Malaysian Journal of Analytical Sciences, Vol 23 No 1 (2019): 124 - 130
DOI: https://doi.org/10.17576/mjas-2019-2301-15

MALAYSIAN JOURNAL OF ANALYTICAL SCIENCES
Published by The Malaysian Analytical Sciences Society
ISSN 1394 - 2506

DEHYDRATING ETHANOL USING A TERNARY SOLUTE AND EXTRACTIVE BATCH DISTILLATION

(Pengeringan Etanol Menggunakan Zat Larut Ternari dan Penyulingan Kelompok Hasil Ekstrak)

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Received: 13 April 2017; Accepted: 17 April 2018

Abstract

Anhydrous bioethanol is a material used in many applications including biofuel. Commonly, bioethanol is produced through sugar fermentation which results in a low concentration of ethanol. For utilization as biofuel, the lowest ethanol concentration should be 99.5%. Distillation is common technique to dry a mixture solution, however, the mixture of bioethanol and water is forming an azeotrope that limit the concentration of 96% ethanol. This paper discusses ethanol dehydration through extractive batch distillation by the addition of a ternary solute sodium hydroxide, citric acid, sulfuric acid, glycerol or ethylene glycol to ethanol. The initial concentration of ethanol used was 86% v/v, and the amount of ternary solute added was selected based on the colligative properties of the solution, which included a boiling point elevation (ΔT_B) that ranged from 5 to 25 °C. All the ternary solutes could break or shift the ethanol-water azeotrope. The highest concentration of ethanol was 99.91% v/v at ΔT_B = 25 °C with sulfuric acid as the ternary component. The resulted ethanol concentration exhibited a linear relationship with ΔT_B, which was also affected by the boiling point of the ternary solute. This study successfully produced anhydrous bioethanol by low cost and simple distillation process.

Keywords: bioethanol, azeotrope, colligative properties, ternary solute

Abstrak

Bioetanol anhidrat adalah bahan yang diperlukan dalam pelbagai aplikasi termasuk biofuel. Biasanya, bioetanol dihasilkan melalui penapaian gula, yang menghasilkan kepekatan etanol yang rendah. Supaya boleh digunakan dalam aplikasi biofuel, diperlukan kepekatan etanol sekurang-kurangnya 99.5%. Distilasi adalah kaedah yang umum digunakan untuk mengeringkan larutan, namun campuran bioetanol dan air membentuk azeotrop yang membatasi kepekatan 96% etanol. Kajian ini membincangkan pengeringan etanol dengan penambahan zat larut ternari: natrium hidroksida, asid sitrik, asid sulfurik, gliserol atau etilena glikol. Kepekatan awal etanol yang digunakan adalah 86% v/v. Jumlah zat larut yang ditambahkan dipilih berdasarkan sifat koligatif pelarut, termasuk ketinggian titik didih (ΔT_B) yang berkisar antara 5 hingga 25 °C. Semua bahan terner didapati boleh memecahkan atau mengalihkan azeotrop air etanol; kepekatan tertinggi etanol yang diperoleh ialah 99.91% pada ΔT_B = 25 °C dengan asid sulfurik sebagai komponen ternari. Kepekatan etanol yang dihasilkan memperlihatkan hubungan linear dengan ΔT_B, yang juga dipengaruhi oleh titik didih zat larut ternari. Kajian ini telah berjaya menghasilkan bioethanol kering melalui kaedah penyulingan yang murah dan sederhana.

Kata kunci: bioetanol, azeotrop, sifat koligatif, zat larut ternar

Introduction

Anhydrous ethanol is widely used in the chemical industry as a solvent, a raw material in the synthesis of esters and as an additive in detergents, paints, cosmetics, aerosols, perfumes, medicines, and organic food [1]. Anhydrous ethanol, with a purity exceeding 99.5%, is commonly called fuel-grade ethanol, and it is a biofuel material that can be used as a direct fuel replacement in vehicles and gasoline-powered machinery or can be mixed with conventional fuels. Fuel-grade ethanol with a higher-octane number (116-129) can be used as an octane booster for fuel with a lower octane number [2-6].

Bioethanol is often produced by fermenting sugar from a sugar source or starch with the help of *Saccharomyces cerevisiae* yeast, resulting in low-ethanol-concentration products that must then undergo purification. Molasses is a commonly used raw material or sugar source because processing molasses to bioethanol requires less time compared with the processing of other raw materials [7, 8]. The conventional method used to obtain pure ethanol is distillation. However, purification of ethanol by distillation is limited to a purity less than 96% ethanol, because the water-ethanol mixture under atmospheric pressure produces an azeotrope of 96% wt. ethanol and 4% wt. water at 78.1 °C [3, 9]. Dehydration is then carried out to obtain ethanol anhydrate or fuel-grade ethanol. The dehydration methods employed include the use of molecular sieves, membrane pervaporation separation, and extractive distillation using ternary solutes to break the azeotrope.

