Efficient Separation Coupled with Ultrasonic Atomization Using a Molecular Sieve

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Introduction

We previously reported a phenomenon in which ethanol concentration in atomized mist increases in comparison with ethanol concentration in the original solution with 2.4-MHz ultrasonic wave irradiation from under the surface of an ethanol–water solution.[1–4] The separation efficiency of ultrasonic atomization was superior to the vapor–liquid equilibrium of an ethanol–water system. Additionally, the energy required to atomize a unit volume of the solution was lower than the vaporization energy. Kirupalani et al.[5–7] obtained similar data. However, to establish industrial separation equipment, atomized mist and vapor have to be collected by some practical means. To this purpose, we reported a mist collection method using thermal swing adsorption (TSA),[2] in which the concentrations of ethanol solution directly collected are sufficiently high. However, it is necessary to heat activate carbon fiber in the TSA system to desorb adsorbed ethanol. In such a case, the merit of separation through ultrasonic atomization without heating is abandoned.

The conditions necessary for the rational collection method to adopt separation through ultrasonic atomization are as follows:

(1) It should be operational at normal temperatures.
(2) It should operate continuously.
(3) It should enable the dehydration of ethanol–water mist and vapor generated by ultrasonic atomization.
(4) The required energy for collection should be small.

With the above requirements, we investigated pressure swing adsorption (PSA)[8,9] as a rational collection means of ultrasonic atomization. The strategy to achieve our purpose is to dehydrate atomized mist and vapor using a 3-Å molecular sieve.[10]

Experimental

Separation through ultrasonic atomization and PSA system

A 2.4-MHz oscillator for ultrasonic atomization (Honda Electric Co., Ltd., Toyohashi, Japan) was used at a 16 J/s power output. One oscillator can atomize a mist of water at 20–40 × 10^{-6} kg/s atomization rates. For pure ethanol atomization, one oscillator can atomize at 50–100 × 10^{-6} kg/s atomization rates. The atomization efficiency achieved under these conditions using a 16 J/s oscillator output is higher than that achieved by heating at the vaporization energy of water or ethanol.

As shown in Figure 1, ultrasonic waves produced by an oscillator were irradiated from the bottom of the ethanol–water solution (5) to the surface (6). When the solution pillar or jet (8) was formed on the surface with the input of a 30-V direct current to the circuit (2), mist was atomized around the pillar (8). The atomized mist was discharged from the vessel (4) by blowing away the gas phase and condensed by the cooler (9). Two demisters were used to eliminate the mist after atomization and cooling. After cooling and eliminating the mist, the gas phase including ethanol vapor and

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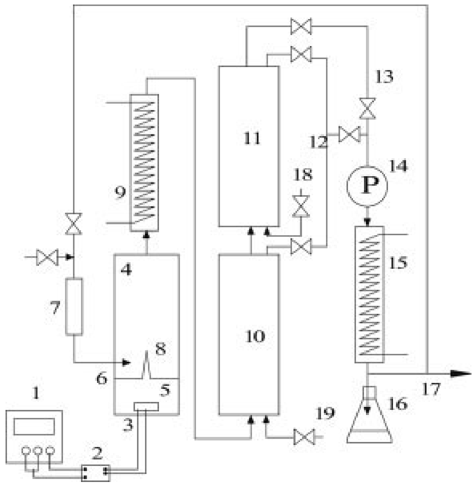

Figure 1. Experimental apparatus for separation by ultrasonic atomization using PSA system.

Legend: 1, electric source; 2, circuit; 3, oscillator; 4, atomizer; 5, solution; 6, surface of solution; 7, flow meter; 8, pillar; 9, condenser; 10, 3-Å column; 11, hydrophobic column; 12, desorption line; 13, adsorption line; 14, vacuum pump; 15, condenser; 16, flask; 17, exhaust; 18 and 19, purge lines for desorption.

mist was introduced into a packed column with 1.4 kg of 3-Å molecular sieve. A dehydrated gas phase was also introduced into a column packed with 1.4 kg of hydrophobic adsorbent.

