International Journal of Emerging Technology and Advanced Engineering
Website: www.ijetae.com (ISSN 2250-2459, ISO 9001:2008 Certified Journal, Volume 5, Issue 11, November 2015)

Dehydration of Ethanol-Water Mixture Using 3a Zeolite Adsorbent

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***Abstract*— There are several methods of separation of water from dilute ethanol solution. Among the separation methods, adsorption process would be a simple and economical alternative. Zeolite type 3A molecular sieves have the largest surface area and it possess selective micro-pores whereon, due to the small size of their pores, the water molecules are adsorbed while the ethanol molecules are excluded. In this paper, adsorption of water from liquid phase water-ethanol azeotrope using 3-A zeolite molecular sieve adsorbents was investigated. The objective of this work was to increase concentration of alcohol of liquid water-ethanol mixture (azeotrope). The experimentation was carried out comparatively by soaking the adsorbents in azeotrope at rest and soaking with mechanical shaking. The experiment on adsorbent contact time (soaking) effect on azeotrope and its effect on concentration was studied. The Solar parabolic concentrator was used to regenerate the molecular sieve granules.**

***Keywords*—Adsorbent, Azeotrope, Ethanol, Molecular sieve, Adsorption, zeolite.**

I. INTRODUCTION

The recent depletion of fossil fuels along with the problem of global warming has made bio-ethanol receive an increasing attention as an alternative chemical source in addition to its potential for providing renewable energy. Distillation is a relatively simple technique used to purify liquids. Distillation is used to concentrate the alcohol in wines and other beverages obtained from the natural fermentation of fruits and vegetables

Various techniques have been developed to break the azeotrope of ethanol and water for preparation anhydrous ethanol, such as azeotropic distillation, extractive distillation, reactive distillation and adsorptive distillation. Among the methods, the adsorptive option is particularly attractive because of its low energy consumption, which takes up 50–80% of the overall energy required by the fermentative plan. Anhydrous ethanol is normally produced by distilling the solution.

Ethanol dehydration by adsorption requires far less energy than the conventional azeotropic distillation

Bioethanol purification process after the fermentation process was done in two stages, namely distillation and dehydration. Then dehydration can be carried out with molecular sieves. Of the purification processes used for bioethanol, dehydration consumes the most energy. Adsorptive dehydration is one of the most energy-efficient methods for this purpose.

Basic characteristic of an adsorbent material is a stronger affinity for one type of atom or molecule than for the other types. In the case of a molecular sieve ethanol dehydrator, we select an adsorbent with a strong affinity for water and little affinity for ethanol. When comes in contact, the desiccant adsorbs the water molecules but not the ethanol molecules from ethanol-water azeotrop. This process cannot continue indefinitely, because the desiccant has a finite capacity for water

Adsorbed component of the fluid is known as the adsorbate. To separate ethanol using adsorption from a feed mixtures containing ethanol-water, the mixture is contacted with the adsorbent and the water is more selectively adsorbed and retained by the adsorbent while ethanol is relatively un-adsorbed and is removed from the interstitial void spaces between the particles of the adsorbent and the surface of the adsorbent

Heat energy is also required to evaporate the liquid remaining in the void of the beds and raise the temperature of the adsorbent. All adsorption processes include two major steps, adsorption and desorption, and almost the process is named by the desorption step

Adsorbents used for drying liquids, such as silica gel, activated alumina, and molecular sieves. Unlike molecular sieves, silica gel and activated alumina have larger pores and a wide distribution of pore sizes in the range of 100 to 500 nm. The pores sizes of the zeolite molecular sieves type 3A, 4A, 5A, and 13X are 0.3, 0.4, 0.5, and 1.0 nm, respectively.

