

Biofuel Production by Dehydration of Ethanol-Water mixture using Biobased Adsorbents

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ABSTRACT: Bioethanol is considered to be the most optimistic biofuel. Hydrated ethanol with more than 2% (v/v) of water is not completely miscible with gasoline, so complete dehydration of ethanol is required. Distillation alone cannot concentrate ethanol beyond its azeotropic point so various other methods are used to concentrate ethanol to completely anhydrous state in short span of 93-99.80% (w/w) ethanol. Among the separation methods, adsorption process is a simple and economical alternative. The potential of new Biobased adsorbents was assessed in separation of ethanol-water mixture. Biobased adsorbents such as bleached banana stem pulp, sodium hydroxide promoted soyabean meal and potato starch based adsorbents were used in this study. The water concentration in the feed solution was varied from 5% to 18% (weight basis). A glass adsorption column with an inside diameter of 1.54 cm was used to generate breakthrough curves to determine the effectiveness of the adsorbents. Heating jacket was provided to maintain the packed-column at constant temperature. In addition maximum water uptake and surface area of adsorbents were examined. Dehydration of ethanol vapour achieved is due to an interaction between free hydroxyl group of starch and the water molecules.

KEYWORDS: Bioethanol, molecular sieve, dehydration, biobased adsorbents.

I. INTRODUCTION

Ethanol fuel has potential of providing renewable energy that solves the major problems such as fossil fuels depletion and global warming [1]. Gasohol, a blend of ethanol and gasoline is a promising alternative to gasoline. The addition of ethanol to conventional fuel leads to decreased emissions of CO (carbon monoxide) and carcinogenic volatile organic compounds causing potential reductions in ozone precursors by 20 – 30 %. Furthermore, the ethanol, raises the octane number of gasoline, is an antiknock agent and also has high engine compression ratios that increase engine efficiency and performance [2]. In many countries the government provides strong support for Bioethanol programs which includes tax credits and regulations making use of biofuel obligatory. According to some estimates, a protective biofuel policy could ensure a fivefold increase in proportion of biofuel used in world transport [3]. Bioethanol is a clear, colorless liquid obtained from renewable sources, such as cellulosic biomass. Bioethanol can be produced from agricultural feedstocks like hemp, sugarcane and potato, as well as many types of cellulose waste. Several processes are being developed that are able to convert cellulosic biomass into Bioethanol by fermentation. To be competitive and for economical acceptance, cost for Bioethanol conversion from biomass must be lower than gasoline prices, so more attention is given towards improvement in energy efficiency of biomass conversion techniques[2]. For blending with gasoline ethanol to be used must be anhydrous since hydrated ethanol with more than 2% (v/v) water is not completely miscible with gasoline. Distillation can concentrate the ethanol up to azeotropic point but further dehydration technique adds costs to Bioethanol production.

The energy consumption in process of azeotropic distillation of ethanol-water azeotrope is about 88 kJ per m³ of ethanol, which is much higher than the energy consumption needed for the adsorption process using corn grits by 32 kJ per m³ of ethanol [4]. This clearly indicates that the adsorption is less expensive than the azeotropic distillation process

[5]. The energy efficiency can be improved by integrating a distillation process with a pertinent adsorption system [6]. One possible way is distilling fermentation strength ethanol to obtain 75–92 wt % ethanol–water product which is below the azeotrope (95.6 wt % ethanol) and then, using adsorption to obtain anhydrous ethanol.

Adsorbents having ability to adsorb water have already been studied. These include molecular sieves, chloride or oxide salts, silica gel, and starchy and cellulosic materials from biomass. The adsorbents currently used in industry are the commercial 3-A molecular sieves. The water saturated molecular sieves need high regeneration temperature in the range of 190–210 °C for regeneration. The biggest drawback with molecular sieves is the high cost of regeneration [7],[8],[9]. In addition disposal of exhausted molecular sieves is one more problem to the environment. It was found that biomass materials were generally less expensive to regenerate as compare to molecular sieves [10]. In addition, if regeneration was not practical and economical, the used adsorbents could be added as a feedstock of a fermenter to produce ethanol or biogas. Deposition of the biobased adsorbents is also environmental friendly as these are biodegradable [11]. This has driven the search for new and more efficient adsorbents, so use of natural materials as adsorbents has been investigated [12]. Ability of starch and cellulose in selectively adsorption of water is a result of interaction in the form of hydrogen bonding between free hydroxyl groups (-OH) units and the water molecules [13].

There has been an extensive research on using biobased adsorbents for ethanol dehydration process, and it has been reported that corn grits have been used for ethanol dehydration in the industry. However, use of corn puts pressure on food consumption. There is an incentive to find new cost effective biobased material sources for this application, which drives the current work. In this work, new biobased adsorbents that are able to separate the azeotropic water–ethanol mixture are developed. The water content in the feed solution was varied and the breakthrough curves of each water concentration were obtained. The isotherms of water sorption are also presented at different inlet water contents and maximum water uptake and surface area of adsorbents were also examined.