In the adsorption mode, the gas phase was introduced into the 3-Å (10) and hydrophobic (11) adsorption columns; exhaust from the adsorption column was aspirated by vacuum pump (14). In the desorption mode, a condensed-water-rich solution from column 10 and a concentrated ethanol solution from column 11 were collected at the condenser (15) through an individual line using a vacuum pump (14). The pressure in the column in the desorption mode was 10 Pa. Inlets and valves (18 and 19) show the purge lines into each column. The role of the purge lines is for the small-volume gas flow into the adsorption column to produce an adsorbate in column transport to the vacuum pump in the desorption mode.

Ethanol and water analyses

The ethanol used was of special grade (99.5 v/v%, 98.4 mol %). Water was filtered using an ultra-filtration membrane before use. The concentrations of ethanol and water were analyzed by gas chromatography (GC-14A; Shimadzu, Kyoto, Japan); the areas of the peaks of water and ethanol were determined using a thermal conductivity detector (TCD).

Results and Discussion

Ethanol concentration in gas phase

In this study, we intended to directly dehydrate atomized mist and vapor by an adsorption operation after atomization. When mist is introduced into an adsorption column, clusters of ethanol and water coadsorb onto the 3-Å adsorbent. The coadsorption of water and ethanol molecules decreases ethanol concentration in the product. Therefore, we should consider the phase of the mist and vapor mixture in the carrier gas.

When an ethanol–water mixture is atomized into a carrier gas, the contents of mist diffuse into the carrier gas. This is the second vaporization from the surface of mist to the gas phase. In the Gibbs–Thomson effect,[11] an increase in vapor pressure from the surface of nanoscale aerosol depends on aerosol diameter. The carrier gas after atomization must be immediately saturated with ethanol or water vapor according to the Gibbs–Thomson effect. The carrier gas includes both vapor and mist. We compared the concentration of ethanol or water in saturated gas with the ratio of the atomized solution to the volume of the carrier gas. Figure 2 shows the relationship between carrier gas velocity U_G and the amount of accompanying mist per weight of dry air h_Y. Bold lines in Figure 2 show the amounts of mist in the carrier gas at the atomization rates D (kg/s) indicated in Figure 2. Dotted line A indicates the saturated ethanol concentration in vapor in the gas phase at 303 K as calculated using Antoine's equation; dotted line B indicates the saturated water concentration in vapor in the gas phase at the same temperature.

If pure ethanol solution is atomized and the temperature at the gas outlet of the mist atomizer is 303 K at an atomization rate $D = 28 \times 10^{-6}$ kg s^{-1} oscillator^{-1}, all the mist atomized in the carrier gas will be vaporized regardless of carrier gas velocity. On the other hand, the concentration of mist in the gas phase increases with increasing D (upper area of dotted line A). In particular, in the case of the atomization of an ethanol–water solution, the saturated water concentration in vapor in the gas phase is much smaller than that in ethanol. Therefore, the atomized ethanol–water solution will exist as mist at the atomization rate of the upper area of dotted line B and as vapor at that of the lower area of dotted line A.

With the above consideration, in the case that the amount of the atomized solution introduced into the carrier gas is greater than the saturated concentration, the atomized solution will exist as mist. If the mist is not eliminated before the introduction into the 3-Å column, the surface of the 3-Å

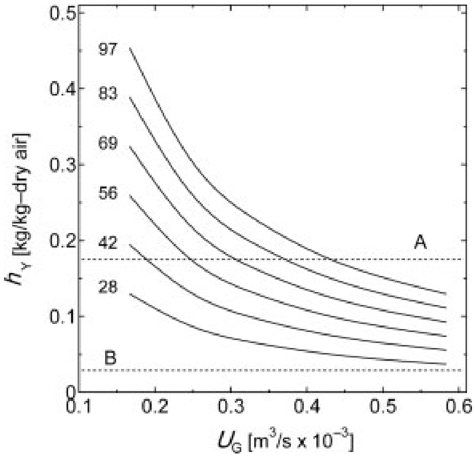

Figure 2. Relationship between humidity and flow rate of carrier gas.

Numbers in the figure indicate the atomization rate D [kg/s/oscillator, $\times 10^{-6}$]. Dotted lines A and B denote the saturated concentrations of ethanol and water in air, respectively.

