Cassava-Based Adsorbent for Removing Water from Ethanol Vapor

Panarat Tomanee, School of Chemical Engineering, Suranaree University of Technology

Abstract

Cassava pulp is a by-product of cassava starch production that contain sufficient amount of fiber and starch. This material, which is normally abundantly produced, is mostly sold very cheaply to animal feed manufacturers. When demand from animal feed industry is low, cassava pulp accumulates, rots and smells badly, especially in a humid rainy season. This causes serious odor pollution, an environmental problem commonly observed around cassava-starch factories.

Starch, starch-based material, cellulose, and hemicelluloses have been reported to have affinity for water and can selectively adsorb water from various organic solutions. It has beed demonstrated the separation of ethanol-water vapor mixture over cracked corn, starch, and carboxymethyl cellulose. Other biomass materials, including corn grits, corn meal, corn cobs, xylan, crystalline cellulose, and wood chips, have been shown to separate water from ethanol. Water was also removed from others alcohols such as methanol, isopropyl alcohol, and tert-butyl alcohol.

This research aims to study the potential of using cassava pulp as adsorbent for removing water from ethanol vapor. Parameters investigated include characteristics in water adsorption of cassava-based adsorbent in packed-bed adsorption column and adsorption capacity. Adsorption isotherm and breakthrough curve for water adsorption over this adsorbent are presented here. It is found that adsorbent prepared from cassava starch and pulp was able to selectively remove water from ethanol solution, and it was possible to obtain anhydrous alcohol, with ethanol concentration higher than 99.5 %wt from this process.

Introduction

Large quantities of water are produced during fermentation process for ethanol production. Anhydrous ethanol, i.e. solution with ethanol concentration of 99.5 wt% or higher, is required for automobile usage (Benson and George, 2005), therefore the water must be removed. Conventional techniques to remove the water are low-pressure distillation and azeotropic distillation with third component addition. However, it has been reported that distillation of ethanol could consume up to 50% of the overall energy used in a typical grain alcohol plant. Distillation of water-ethanol mixture to a concentration near azeotrope, followed by adsorption to remove the remaining water, referred to as dehydration step, has proved to be more energy-efficient alternative. The energy consumption in azeotropic distillation of ethanol-water azeotrope is about 88 kJ per m³ of ethanol, which is higher than the energy consumption needed for the adsorption process using corn grits by 32 kJ per m³ of ethanol (Ladisch and Dyck, 1979).

Adsorbents that readily adsorb water have already been studied, and some are being used commercially. These include molecular sieves, chloride or oxide salts, silica gel, and starchy and cellulosic materials from biomass, such as corn grits, ground corn, potato starch, maize starch, wheat straw. It was found that biomass materials were generally less expensive to regenerate when compared to molecular sieves (Ladisch and Tsao, 1982). In addition, if regeneration was not practical and economical, the spent adsorbents could be used as a feedstock of a fermenter to produce ethanol. Deposition of the biobased adsorbents is also environmental friendly as these materials are biodegradable (Benson and George, 2005).

There are two types of starch, amylose and amylopectin (Kyle and Ladisch, 2001). Amylose consists of D-glucos units bound together by α -1,4 O-glucosidic bonds and has about 9-20 α -1,6 O-glucosidic branch point on each amylose chain. Amylopectin is similar to amylose but it has many more α -1,6 O-glucosidic branches. Starch's ability to adsorb water is a result of interaction between free hydroxyl (-OH) groups on the glucose units and the water molecules, as depicted in Figure 1.

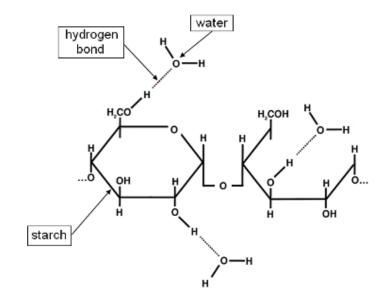


Figure 1. Hydrogen bonding between starch and water

Cassava pulp is a by-product of cassava starch production that contain sufficient amount of fiber and starch. This material, which is normally abundantly produced, is mostly sold very cheaply to animal feed manufacturers. When the demand from animal feed industry is low, cassava pulp accumulates and rots, causing a serious strong odor problem, which is an environmental problem commonly observed around cassava-starch factories. to community near cassava starch plant, especially during a humid rainy season.

In this work, starch-based adsorbent capable of removing water from ethanol vapor was developed. It was found that adsorbent prepared from cassava pulp was able to selectively remove water from ethanol solution. Efficiency of adsorption is affected by particle size of the adsorbent, as well as the starting concentration of ethanol feed. Isotherm for water adsorption over this adsorbent is also presented and discussed here.

