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Xien Hu[a]; Weiguo Xie[a]
[a] Institute of Nuclear Energy Technology, Tsinghua University, Beijing, People's Republic of China

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FIXED-BED ADSORPTION AND FLUIDIZED-BED REGENERATION FOR BREAKING THE AZEOTROPE OF ETHANOL AND WATER

Xien Hu* **and Weiguo Xie**

Institute of Nuclear Energy Technology, Tsinghua University, Beijing 102201, People's Republic of China

ABSTRACT

Two kinds of Chinese cornmeal used as the adsorbent of a fixed bed were examined with a pilot test system for breaking the azeotrope of ethanol and water. The results showed that the adsorption capacity of water depends on the vapor superficial velocity in the fixed bed, the temperature, and the particle size distribution of cornmeal. When 99.5 wt.-% ethanol at outlet was defined as the breakthrough point in a fixed bed, the adsorption capacity of water was 0.014–0.025 g water/g adsorbent. The service time equation was also given. Instead of down-flow drying in general fixed-bed, up-flow fluidized drying was developed for regeneration. The fluidization would favor the regeneration process in controlling channel and speeding up the operation. It is expected that the Chinese cornmeal as a renewable material would be commercially used in the near future.

Key Words: Adsorption; Adsorbent; Cornmeal; Anhydrous ethanol.

*Address correspondence to Xien Hu. E-mail: huxien@mail.tsinghua.edu.cn

INTRODUCTION

To break the azeotrope of ethanol and water and prepare anhydrous ethanol, many processes have been developed for fermentation ethanol recovery. The process used most in industrial scale is azeotropic distillation with benzene or extractive distillation with ethylene glycol and salt, such as potassium acetate. For all the distillation processes a reflux ratio over 2 should be used. Furthermore, the solvent recovery system attached is also a distillation process, so that the energy consumption is considerable (1). On the other hand, benzene is poisonous and flammable, so the azcotropic distillation is not satisfactory. Although the membrane pervaporation process was developed as an alternative technique, the energy consumption for ethanol product is still high. For those reasons, the adsorption process in vapor phase to produce anhydrous ethanol from the azeotrope of ethanol and water has been developed since 1980s. The advantage of the vapor phase adsorption process over distillation is lower energy consumption, because only one-time vaporization is needed without reflux. The comparison of energy consumption for the production of anhydrous ethanol by various processes and a comprehensive review were given by Serra (2).

Many solid materials were tried as adsorbents. The molecular sieve has high separation factor for ethanol and water, but the adsorption temperature is as high as 120°C, and the desorption temperature is over 200°C (3). The cornmeal as a potential starch adsorbent is attractive not only due to the moderate operation temperature and low cost, but also because it is a biodegradable material derived from renewable resources. The research on cornmeal has been active in recent years to extend the scope of application and modify the property (4). The adsorption isotherm of ethanol–water on cornmeal using a small-bore column under isothermal condition was given by Hong (5). In order to develop a commercial process a bench scale study and a pilot scale adsorption experiment were carried out by Ladisch. The temperature profile and the concentration profile in a fixed-bed adsorber were also determined (6,7).

Corn is a biomass material, and the composition of corn that comes from various areas is also different. Therefore, the adsorption property of the cornmeal might be affected by the production area. The fixed bed is available for adsorption, but the uniformity of packed adsorbent in fixed bed would make a notable impact on adsorption. When a channel appears in the bed or along the bed wall, it would cause short contact between vapor and adsorbent. The down-flow drying in fixed bed was used for regeneration in Ladisch's work (6). It was known that the channel in a fixed bed operating for a long time would usually appear. The aim of this work is to experimentally examine the adsorption behavior of Chinese cornmeal for ethanol–water separation and to improve the regeneration process by fluidization.

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EXPERIMENTAL

Materials

The cornmeal used as adsorbent was prepared from corn planted in Hebei province and Heilongjiang province, which are the main corn-producing area in China. The two kinds of cornmeal were named the Hb cornmeal and the Hl cornmeal, respectively. The corn was ground and sized by a sieve shaker to obtain suitable size for use in this work.