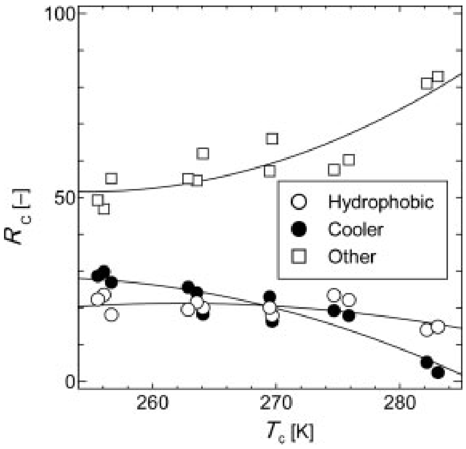

Figure 3. Collection ratios of ethanol in cooler, hydrophobic column, and other parts at cooling temperature T_C.

The total collection amounts in the cooler, hydrophobic column, and other parts were equal to the total atomization amounts.

adsorbent will become wet and water molecules will not be able to enter the pores of the 3-Å adsorbent. For molecular water to adsorb onto the 3-Å column, the ethanol–water solution should be atomized between dotted lines A and B, the water-rich mist should be eliminated at the demister, and an ethanol-rich gas should be introduced into the 3-Å column. The operating region of atomization should also be restricted by adjusting the critical gas velocity at the adsorption column.

Conditions for adsorption onto 3-Å molecular sieve column

Figure 3 shows the collection ratio R_C of the amount of ethanol collected in each step [that is, demister (other), cooler, and hydrophobic column] to the amount of atomized ethanol mist when the set temperature of the cooler was changed. Hydrophobic in Figure 3 indicates the R_C of the solution collected at the hydrophobic column through the 3-Å column. The cooler and demister in Figure 3 indicate the R_C, which also indicates the amount of ethanol collected relative to the atomized ethanol mist amount. The amount of mist or vapor collected at the condenser decreased with the temperature of the cooler. No change in hydrophobic R_C (Figure 3, ○ symbol) was observed below 275 or 276 K. Hydrophobic R_C (Figure 3, ○ symbol) decreased toward 283 K. The other collection ratios except for the cooler and hydrophobic increased with temperature. In particular, above 273 K, the amount of mist or vapor not collected at the cooler or hydrophobic column significantly increased. This indicates that the amounts of condensation and adsorption decreased. Considering the isotherm equilibrium curve for adsorption to the 3-Å adsorbent, it is necessary that—before their introduction into the 3-Å column—both mist and vapor are appropriately cooled. Figure 4 shows the atomization rate in the case that the exhaust outlet (17) of the equipment shown in Figure 1 is connected to the inlet of the ultrasonic atomization vessel. The reasons gas circulation is required are as follows:

(1) Volatile organic compounds such as ethanol should be enclosed within the equipment to prevent air pollution.

(2) The heat generated as adsorption heat is used for atomization heating by recovery of the carrier gas. This is because the atomization rate increases with increasing temperature of the carrier gas.

However, as shown in Figure 4, the atomization rate decreased with an increase in the temperature of the cooler. This is attributed to the inflow of ethanol and water vapor to the inlet of the atomizer, which has a high humidity in the carrier gas through PSA columns because this set temperature of the cooler is too high to sufficiently induce the collection of mist and vapor at the cooler and PSA. When the water or ethanol content in the carrier gas is high, atomization is inhibited by high humidity. Therefore, to maintain both a high atomization rate and a high adsorption rate, it is necessary to cool the carrier gas introduced into the 3-Å column.

Dehydration of ethanol–water solution gas flow by PSA system

On the basis of the results of the above examination to determine the operating conditions for separation using ultrasonic atomization and the PSA system using a molecular sieve, the operation conditions were set such that carrier gas velocity is determined between two constraints. The carrier gas has to be maintained at a velocity higher than that necessary to vaporize atomized mist as shown in Figure 2. The second constraint is that the velocity has to be operated at a critical linear velocity for adsorption. Carrier gas velocity was set at 12 L/min or 0.2×10^{-3} m^3/s; the linear velocity in the PSA column was 0.006 m/s. The temperatures of the atomized solution and cooler were controlled at 303 and 256 K, respectively. No control of PSA temperature was performed. Under these conditions, the atomization in PSA (hydrophilic through 3 Å) was carried out for 1800 s. After

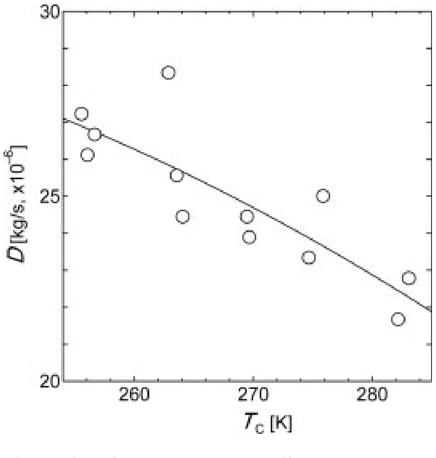

Figure 4. Atomization rate at cooling temperature T_C.