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Zeolites molecular sieve are widely employed in separating ethanol–water mixture. 3A zeolite molecular sieves which has a nominal pore size of 3 Angstroms (0.30 nm) can be used for dehydration of polar liquids such as ethanol. Water molecules, with an approximate molecular diameter of 0.28 nm, can easily penetrate the pores of the molecular sieve adsorbent, while ethanol, with an approximate molecular diameter of 0.44 nm, simultaneously retained

Teo and *Ruthven* confirmed experimentally that fuel grade ethanol could be produced by liquid phase adsorption of water from aqueous ethanol using 3A molecular sieves. The heat of adsorption could be stored in the bed of molecular sieve to be used subsequently in the desorption stage. Water adsorption is one of energy-efficient techniques that are widely used for dehydration of ethanol

Zeolite is a mineral consisting of SiO_2, AlO_2 groups and alkali-ions. It is capable of adsorbing water vapor and other gas molecules in the cavities of its complex crystal structure. Water content up to 25 % (kg water/kg zeolite) can be adsorbed and then the zeolite is heated up by the adsorption enthalpy. These processes are reversible. By heating up the zeolite to 150 -250^{o}C the water can be desorbed

Porosity plays a critical role in adsorption and desorption rates. The ethanol-water mixture must pass through the binder and zeolite particles, into the zeolite crystal and ultimately into the zeolite cage, where separation occurs

Zeolites are hydrated crystalline aluminosilicates that form a crystal with an ideal structure and uniform pore size following the hydration process. The pore size depends upon the type of zeolite, the cations present its structure and on the nature and conditions of the treatments that are carried out during the preparation

The molecular sieves can be used repeatedly and have the advantages of a high degree of dehydration, low energy consumption, permanence of the bed and the absence of harmful emissions to the environment. In addition to this molecular sieve has lower operating costs, no external chemicals required and gives high alcohol recovery.

In adsorption, molecules diffuse from the bulk of the fluid to the surface of the solid adsorbent forming a distinct adsorbed phase. These adsorbed molecules adhere to the surface of adsorbents due to weak cohesive forces called van der Waals forces. Separation by adsorption relies on one component being more readily adsorbed than the other. In an ethanol-water mixture, water is more readily adsorbed on zeolite than ethanol.

II. Materials And Methods

Ethanol used in this study was of 40 % (v/v) concentration range produced from fermented cashew apple juice and to increase the concentration of this ethanol, zeolite 3-A molecular sieve adsorption method was undertaken.

Table 1:
Absorbent characteristics

Adsorbent Type	Zeolite 3A
Shape	Sphere
Particle diameter	3-5 mm
Bulk density	779 kg/m3
Attrition / Abrasion resistance	< 0.15 %
Water adsorption capacity (17 mm of Hg)	23.5 %

In the initial stage, the adsorbents were tested for their liquid uptake and holding capacity, in which the experiments were conducted for the soaking of the adsorbent in azeotrope for different time periods. The liquid uptake for 15, 30, 45, and 60 minutes was 9.5, 6, 10.5 and 12.5 % respectively. It was observed that, when adsorbent comes in contact with azeotrope, as an immediate reaction it adsorbs the liquid but the rate of liquid uptake slightly decreased and then increased over an increase in soaking time. Hence it was decided to go for the larger retention time period and different method of soaking the adsorbent in azeotrope.

Procedure:

The zeolite 3-A molecular sieve granules were oven dried at 105°C for 24 hr, to make sure that all humidity within the crystals of molecular sieves gets evaporated.

The dried molecular sieves granules were kept in bottles, which then were stored in a glass chamber, to make sure that no humidity would be sorbed on the molecular sieves.

Ethanol-water azeotrope was analyzed for its initial alcohol concentration then samples were examined for its volume and weight determination.

Soaking at rest: In the first investigation method, the molecular sieve granules of 75 g weight were soaked in 150 g water-ethanol azeotrope in container and allowed to settle it for different time periods from 0 hr to 10 hrs.

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Shaking while soaking: In the second investigation method, the molecular sieve of 75 g weight was soaked in 150 g water-ethanol azeotrope in container and for different time periods from 0 hr to 5 hrs, the samples were stirred on a mechanical shaker.