The AR grade 95 wt.-% ethanol and anhydrous ethanol as reference reagent were produced by the Beijing Chemical Corp. The ethylene glycol of the industrial grade was used in the bath of the experimental system.

Apparatus

A fixed-bed adsorber for the pilot test was made up of a glass pipe of 102 mm inside diameter (i.d.) and 100 cm in length with a jacket for ethylene glycol bath and flanged connection outlets. The adsorbent in the fixed bed was supported by a sieve plate and glass beads of various sizes. The top of the fixed bed was free, so that the bed can be operated in fluidization for regeneration. An electroheating boiler of 15 L made of stainless steel was connected with the bottom of the bed. The outlet pipe of vapor from the top of the bed was wound by an electroheating belt to keep the vapor temperature above dew point. The ethylene glycol bath system was composed of an electroheater, a thermostat, and a recycling pump. The pressurized air through a flowmeter and a silica gel bed was used for regeneration (see Fig. 1). In the preparative experiment for selecting suitable operation condition, the setup was similar to the pilot test apparatus, but a fixed-bed adsorber with an i.d. of 25 mm was used.

Procedure

In this work the breakthrough curve of adsorption for the fixed bed was determined experimentally under each condition, while changing the vapor superficial velocity, temperature, and particle size of the cornmeal. The azeotrope of ethanol and water, 95.6 wt.-% ethanol, was filled in the boiler located at the bottom of the fixed bed in order to keep the constant composition of the feed vapor and exclude the rectification effect in the boiler. The operation procedure

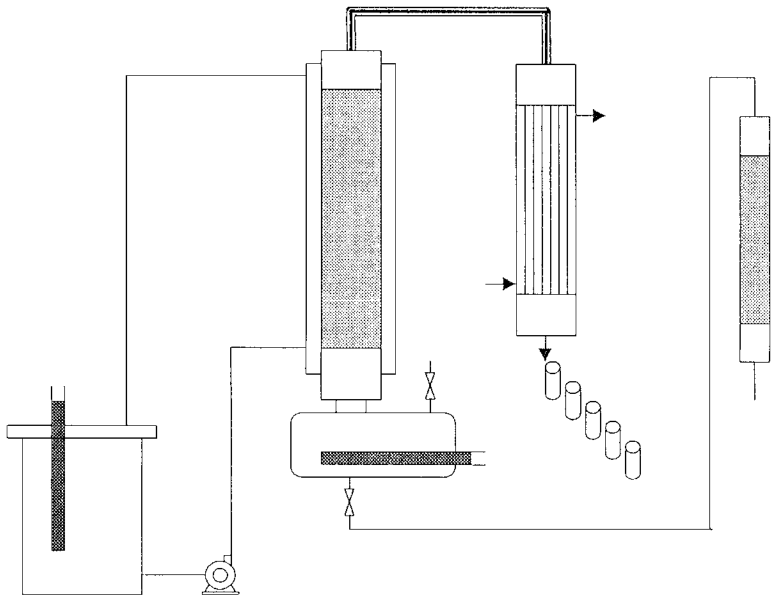

Figure 1. Fixed-bed adsorption system.

was as follows. First, by heating the ethylene glycol in the bath loop, the fixed-bed adsorber was preheated to attain the set temperature. Then, by heating the boiler to boiling temperature, the vapor of ethanol–water passed through the fixed bed. The vapor velocity was controlled by the voltage of the electro-heater in the boiler. The condensate of the vapor from the outlet of the fixed bed was collected by a step-sampler at set interval. The superficial velocity of the vapor in the fixed bed was obtained by the condensate flow rate under the steady state.

For regeneration operation, the feed was discharged from the tank located at the bottom of the fixed bed, then the fixed bed was heated to 105°C. The preheated air passed through a silica gel bed for drying, then flowed upward into the fixed bed. The up-flow operation was used for recovery of the ethanol held in the bed by the condenser located at the outlet of the fixed bed.