Research on ethanol dehydration and fuel-grade ethanol has been conducted by many researchers. Kusmiyati and Susanto [10] using a membrane pervaporation setup comprising an evaporator tank, a membrane pervaporation module (diameter × height = 20 × 120 cm), vacuum pump, and cooling column. They evaporated and then pumped bioethanol into the membrane module under 6 bars of permeate pressure, resulting in 99% v/v ethanol. Al-Asheh et al. [11] researched the potential of using bio-based adsorbents corn cop, stone palm, and oak tree, after activation through various zeolite molecular sieves (types 3A, 4A, and 5A) to separate the ethanol-water azeotrope. Type 3A molecular sieves possess the greatest surface area and exhibit the highest water absorption capacity among various bio-based adsorbents. Meanwhile, the process of ethanol dehydration using molecular sieves begins with the adsorption of water until the molecular sieves are saturated. A commercial NaA zeolite membrane showed a relatively high and efficient dehydration performance that was economical. The product obtained at pilot-plant scale was ethanol anhydrate with a purity >99.7%. [9, 12].

The total component splitting of the azeotrope solution requires the addition of a ternary solute, which changes the behavior of the liquid vapor in the distillation column. Several liquid and solid ternary solute materials can be used in ethanol dehydration, including benzene, pentane, furfural, ethylene glycol, diethyl ether, toluene, glycerol, salt, and ionic liquids (ILs) [13-18]. At the industrial scale, ILs offer the greatest potential in extractive distillation. The result of ethanol dehydration using sodium chloride, calcium chloride, potassium acetate, calcium nitrate, and a mixture of sodium and potassium acetates as the third component of the ternary system shows that with similar treatments, they can break the azeotrope and increase the ethanol concentration obtained by extractive distillation [1, 19]. Restrepo and Arias (2003) used an extractive distillation column to produce absolute ethanol with a $CaCl_2$ salt to break the water-ethanol azeotrope [20]. Ligero and Ravagnani studied the recovery of potassium acetate salt as a ternary substance in water-ethanol extractive distillation. They carried out the separation using a double evaporator and a single spray dryer. The single spray dryer is more attractive from an energy consumption viewpoint. One of the advantages of salt extractive distillation is the production of a distillate that is completely free from the substance used in the separation [21]. Gomis et al. performed ethanol dehydration in a pilot-plant-scale azeotropic distillation using four hydrocarbon entrainers—hexane, cyclohexane, isooctane and toluene, which represent the hydrocarbons in gasoline—in attempts to obtain a ready-to-use, ethanol-hydrocarbon fuel mixture [4]. Lie et al. studied two methods to separate a ternary azeotrope with a heterogeneous azeotrope using toluene that exists in that system as an entrainer and extractive distillation using glycerol as the solvent. They found that extractive distillation reduced the energy expended by as much as 27.7%. In addition, extractive distillation can reduce the energy used by as much as 18.8% compared with the energy consumed during conventional heterogenic azeotropic distillation [22].

The process of ethanol dehydration by various methods such as adsorption by molecular sieves, pervaporation membranes, azeotropic distillation and extractive distillation all require energy at substantial expense for

evaporation, regeneration, or distillation. Ethanol-water dehydration using extractive distillation ternary solutes will affect the expense of the process. Here, we explain how to determine the amounts of liquid and solid solute ternary components needed based on the colligative properties of the solutions. Colligative property is a property that is determined by concentration of the solute, and it does not depend on the kind of solute molecule, such as vapor pressure, osmosis, and boiling point. The presence of a ternary solute in the mixture can affect the arrangement of the liquid phase, which changes the composition of the vapor and liquid in equilibrium. This change in equilibrium composition can change the relative volatility of the solution, shifting or omitting the azeotrope and thus making the distillation separation system easier [1,12]. The selection of ternary solutes in this research is based on using colligative properties to determine the boiling point elevation of the solvent (i.e., water) shown by equations 1-6 below.

$$\Delta T_B = K_B . m \tag{1}$$

$$\Delta T_B = K_B . \frac{G_{sl}}{MW} . \frac{1000}{G_{sv}} \tag{2}$$

$$G_{sv} = (1 - X_e) . V_e . \rho_w \tag{3}$$

$$G_{sl} = \frac{\Delta T_B . MW . (1 - X_e) . V_e . \rho_w}{1000 . K_B} \tag{4}$$

For a liquid:

$$G_{sl} = V_{sl} . x_{sl} . \rho_{sl} \tag{5}$$

$$G_{sv} = (1 - X_e) . V_e . \rho_w + V_{sl} . (1 - x_{sl}) . \rho_{sl} \tag{6}$$

ΔT_B: boiling point elevation (°C), K_B: molal boiling point elevation constant (°C/m), m: molality of the solution (mol/kg), G_{sl}: mass of the solute (g), G_{sv}: mass of the solvent (g), MW: molecular weight (g/mol), X_e: percent by volume of ethanol (v/v), X_{sl}: percent by mass (g/g), ρ_w: density of water (g/mL) and ρ_{sl}: density of solute (g/mL).

