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Separation of ethanol/water azeotrope using compound starch-based adsorbents

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ABSTRACT

Comparing breakthrough cures of five starch-based materials experimentally prepared for ethanol dehydration, a compound adsorptive agent ZSG-1 was formulated with high adsorption capacity, low energy and material cost. The selective water adsorption was conducted in a fixed-bed absorber packed with ZSG-1 to find the optimum conditions yielding 99.7 wt% anhydrous ethanol with high efficiency. The adsorption kinetics is well described by Bohart–Adams equation. The adsorption heat, ΔH_{abs}, was calculated to be $-3.16 \times 10^4\ \text{J mol}^{-1}$ from retention data by inverse gas chromatography. Results suggested that water entrapment in ZSG-1 is a exothermic and physisorption process. Also, ZSG-1 is recyclable for on-site multiple-use and then adapt for upstream fermentation process after saturation, avoiding pollution through disposal.

1. Introduction

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 (Banat et al., 2000; Hassaballah and Hills, 1990).

The removal of water from ethanol using a fixed-bed adsorbent, mainly molecular sieves, is a well-known process (Sowerby and Crittenden, 1988). However molecular sieves are expensive and can only be discarded after saturated with water, which makes the process less economical. So an increasing interest has been focused on the cheaper and recyclable adsorbents. Ladisch and Dyck (1979) first found that the biomass adsorbents, composed of cellulose and starch, could be used to remove water from a wide range of organics. Since then, many approaches have been developed in ethanol dehydration using various biomass materials such as corn (Robertson et al., 1983; Crawshaw and Hills, 1990), corn meal (Hong et al., 1982; Ladisch et al., 1984; Hills and Pirzada, 1989; Hassaballah and Hills, 1990) corn grits (Bienkowski et al.,1983; Neuman et al., 1986; Crawshaw and Hills,1990), cellulosics (Hong et al., 1982; Walsh et al., 1983) and starch (Hong et al., 1982; Crawshaw and Hills, 1990). The advantages of these adsorbents include high efficiency, relatively less raw material cost and energy consumption. For instance, the energy of ethanol dehydration is $3669\ \text{kJ kg}^{-1}$ ethanol by calcium oxide, and 2873 by cellulose. Whereas, the authors also found that the adsorption process, consuming only $32\ \text{kJ m}^{-3}$ ethanol by corn grits, was more energy-saving than the $88\ \text{kJ m}^{-3}$ ethanol by azeotropic distillation (Hassaballah and Hills, 1990; Lee et al., 1991). Consequently corn grits were widely used in industry to produce anhydrous ethanol of 99.8 wt% over 750 million gallons per year (Beery and Ladisch, 2001). Recently, compound starch-based adsorbents were found still more efficient in anhydrous ethanol preparation. As one of the progress, Ma (2006) developed a granular adsorbent, composed of dry pachyrhizus, dry cassava, dry potato, wheat, pachyrhizus seeding, xanthan gum and carboxymethyl amylum. The product ethanol concentration reached 99.7 wt% from initial concentration of 92.4 wt%.

Starch, starch-based materials, cellulose and hemi-cellulose were reported to have an affinity for water (Ladisch and Dyck, 1979; Hong et al., 1982; Westgate and Ladisch, 1993). As such, the objective of this study is to develop a optimum compound adsorbent by evaluating adsorption capacity of corn, sticky rice, sweet potatoes, durra, and crystal sugar. A new compound cheaper compound ZSG-1 consisting of corn, sweet potatoes and foaming agent was obtained through screening in a fixed-bed absorber. The best values for the process parameters was sought to increase the capacity of ZSG-1, and kinetic and thermodynamic analyses were conducted to investigate the adsorption property of ZSG-1.

2. Methods

2.1. Raw materials

All raw materials, corn, sticky rice, sweet potatoes, durra, and crystal sugar, were of food quality and purchased in the market.

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These materials were dried in a vacuum oven at 90 °C for 12 h, and stored in sealed package for future screening experiment.

2.2. Zsg-1

Corn flour (90–40 mesh) and the sweet potato powder (120–90 mesh) were selected as basic components for ZSG-1. To prepare the absorbent, 5 g sweet potato powder was dispersed in 120 ml boiling water under stirring for 1 min. 4 ml H_2SO_4 (0.1 mol l^{-1}) was dripped into 82 ml above solution in a beaker, and 75 g corn flour was added into the solution by stirring to form a paste. Then the paste was squeezed into $\varnothing 3 \times 4$ mm columns within 1.5 h. Finally, the columns was kept drying first at room temperature in the ventilated cabinet for 7 days, and then at 90 °C in a vacuum oven for 12 h.

The finished adsorbent columns were measured through the dead weight pressure test (static pressure over 313 kPa) at room temperature. 10 cm high ZSG-1 was placed in a 100 ml measuring tube and with 5 kg stainless steel column ($\varnothing$2.5 cm) on it. Samples with height shrinkage of less than 2 mm (2%) after 24 h are considered to pass the test.

