



Adsorption characterisation of water and ethanol on wheat starch and wheat gluten using inverse gas chromatography

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ABSTRACT

Adsorption of water and ethanol on wheat starch and wheat gluten has been studied in the temperature range of 60–150 °C using inverse gas chromatography (IGC). From the chromatographic retention data it is able to calculate the separation factors for the two solutes and obtain values for thermodynamic parameters such as Gibbs free energy (ΔG_s) and the enthalpy (ΔH_s) of adsorption of water and ethanol. The results indicate that water is adsorbed more strongly than ethanol at all temperatures, and the low temperature is found to facilitate the adsorptive separation of water from ethanol. It is also shown that the starch definitely plays a crucial role for the water and ethanol separation, despite that wheat flour includes both gluten and starch. The wheat starch is seen to have potential application in biomass water–ethanol separation to obtain fuel ethanol through the preferential adsorption of water from aqueous ethanol.

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1. Introduction

With the excessive consumption of non-renewable fossil oil resources and aggravation of energy crisis, using renewable resources to replace non-renewable ones is receiving more and more attention all over the world. Due to high-energy values, ethanol is the most promising future biofuel. Presently, it is used in fuel industry as an additive to petrol that raises its octane number and combustibility. The only barrier for a broad application of production capacities of ethanol and installations for composing petrol on the basis of ethanol is a high production cost. Production of anhydrous ethanol requires overcoming the barriers of a positive homoazeotrope. Traditional distillation units often consumed almost as much energy as the fuel value of the ethanol produced through combustion. Further improvement upon traditional methods is observed and methods to reduce the cost of dehydrated ethanol production are still ongoing.

The separation of ethanol–water mixtures by passing the vapours over cellulose or starch adsorbents was first demonstrated by Ladisch and Dyck (Ladisch & Dyck, 1979). They proposed distillation of the fermentation broth to between 75 and 90 wt.% ethanol, followed by adsorption of the remaining water onto adsorbents (silica gel and biomass materials) (Ladisch & Tsao, 1982). The energy consumption of this combined process is less than that obtained from combustion of ethanol. Since then, numerous similar approaches for ethanol dehydration have been carried out with various biomass materials, such as corn, corn meal, cellulose, etc. (Beery & Ladisch, 2001; Carmo,

Adeodato, Moreira, Parente, & Vieira, 2004; Chang, Yuan, Tian, & Zeng, 2006; Crawshaw & Hills, 1992; Han, Liu, Ma, & Fang, 2008; Hassaballah & Hills, 1990; Ma et al., 2006; Vareli, Demertzis, & Akrida-Demertzi, 2000). The aforementioned ethanol-dehydration adsorbents have such advantages as efficiency, relatively low adsorbent cost and ready disposal of spent adsorbent as fermentation or animal feeding. These adsorbents are also environmentally attractive for drying applications since they are nontoxic, biodegradable materials derived from renewable resources.

Although, wheat flour has been used as adsorbent (Erbas, Ertugay, & Certel, 2005; Ma et al., 2006; Vareli et al., 2000), no systematic efforts have been made to elucidate either the wheat starch and the wheat gluten separation potential, or the adsorptive mechanism on selective adsorption of water and ethanol.

In this work, the experiments of adsorption of water and ethanol on the wheat starch and the wheat gluten are separately performed. The aim of this work is to study the adsorption thermodynamic parameters of wheat starch and wheat gluten adsorbent by separating wheat starch and wheat gluten from wheat flour. Inverse gas chromatographic method (IGC) is used to determine the vapour sorption of water and ethanol on wheat starch and wheat gluten particles in the temperature range of 60–150 °C.

2. Materials and methods

2.1. Inverse gas chromatography

IGC is an inversion of conventional gas chromatography. The main difference between GC and IGC is that the interested species

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is the material acting as the stationary phase in IGC column. IGC has been widely used to determine the physicochemical properties of the stationary phase by its interaction with a moving phase (solute) (Askin & Bilgic, 2005; Shi, Zhao, Jia, & Wang, 2007; Wu, Que, & Al-Saiigh, 2007). If very small amounts of a solute are used, then the solute undergoes partitioning during elution. Although, chromatographic systems are usually not in true equilibrium, use of small amount of solute and low flow rate of carrier gas allows the approximation of equilibrium conditions. The time that elapses from injection of the sample to the recording of the peak maximum is the retention time. The retention time and the peak elution profiles of standard solutes, affected by interactions between the solute and stationary phase, are used to estimate those interactions. The net retention time is difference between the retention of a solute and that of an unretained indicator. In this work, air is used as the unretained compound. The separation factor can be expressed as:

$$\alpha = \frac{t_{N1}}{t_{N2}} \quad (1)$$

where α is the separation factor, t_{N1} and t_{N2} represent the net retention time of solute 1 and 2, respectively.