II. METHODS AND MATERIALS

Bench-Scale Packed Bed Adsorption

The glass adsorption column with an inside diameter of 1.54 cm and a length of 35 cm was packed with 10 g of adsorbent. The column wall temperature was maintained constant at about 90°C by circulating hot water through the jacket. The temperature of the mixture in the boiling flask was measured constantly using thermocouple. Ethanol–water mixtures of 300 ml in each run with various water contents were used as starting solutions and were heated from a 500-ml flask surrounded by an electric heating mantle. The vapor was passed through the column, and the exit stream was condensed using cold water. The condensate was removed after every two minutes analyzed for finding ethanol concentration. The average flow of the condensate was calculated for each run. The adsorbent was removed from the bed and dried for further use at the end of experiment. The adsorbents were efficient even after 5 cycles of the adsorption–drying process. The aqueous ethanol mixtures were prepared at four water levels, namely, 5 (the azeotropic concentration), 10, 14 and 18 wt%. The ethanol/water mixtures were blended using 200- proof ethanol and distilled water to make about 300 ml of solution as per required concentration at start of run. The time for completion of run depends upon the adsorbent and the feed composition.

Adsorbent Preparation

Bleached banana stem pulp

The raw banana fibers were washed with distilled water and then dried in an oven at temperatures of 70–80°C for 24 hours. The dried banana fibers were crushed and dried again. Banana stem fiber based adsorbents were prepared by pretreatment. This pretreatment include three stages mainly: dewaxing, alkali treatment and bleaching. Raw banana stem fibers were treated in soxhlet extractor for removal of wax and oil in dewaxing process. The alkali treatment was done on dewaxed fibers for removal of unwanted alkali soluble material. Bleached banana stem pulp which was used as adsorbent was produced after final treatment of bleaching.

Sodium hydroxide promoted soyabean meal adsorbent

The Soyabean meal is dried in oven at temperatures of 70–80°C for 24 hours. The dried soyabean meal weighted and added to the 0.1 M NaOH solution in ratio of 1:2. Small pellets of equal size were made from resulting mixture and used as adsorbent.

Potato starch based adsorbents

Corncoobs were cut into small pieces with a knife and washed with distilled water and then dried in an oven at temperatures of 70–80°C for 24 hours. The dried corncoobs were crushed and dried again. The dried corncoobs grits were then kept in bottles that are stored in a glass chamber containing silica gel to avoid moisture absorption. The wood powder dried in oven at 70–80°C for 24 hours. The baggase was dried in an oven at temperatures of 70–80°C for 24 hours and then grounded, sieved and again dried.

Potato starch is dissolved in 0.1 M NaOH and the mixture was stirred while being heated for 10 min. The dried and ground corncoobs were added to the mixture. For another adsorbent preparation instead of corncoobs wood powder added to potato starch and NaOH mixture. Similarly addition of baggase gave another adsorbent. The pellets of the mixture were used as the adsorbent in this study.

III. EXPERIMENTAL RESULTS

Biobased adsorbents were used to study the breakthrough behavior of water sorption using four different water concentrations of ethanol–water mixtures. The results are examined for water contents of 5, 10, 14, and 18 wt%, respectively. The final concentration of ethanol in sample also can be calculated from the density data as shown in Fig 1 and Fig 2. It is seen that the time required to reach a plateau value varies as a function of the inlet water content of ethanol–water mixture. It is important to emphasize that the data are plotted as (C/C0) versus time that is water content in effluent stream divided by initial water content, therefore, the breakthrough time varies depending on the initial water content. Calculation of partial equilibrium of water vapor and the water uptake on the adsorbent at each inlet water content allows determination of isotherms for such results.

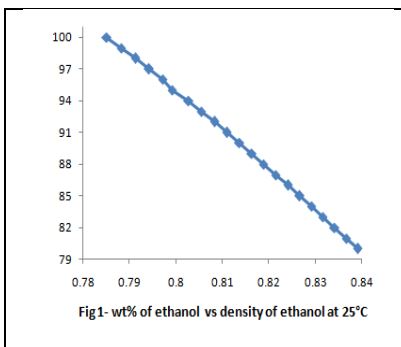


Fig1

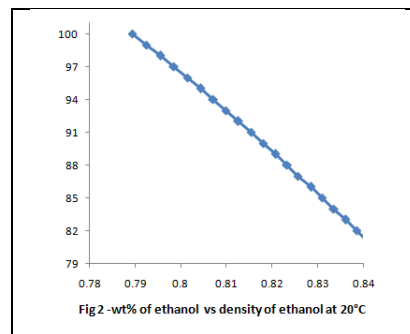


Fig 2

IV. CONCLUSION

Ligno-cellulosic materials possess strong affinity towards water. Their hygroscopic nature allows for the uptake of water molecules from ethanol-water mixtures. Adsorption isotherm of water over bleached banana stem pulp, sodium hydroxide promoted soyabean meal and potato starch based adsorbents, was constructed using a packed-bed adsorber. It was found that these adsorbents were able to selectively adsorb and removed water from ethanol vapor. The effects of operating conditions including temperature, vapor feed concentration, type of adsorbent, and adsorbent particle size on the adsorption performance were examined. It is concluded that among all Langmuir isotherm gives best result for water adsorption from ethanol-water mixture. It is possible to obtain anhydrous alcohol, with ethanol concentration higher than 99.5 %wt from lower grade feeds containing 80–95 wt % in this process. This study elucidates that banana stem fibers could be a raw material for preparation of adsorbent with target use of water adsorption. In conclusion,

water adsorption with cellulose-based adsorbent could be an economical technique to produce anhydrous ethanol in country with large area of banana plantation.

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