Atomization was inhibited by an increase in cooler temperature when exhaust gas from the PSA system was circulated to the inlet of the atomizer because the humid carrier gas at a higher temperature repressed such atomization.

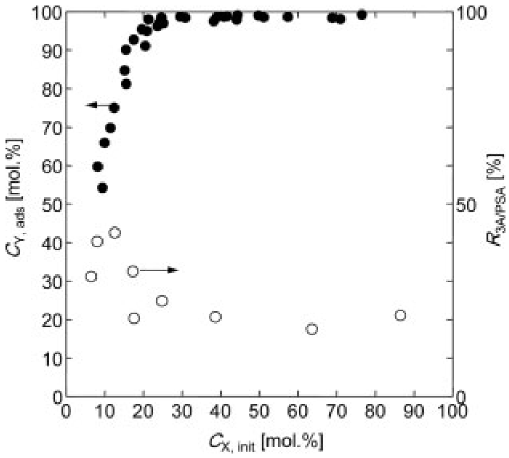

Figure 5. Result of dehydration for 3-Å molecular sieve.

$R_{3A/PSA}$ indicates the ethanol collection ratio at the 3-Å column to the PSA system. 100% of $R_{3A/PSA}$ ratio denotes that all ethanol introduced into the 3-Å column was collected.

adsorption, desorption was performed at the temperature (253 K) of the condenser set at the outlet of the vacuum pump. The ethanol concentration in the solution condensed in the flask (Figure 1, 16) was compared with that in the original solution, as shown in Figure 5. When the concentration of the original ethanol–water solution was <20 mol %, the concentration of the solution collected at the hydrophobic column of the PSA system increased with increasing concentration of the original solution. When the concentration of the original solution was 20 mol %, the concentration of the solution collected at PSA reached 97 mol %. At more than 40 mol % of the original solution, the collected solution was almost dehydrated to 99.5 v/v% or 98 mol %. Even though it was not completely dehydrated, it is of sufficient concentration for practical use.

The collection rates for 98 mol % ethanol at the hydrophobic column are shown in Figures 3 and 4. The total collection amounts in the cooler, hydrophobic column, and other parts (Figure 3) were equal to the total atomization amounts (Figure 4) and the collection rates for 98 mol % ethanol were 5–6 × 10^{-6} kg/s for one ultrasonic oscillator. We performed the numbering-up of this system to a 300-oscillator scale.

Phase change of mist or gas at inlet of 3-Å column

The vapor–mist mixture introduced into the 3-Å column contained several tens of % ethanol. The symbol ○ in Figure 5 shows the ratio of the amount of ethanol collected at the 3-Å column to the total amount of ethanol collected at the 3-Å and hydrophobic columns. From the result shown in Figure 5, in the lower concentration range of the original ethanol–water solution, a water molecule adsorbed onto a pore in the 3-Å adsorbent must be hydrogen-bonded to several ethanol or water molecules. The adsorbate adsorbed onto the porous structure of the 3-Å adsorbent consisted of water molecules trapped in the pores of the adsorbent and ethanol molecules hydrogen-bonded to the trapped water molecules. These results indicate that all the mist was not vaporized to gas. The carrier gas inflow to the 3-Å column contained both gas and liquid (mist).

With increasing ethanol concentration in the original solution, the amount of ethanol collected at the 3-Å column decreased. The mist at the inlet to the 3-Å column was vaporized to gas.

Acknowledgments

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Notation

C = ethanol concentration, mol %
D = atomization rate, kg/s
h = humidity of dry air, kg/kg-dry air
R_C = amount ratio of ethanol collected to atomized ethanol
$R_{3A/PSA}$ = ethanol collection ratio in 3 Å to 3 Å + hydrophobic
T_C = temperature of cooler, K
U_G = carrier gas flow rate, m^3/s

Subscripts

ads = adsorption
init = initial
X = liquid phase
Y = vapor or mist phase

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