The water content in samples was determined by Karl-Fisher titration, and an MCl Model CA-01 titrator, made by Ikegami Tsushinki Co., Japan, was used. It should be noted that the condensate reflux into the fixed bed would destroy the adsorption operation of the fixed bed.

RESULTS AND DISCUSSION

Selection of Suitable Operation Condition

In the preparative experiment for selecting suitable operation conditions, the variables were the vapor superficial velocity in the fixed bed, the temperature, and the particle size of cornmeal. The plateau length and the height of the breakthrough curve were taken as the criterion of suitable operation for each condition. The product of the plateau length by the height means the obtained amount of anhydrous ethanol in adsorption.

Vapor Superficial Velocity in Fixed Bed

The 25-mm i.d. fixed bed was packed with 60 g cornmeal. The bed length was 20 cm, and the bath temperature was 100°C. The breakthrough curves were determined at the sampling flow rates, 1.5, 2.1, and 3.4 mL/min corresponding to the superficial velocities of 4.4, 6.1, and 9.9 cm/s, respectively. It was shown that ethanol over 99.5 wt.-% was obtained for 6.1 cm/s, whereas lower-content ethanol was obtained for other superficial velocities, as shown in Figure 2.

The vapor superficial velocity in the following adsorption operations was then set to about 6.1 cm/s. The drying of ethanol vapor by adsorption on cornmeal is dominated by mass transfer rate of ethanol and water (8), so that the vapor

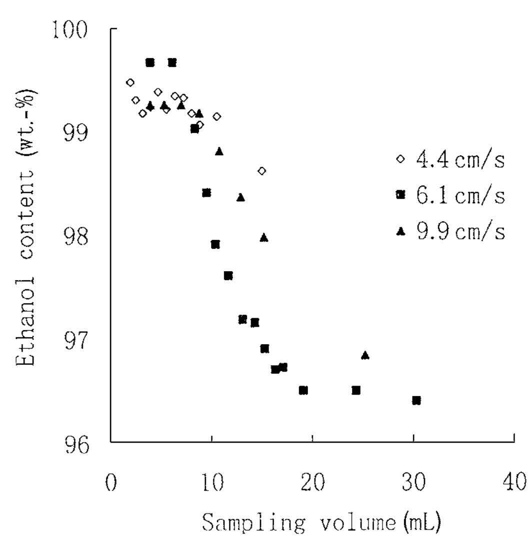

Figure 2. Breakthouth curve at variable vapor superficial velocity.

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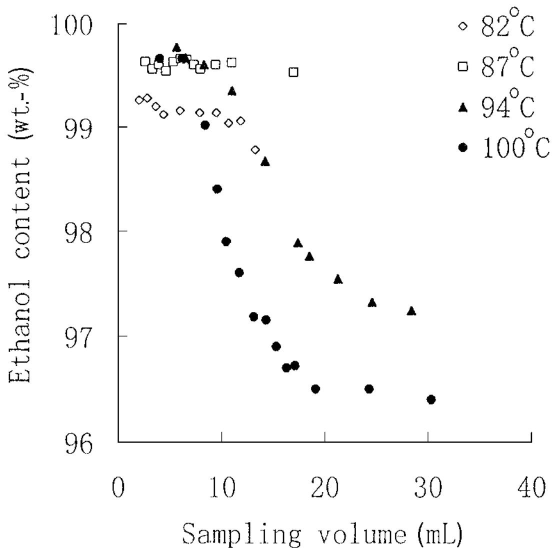

Figure 3. Breakthouth curve at variable temperature.

superficial velocity would be a sensitive factor. According to the Van Deemter plot of gas chromatography, the relation between height equivalent to one theoretical stage (HETS) and gas superficial velocity has a valley (9). Based on the these reasons, a suitable vapor superficial velocity would exist for the adsorption process.