Then sample was filtered through simple sieve and granules (solid) and solution (liquid) parts were separated.

Weight of molecular sieve granules and solution was measured and the alcohol concentration of solution was measured by using standard test procedure reported by Natu *et al*. (1986).

The investigation was carried out to check the feasibility of Parabolic Solar Concentrator (SK - 14 type) to use as regeneration technology for Molecular sieve granules. In this system solar radiation were concentrated at the focal point and used for heating the granules. The concentrating system followed the sun so that the sun rays were always focused on absorber surface. The temperature range inside the container of this system was 150 - 220^{o}C range without load.

To determine the water uptake of in zeolite 3-A molecular sieve granules, the weight difference of wet and dry adsorbent, weight difference of solution before and after soaking and also the initial and final alcohol concentration was investigated.

III. Results And Discussion

Observations:

It was observed that, colour of the ethanol-water azeotrope was changed, it may be due to the higher concentration of water and the longer retention time the adsorbent was slightly dissolved in azeotrope. During experiments heat was being released from the reaction when adsorbents were mixed with azeotrope, which known as heat of adsorption.

In the first investigation method that, soaking the adsorbents in azeotrope at rest for different time periods from 0 hr to 5 hrs, resulted in the alcohol concentration increase in the range of 8 to 14 % from the initial concentration. Water uptake was found to be higher for the 4 hour soaking at rest, but in first hour itself it gave satisfactory output. The trial showed the slightly increasing trend with increasing retention time for rest of the experiments.

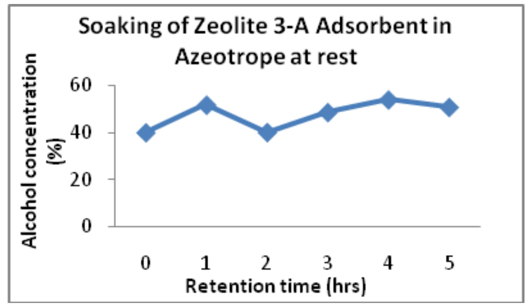

Figure 1. Effect of adsorbent soaking time on azeotrope concentration

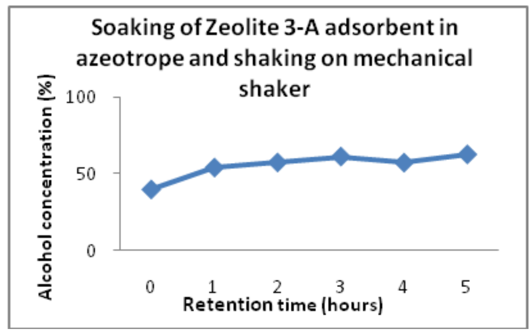

Figure 2. Effect of adsorbent soaking time on azeotrope concentration

In the second investigation method that soaking the adsorbents in azeotrope while shaking it on mechanical shaker for different time periods from 0 hr to 5 hrs, resulted in the alcohol concentration increase in the range of 14 to 21 % range from the initial concentration. Maximum water uptake was found for the 3 hours of mechanical shaking, but in first hour itself it gave satisfactory output.

Regeneration using the Parabolic Solar Concentrator (SK-14 type) in a single day could be possible and its performance was satisfactory. The temperature achieved inside the container during the regeneration process was in the range of 90 to 160^{o}C, and it was suggested that the slow heating can be effective from the life of granules point of view.

IV. Conclusion

1. Zeolite 3-A molecular sieve was able to adsorb water from ethanol-water liquid mixture range of 8 to 14 % at stationary soaking and 14 to 21 % by mechanical shaking.
2. Water uptake was fast within the first 60 minutes of adsorption.

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3. Regeneration of zeolite molecular sieve granules could be possible using Solar concentrating collector.
4. Zeolite 3-A molecular sieve has a potential for ethanol upgradation. Molecular sieve technology reduces energy requirement and leads to significant savings.

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Zeolite 3-A Molecular Sieve

Soaking at rest

Shaking while soaking

Azeotrpe before and after treatment