IGC method is used to determine the thermodynamic parameters. The first step is to determine the net retention volume, V_N , which is the volume of carrier gas necessary to elute an adsorbed solute from the column under the specific conditions of temperature and pressure, and it is calculated from:

$$V_N = F_c(t_R - t_A) \quad (2)$$

where t_R is the measured retention time at maximum peak of the solute, t_A is the retention time of the non-adsorbing air and F_c the corrected flow rate under the conditions within the oven. And F_c can be expressed as,

$$F_c = \frac{T_{ov}}{T_{fl}} \times \frac{P_o - P_w}{P_o} \times j \times F \quad (3)$$

where F is the flow rate measured under flow meter conditions, T_{ov} and T_{fl} are the temperatures of the oven and the flow meter, respectively. P_o is the outlet pressure of the column, and P_w is the vapour pressure of water inside the soap bubble flow meter. The parameter j represents the compressibility factor and is given by:

$$j = \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \times \frac{3}{2} \quad (4)$$

where P_i is the inlet pressure of the column. The specific retention volume, V_g^0 , is the net retention volume corrected to standard temperature and pressure and is given by the following equation:

$$V_g^0 = \frac{V_N}{w_s} \times \frac{273.15}{T} \quad (5)$$

where w_s is the weight of stationary phase and T is the temperature of the column. Finally, the partition coefficient K_p is calculated using:

$$K_p = \frac{V_g^0 \rho T}{273.15} \quad (6)$$

where ρ is the density of the packing material.

The free energy of adsorption of a solute on the column packing can be estimated using:

$$\Delta G_s = -RT \ln K_p \quad (7)$$

The heat (enthalpy) of adsorption ΔH_s is given by:

$$\frac{-\Delta H_s}{R} = \frac{d \ln V_g^0}{d(1/T)} \quad (8)$$

$$\text{or } \ln V_g^0 = \frac{\Delta H_s}{RT} + C \quad (C \text{ is a constant}) \quad (9)$$

The ΔH_s can be obtained by linear fit of the $\ln V_g^0$ vs. T^{-1} .

2.2. Materials and columns

The sample wheat is from one of the local farms in Zhengzhou, China, and is milled into flour. Wheat gluten is obtained by separation of wheat flour into starch and gluten through the wet-milling process. It comes in the form of a whitish viscous paste ("moist" gluten) or a cream-coloured powder (dry gluten). It consists essentially of a mixture of various proteins, the main ones being gliadin and glutenin. The starch slurry from the extraction of the gluten, is further processed to extract premium wheat starch and is dried into powder.

The starch and gluten samples were dried in a vacuum oven at 50 °C for 4 h, then the 80–100 mesh starch and gluten fractions were obtained and stored in a desiccator. The samples prepared in this way were diluted with an inert support (Chromosorb W AW, DMCS, 80–100 mesh) purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai. The inert support was dried under the same conditions and stored in the desiccator.

In order to measure the retention time on these materials, samples were diluted to 30 parts of adsorbent to 70 parts of Chromosorb W AW, DMCS. The water retention time was very long, which would otherwise make the experiments extremely time consuming if the column was packed with 100% adsorbent. In order to measure the retention time of water on these materials, samples were diluted with Chromosorb as the dilution could reduce the time required for the experiment. And it is obvious that the error from the dilution can be negligible based on the fact that the water retention time on a 100% Chromosorb W AW column ranged from 0.22 min g⁻¹ Chromosorb at 60 °C to 0.12 min g⁻¹ Chromosorb at 150 °C, while the water retention time on starch ranged from 90.85 min g⁻¹ at 60 °C to 1.57 min g⁻¹ at 150 °C.

The retention time of ethanol per gram for a 100% adsorbent column could be estimated from the following equation due to the relatively low retention times of ethanol on both the Chromosorb and the adsorbent, respectively:

$$t_{Ns/g} = \frac{t_{NT} - t_{NA/g} \times m_A}{m_s} \quad (10)$$

where t_{NT} is the net retention time of the solute in the diluted-sample column, and $t_{NA/g}$ is the net retention time per gram of the solute in the 100% Chromosorb column at the same temperature as that of the diluted-sample column. Parameter m_A is the mass of the Chromosorb in the diluted-sample column, and m_s is the mass of the adsorbent in the diluted-sample column.

The net retention time of water in the diluted column is estimated by Eq. (10) in this work despite the negligible influence of Chromosorb on it.

The chromatography columns used were constructed from stainless steel tubing with an inside diameter of 3 mm and a length of 2 m. The empty column was weighed and then a few grams of stationary phase were put into the column. The supporting stationary phase was continually added and packed until the column was filled, then the column was weighed again. Each analytical column was conditioned for at least 12 h by passing nitrogen carrier gas through the column.

2.3. Description of the apparatus

A gas chromatograph (Shimadzu, GC-14C, Japan), equipped with a thermal conductivity detector (TCD), was used for measuring the retention times of the water and ethanol. The TCD temperature was set at 200 °C, the injection port was set at 180 °C. Hydrogen was used as the carrier gas with a constant flow-rate 50 mL/min. Flow rates at each temperature were determined for each column upon the equilibration of the column. The probe solvents were injected manually, using a 1.0 μL Hamilton syringe. The injection volumes were 1.0 μL.

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