Fixed-Bed Adsorber Temperature

Keeping the vapor superficial velocity at about 6.1 cm/s, the breakthrough curves corresponding to 82, 87, 94, and 100°C were determined, respectively. It was found that except for 82°C, the plateau length of the breakthrough curve is getting shorter with rising temperature, as shown in Figure 3. The fixed-bed absorber should be operated at a temperature that will keep the vapor in overheated state and exclude condensation. The adsorption was poor at 82°C; one possible reason was that reflux of condensate occurred in the outlet pipe of the fixed bed at the lower temperature. But if the temperature is too high, desorption of water from cornmeal would be favored. Therefore, the operation temperature was set at 87°C.

Cornmeal Particle Size

The Hb cornmeal was sieved and grouped in three groups: <40 mesh, 40–60 mesh, and 60–100 mesh. The breakthrough curve was determined

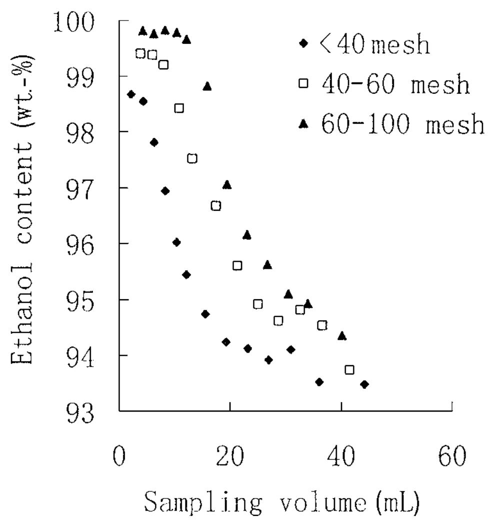

Figure 4. Breakthouth curve at variable particle size.

experimentally for each group at 87°C and the vapor superficial velocity of about 6.1 cm/s. The 60- to 100-mesh group gave better results, as shown in Figure 4. When the size was over 100 mesh, the adsorpton operation failed because of high pressure drop in the fixed bed. The cornmeal particle size distribution would have an effect on adsorption in a complex way, such as the surface area, voidage, vapor flow rate, and pressure drop in the fixed bed.

Adsorption Capacity

The water adsorption capacity of the fixed bed was determined by the breakthrough curve under the condition indicated above. The vapor superficial velocity was about 6.1 cm/s, the fixed-bed temperature was set at 87°C, and the cornmeal particle size was in the range of 60–100 mesh. A fixed bed with an i.d. of 25 mm by depth of 64 cm was used in the experiment. The breakthrough curves for Hb cornmeal and Hl cornmeal are given in Figure 5. It was found that the adsorption capacities were roughly the same for the two kinds of Chinese cornmeal, but the Hb cornmeal saturated by ethanol-water vapor was blocked occasionally.

Based on the mass increment of the packed adsorbent at the breakthrough point, the composition and mass of feed and product, the adsorption capacity of water was calculated by mass balance. For the Hb cornmeal it was 0.014 g water/g adsorbent, which was much lower than the static adsorption capacity (10). Compared with the adsorption capacity range of 0.010–0.115 g water/g adsorbent

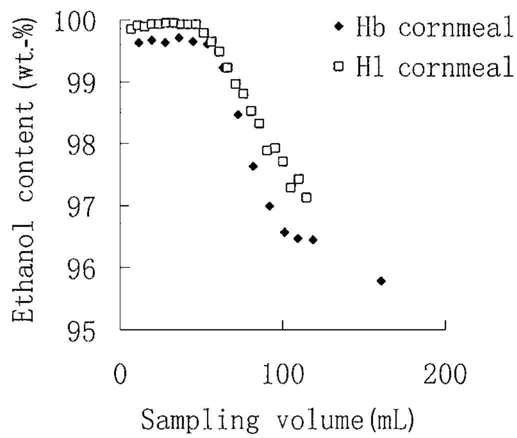

Figure 5. Breakthouth curve of Hb or Hl cormeal.

given by Ladisch (6), this adsorption capacity was located in the lower side, because the 99.5 wt.-% ethanol at outlet was defined as the breakthrough point in this work. When water was adsorbed in the fixed bed, ethanol was simultaneously adsorbed on the surface of the cornmeal. The adsorption capacity of ethanol was also given by the above calculation, which was 0.060 g ethanol/g adsorbent. It should be noted that recovery of the ethanol held on the adsorbent would be important in regeneration.