Materials and Methods

Adsorbent Preparation

Cassava-based adsorbents were prepared in-house by mixing cassava starch and dried cassava pulp at a weight ratio of 1:1 with a solution of 0.1 M NaOH. The mixture was heated for partially gelatinization of the starch before being dried for 12 h in an airconvection oven at 105°C. The dried mixture was then ground and sieved. The adsorbents used in this study have the particle size in a range of 30-40 mesh.

Bench-Scale Packed Bed Adsorption

A bench-scale packed bed adsorber is shown schematically in Figure 2. Adsorption column with an inside diameter of 2.54 cm and a length of 18 cm was packed with 60 g of adsorbent. Column wall temperature was maintained at 85°C by circulating hot water through the jacket. Ethanol-water mixtures 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 water as a cooling medium. The condensate, with an average flow rate of about 0.8 ml/min, was removed every 10 minutes and was analyzed for ethanol concentration using Abbe refractometer.

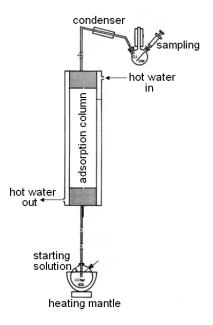


Figure 2. Schematic diagram of bench-scale packed bed.

Scanning Electron Microscopy

Adsorbent samples were fixed on a metal stubs and coated with gold. The morphologies of the samples were then observed using a JEOL JSM-6400 scanning electron microscope operating at 20 kV

Result and Discussion

Breakthrough curve of water from 90 %wt ethanol solution was shown in Figure 3 as an example of breakthrough curves obtained in this study. C/C_0 denotes ratio of water concentration in the condensate to that initially present in starting solution. It can be seen that the adsorbents were able to selectively adsorbed water from ethanol, and it was possible to obtain anhydrous alcohol, i.e. solutions with ethanol concentration higher than 99.5 %wt when this method was used for dehydration of ethanol vapor.

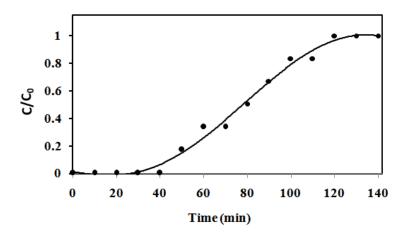


Figure 3. Breakthrough curves demonstrating adsorption characteristics of water over cassava-based adsorbents.

Isotherm for water adsorption was constructed using results obtain from breakthrough curve of water over cassava-based adsorbent. In this study, highest water uptake of about 0.06 $g_{H2O}/g_{adsorbent}$ was achieved. This value, however, could be increased with increasing starch content in the adsorbents

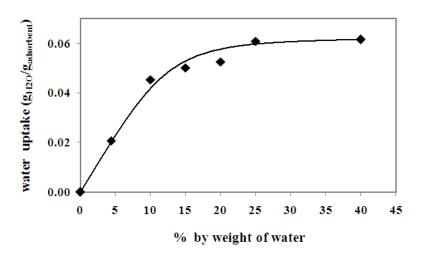


Figure 4. Isotherm of water adsorption on cassava-based adsorbent.

SEM image of cassava-based adsorbent is as shown in Figure 5. Starch can be seen as spherical particles with various sizes. Partially gelatinized starch can also be seen here.

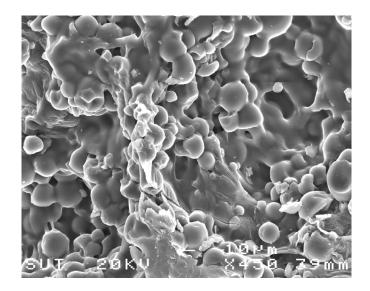


Figure 5. SEM image of cassava-based adsorbent.

Conclusion

Adsorption isotherm of water over cassava-based adsorbents, prepared from cassava starch and cassava pulp, was constructed using a bench-scale packed-bed adsorber. It was found in this study that the adsorbents were able to selectively adsorbed and removed water from ethanol vapor, and it was possible to obtain anhydrous alcohol, with ethanol concentration higher than 99.5 %wt from this process.

References

- 1. Benson, T.J. and George, C. E. (2005), "Cellulose based adsorbent materials for the dehydration of ethanol using thermal swing adsorption," *Adsorption*, 11: 697-701.
- 2. Ladisch, M. R. and Dyck, K. K. (1979), "Dehydration of ethanol: new approach gives positive energy balance," *Science*. 205: 898-900.
- 3. Ladisch, M. R and Tsao, G.T. U.S. Patent No. 4,345,973, 1982.
- 4. Kyle, E.B. and Ladisch, M. R. (2001) Chemistry and properties of starch based desiccants," *Enz. Microb. Technol.* 28: 573-581.