases with water concentration, while the productivity of molecular sieves decreases with water concentration (Cote *et al.,* 2009). Besides its few imitations molecular sieve dehydration remains the most favorable technique for ethanol dehydration. Adsorption of water on Zeolite is a strongly exothermic process. As ethanol water vapor enters the bed, rapid water adsorption followed by significant heat generation takes place. The possibility of using this released heat in evaporating the ethanol water mixture thereby reducing the overall steam consumption in a process can also be explored in near future. Though the process is associated with low energy consumption as compared to distillation; the use of MSDH for recovery of ethanol from fermented wash is never advisable since direct exposure of molecular sieves to fermented wash will result in chocking of the pores on sieves thereby reducing the sites for adsorption of water. MSDH has ability to dehydrate ethanol to the concentration of more than 99.8% (w/w) of ethanol. Figure.2. represents the working of molecular sieve beds used in ethanol dehydration.

Hybrid MPRD-MSDH Technology

The rigorous study of earlier two processes reveals that neither MPRD nor MSDH is capable of producing the purely anhydrous ethanol from fermented wash. MPRD is capable of recovering ethanol from fermented wash but unable to produce completely dehydrated ethanol; on contrary MSDH is capable of producing completely dehydrated ethanol but unable to recover ethanol from fermented wash. It means both these technologies have their own limitations in producing fuel ethanol. However a hybrid technology combining MPRD followed by MSDH has a potential to produce purely anhydrous ethanol. The only fact to decide in hybrid technology is the extent of concentration to which particular technology is used. Consider a graph as shown in figure.3, it cleares that as alcohol concentration in a rectified spirit increases beyond 95%, a rapid increase in energy consumption leading to infinity at azeotropic composition is observed. On contrary, energy consumption in molecular sieve dehydration is independent of ethanol concentration in rectified spirit. Graphical interpretation reveals that up to ethanol concentration of 94% (w/w), MPRD shows less energy consumption as compared to that of MSDH whereas beyond 94% (w/w), MSDH offers less energy consumption as compared to that of MPRD. Therefore a hybrid technology using MPRD up to 94% (w/w) and MSDH beyond it is the most advisable technique. It is observed that the hybrid technology has a potential to reduce steam consumption by 55% to its existing. This technology not only offers the energy savings but also simplifies equipment designs since the distillation column requires only 50 plates as compared to existing 80. It will results in a considerable saving in capital cost also. In overall, these technology offers, considerable savings in operating as well as capital costs thereby offering a least production cost per liter of bioethanol.

RESULTS AND DISCUSSION

Detail study and energy analysis of available dehydration techniques reveals that neither distillation nor sieve dehydration is able to produce purely dry ethanol from fermented wash. It means both these technologies have their own limitations in producing fuel ethanol. However a hybrid technology combining MPRD followed by MSDH has a potential to produce purely anhydrous ethanol with lowest energy consumption. Use of hybrid technology has a potential to reduce the steam consumption by 55% to its present. This technology not only offers the energy savings but also simplifies equipment designs since the distillation column requires only 50 plates as compared to existing 80. It will results in a considerable saving in capital cost also. In overall, these technology offers, considerable savings in operating as well as capital costs thereby offering a least production cost per liter of bioethanol. The comparative study of different parameters of different techniques is as presented in table.2.

Conclusion

The paper after rigorously analyzing the different aspects of dehydration technologies concludes that MPRD and MSDH both have their own limitations and hence unable in producing purely anhydrous ethanol; however the hybrid technology combining both MPRD and MSDH has great potential in energy saving. This hybrid technology is capable of concentrating ethanol from 10 - 99.8% (w/w) with minimum energy consumption as compared to total energy consumption of the individual processes. The hybrid technology seems to be reliable, convenient and economically optimized choice. The reduction in steam consumption is estimated to be 55% of its existing consumption. Moreover reduction in number plate's results in simplified equipment design thereby reducing the capital cost in manufacturing equipments. In overall, hybrid technology brings about reduction in both capital and operating cost thereby resulting in a significant reduction in per liter production cost of ethanol. it can be hoped that with application of this hybrid technology, bioethanol without subsidies could be competitive to gasoline.

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