2.3. Measurement of dynamic saturated adsorbance

To evaluate the sorption capacity for ZSG-1, the dynamic saturated adsorbance was measured. The experiment unit was a glass distillation column packed with steel wire gauze packing caging 1 g adsorbent in it. Vapor was supplied at the bottom from a electrically heated kettle preloaded with enough distilled water. The flow of the distillate at the top total condenser was kept at three drops per minute for 2 h to drive air out and saturate the sample adsorbent. After that, the saturated adsorbent under test was taken out and weighed within 30 s.

2.4. Influencing factors analysis

The influencing factors were evaluated using a fixed-bed absorber, which was a glass pipe with an internal diameter of 25 mm and a height of 20 cm. As shown in Fig. 1, a water jacket was used to maintain the temperature.

The water bath and the circulating pump were switched on 3 h before heating the absorber to the operating temperature. The water jacket temperature should be held above the dew point of the vapor product mixture to avoid condensation. As soon as vapor began to generate, open valve V1 and V3 to let ethanol–water mixture run into the flask from V1 to maintain the concentration in the flask with a peristalsis pump. The mixture was prepared approximately the same ethanol concentration as the evaporation vapor.

To start the experiment, switch vapor into the condenser C1 via valve V3. Samples was taken from S1 once every 2 min, analyzed and weighed to check the concentration and the feed rate. After the ethanol concentration of vapor was stabilized, close V3 and open V2, then let vapor go into the bed and water was adsorbed selectively by the adsorbent ZSG-1. Product coming from the adsorbed was condensed by condenser C2 and collected in receiver 10. The purified product was taken from the sample point S2 once every minute at the first 15 min and once every 2 min in the following 2 h. The samples were weighed and analyzed with gas chromatography.

A column (Φ3 mm, 200 cm long), packed with GDX-203 and 100–120 mesh adsorbent was used in a gas chromatography to analyze the composition. Analysis at 120 °C was monitored by a thermal conductivity detector, and it agreed within 0.2%. The output from the detector was monitored by a recorder.

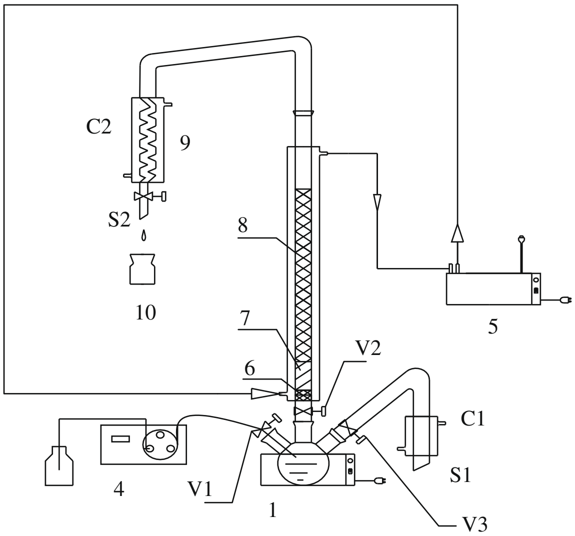

Fig. 1. Diagram of G-S fixed-bed adsorption system: (1) thermostatic waterbath; V1, V2, V3 valves; (4) peristaltic pump; (5) ultrathermostat; (6) steel wire gauze; (7) quartz sand; (8) adsorbent; (9) total condenser; (10) sample bulb.

2.5. Inverse gas chromatography experiment

Inverse gas chromatography (IGC) has been widely used to investigate the interaction properties of volatile compounds (moving phase) with the stationary phase. If very small amounts of a solute are used, the solute undergoes partitioning during elution. Small amounts of solute and low flow rates of carrier gas allow the approximation of equilibrium conditions. The time that elapses from injection of the sample to the recording of the peak maximum is defined as the retention time. The net retention time is the difference between the retention time of a solute and that of an unretained indicator (Vareli et al., 2000).

It is also possible to obtain thermodynamic parameters using IGC. The volume of carrier gas necessary to elute an adsorbed solute from the column under specific temperature and pressure conditions which is called the net retention volume can be calculated from the following equation (Vareli et al., 2000):

$$V_N = jF_c(t_R - t_A) \tag{1}$$

where t_R is the retention time of the solution, t_A the retention time of the air and F_c the corrected flow rate under the conditions within the oven. In Eq. (1)

$$F_c = \frac{T_v}{T_f} \times \frac{P_0 - P_w}{P_0} \times F \tag{2}$$

where F is the flow rate, T_v the temperature of the oven, T_f the temperature of the flow meter, P_0 the outlet pressure of the column and P_w the vapor pressure of water inside the soap bubble flow meter. j is the compressibility factor. So

$$j = \frac{(p_t/p_0)^2 - 1}{(p_t/p_0)^3 - 1} \times 3/2 \tag{3}$$

where P_t is inlet pressure of the column.

The specific retention volume V_g^0 is given by the following equation:

$$V_g^0 = \frac{V_N}{w_s} \times \frac{273.15}{T} \tag{4}$$

where w_s is the mass of stationary phase and T the temperature of the column.