Fluidized-Bed Regeneration

At first, in order to keep the uniform packed density, the top of the fixed bed was filled with glass beads as described in Ladisch's work (6). Unfortunately, it was found that the breakthrough curve was poor for the 102-mm i.d. fixed bed, and the plateau zone was declined; that meant the yield of ethanol over 99.5 wt.-% decreased, Figure 6. The reason was that the visible channeling flow occurred between the bed and the wall. After the glass beads located at the top of the fixed bed were taken out, the upper surface was kept free, and the up-flow air made the fixed bed fluidized, the regeneration operation was improved. The fluidization regeneration has advantage over the down-flow fixed-bed operation as follows: 1) having uniform and loose packed density of adsorbent and depressing channel flow and 2) setting higher air velocity to speed up the regeneration operation. Of course, a suitable separating space above the fixed bed is needed, and excessive fluidization should be avoided. The fluidization curves of fixed-bed adsorber for several bed lengths were shown in Figure 7, which were similar to those of general fluidized bed. To decrease the loss of adsorbent in fluidization, lower superficial

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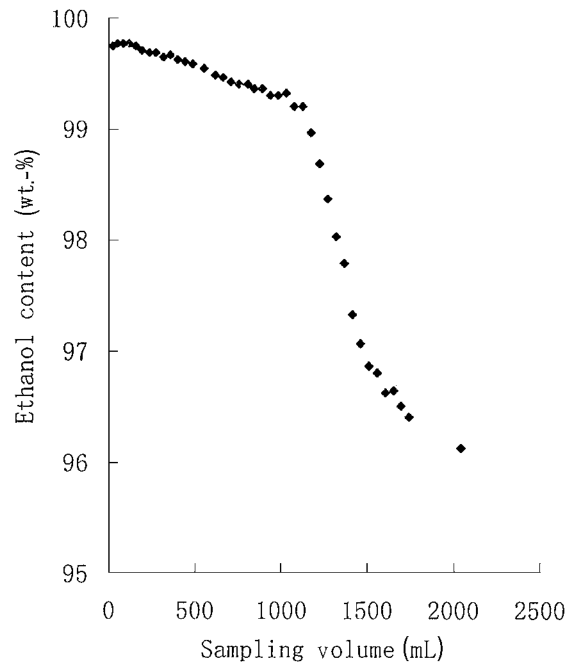

Figure 6. Breakthouth curve of Hl cormeal by down-flow fixed-bed regeneration.

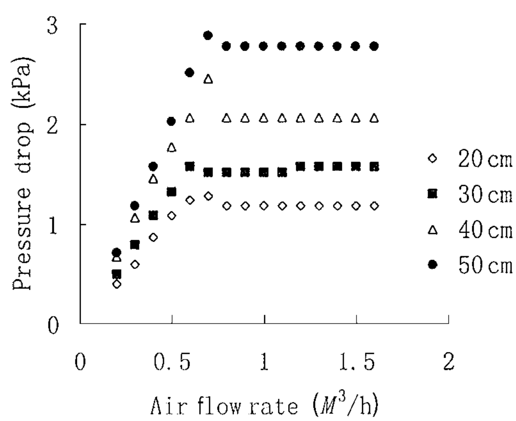

Figure 7. Pressure drop of variable-bed depth.

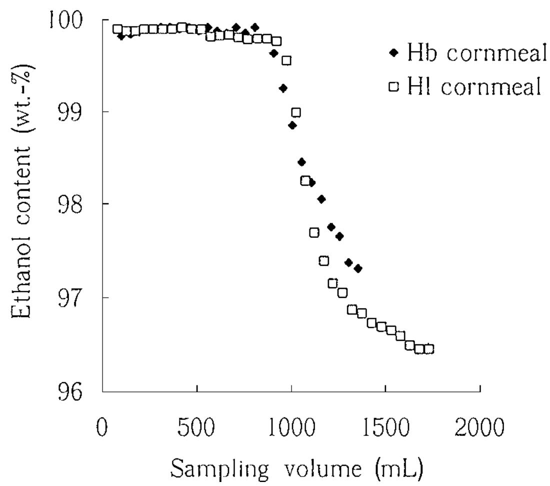

Figure 8. Breakthouth curve by fluidized-bed regeneration.

velocity of air was set, and the fluidized bed worked in the bubble zone having a stable pressure drop. The pressure drop for the depth of 50 cm and the air velocity of 2.7 cm/s was 2.7 kPa.

By using the fluidization regeneration, the adsorption operation of the fixed bed was remarkably improved in stability, as shown in Figure 8. The pilot test system packed with Hl cornmeal worked successfully with the cycle of fixed-bed adsorption and fluidized regeneration for a long time. Even in summertime with high humidity, the adsorption capacity of water for the fixed bed was almost unchanged.

Service Time Equation

For scale-up design, the convenient approach should be the service time equation that gives the relation between adsorption bed depth and service time (11). When both the vapor superficial velocity and the feed composition are constant, the adsorption bed depth, H, in cm, would be proportional to the service time, T, in min.

$$T = \frac{x^{*}\rho_{\mathrm{a}}}{uc} H - T_{\mathrm{o}} \tag{1}$$

In the equation, x^{*} is the adsorption capacity at the breakthrough point, ρ_{a} is the density of adsorbent, u is the vapor superficial velocity, c is the feed composition or water content, and T_{o} is the ordinate intercept. In this work, the breakthrough point or service time was defined as the time when the ethanol composition at the

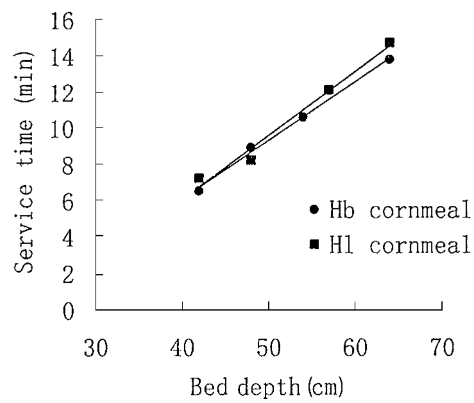

Figure 9. Relation between service time and bed depth.

outlet was 99.5 wt.-%. In the pilot test system, several bed depths were set, and the corresponding service time for each bed depth was experimentally determined. The results are shown in Figure 9.

For the Hb cornmeal the relation obtained was $T = 0.326H - 7.028$; for the Hl cornmeal it was $T = 0.355H - 8.190$.

CONCLUSIONS

As the adsorbent of vapor adsorption process in a fixed bed, two kinds of Chinese cornmeal, Hb cornmeal and Hl cornmeal, were experimentally examined for breaking the azeptrope of ethanol and water. It was shown that the sensitive factors for the vapor adsorption process included the vapor superficial velocity, the temperature, and the particle size distribution of cornmeal. When all of the three parameters were set at suitable value, higher capacity of water adsorption would be attained. In a pilot test fixed bed the adsorption capacity of water for Hb cornmeal or Hl cornmeal was 0.014–0.025 g water/g adsorbent, respectively, with a vapor superficial velocity of about 6.1 cm/s, a temperature of 87°C and particle size of 60–100 mesh. The service time equations of the two kinds of cornmeal were also given. The results show that both the Hb cornmeal and the Hl cornmeal have similar adsorption properties and could be used for commercial process, but sometimes the Hb cornmeal would have blockage in the fixed bed.

The regeneration operation was improved by making the fixed bed fluidized. Compared with down-flow drying in general fixed bed, channeling in the bed could be controlled efficiently by upflow fluidization. The adsorption capacity of the pilot test bed could be recovered at 105°C.

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