Materials and Methods

The raw materials were ethanol (86% v/v) with 14% v/v water. The density (ρ) of water at 105 °C is 0.95106 g/ml, and the molal boiling-point elevation constant (K_B) of water is 0.51 °C/m. Various ternary solutes were investigated: 1). Sodium hydroxide (NaOH), molecular weight 40 gr/mol, density 1.5 g/ml, normal boiling point 318 °C; 2). Citric acid, molecular weight 192.13 g/mol, density 1.665 g/ml, normal boiling point 175°C; 3). Sulfuric acid (H_2SO_4), concentration 95%, molecular weight 98 g/mol, density 1.84 g/mL, normal boiling point 337 °C; 4). Glycerol, concentration 99%, molecular weight 92.0938 g/mol, density 1.26 g/mL, normal boiling point 290 °C; and 5). Ethylene glycol, concentration 99%, molecular weight 62.07 g/mol, density 1.1132 g/mL, normal boiling point 197.3 °C.

The extractive distillation apparatus used in the experiments is shown schematically in Figure 1. The various tools used in the process included a three-necked bottle, a heater, a distillation column filled to 55 cm with a filling material, a reverse cooler as a condenser, a collecting tube as a reflux regulator, a thermometer, and an Erlenmeyer flask to collect the product. Ethanol (86%) mixed with a ternary component was poured into the three-necked bottle for the distillation. First, a total reflux was conducted during the initial heating until the conditions were constant (1 h), as indicated by a constant high and low temperature. Then, the anhydrous ethanol was collected until a certain amount (25 ml) was obtained, and the reflux was kept steady; the anhydrous ethanol was then analyzed.

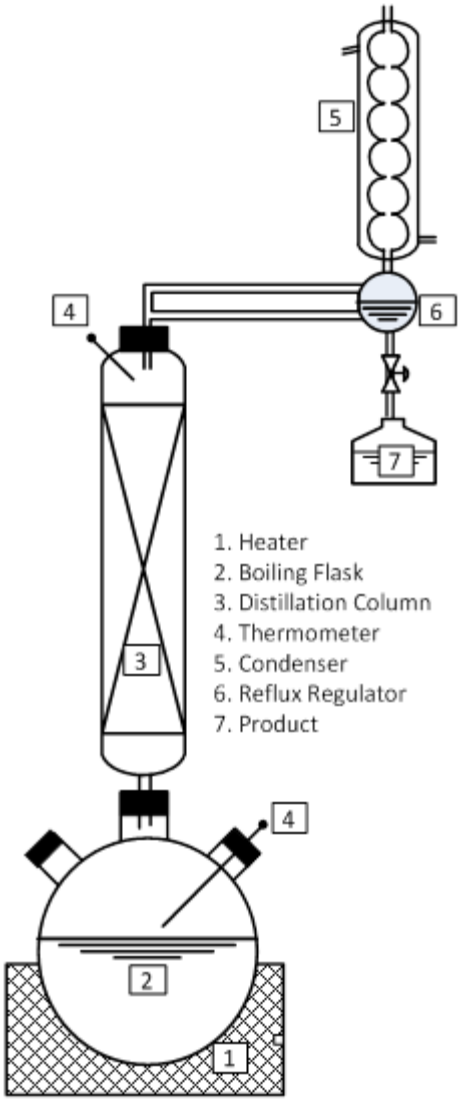

Figure 1. Scheme showing the batch extractive distillation apparatus

Results and Discussion

Before being distilled, the raw ethanol had a concentration of 86%. The raw material was then mixed with a ternary solute. The amount of ternary component necessary to achieve the desired boiling point elevation (ΔT_B) was calculated using the solution colligative property equation. The amount of ternary substance added to 100 ml of the raw ethanol (86%) was calculated using equations (4) and (5). These results are presented in Table 1.

The batch extractive distillation was performed under atmospheric pressure. The column temperature was constant at 62 °C, and the column below ranged from 74 to 76 °C. The addition of a solid ternary system component (sodium hydroxide or citric acid) or a liquid ternary system component (sulfuric acid, glycerol, or ethylene glycol) to 86% v/v ethanol with a water boiling point elevation of 5 °C to 25 °C resulted in anhydrous ethanol, surpassing the azeotrope concentration (>96%) ranging from 98.041 to 99.910% at a boiling point of 25 °C. The resulting anhydrous ethanol concentration arising from extractive batch distillation demonstrates that a ternary solute (either solid or liquid) can break or shift the azeotrope condition. The complete results are presented in Figure 2.

Table 1. Weight/volume of ternary substance on 100 mL ethanol (86%) for various boiling point elevations

ΔT_B (°C)	Weight/Volume of Ternary Solute/100 mL Ethanol 86% v/v				
	Sodium Hydroxide (g)	Citric Acid (g)	Sulfuric Acid (mL)	Glycerol (mL)	Ethylene Glycol (mL)
5	5.1413	24.6949	7.0171	9.4579	7.2035
10	10.2422	49.1957	14.3925	18.9686	14.4242
15	15.3009	73.494	22.1489	28.5284	21.6579
20	20.3156	97.5809	30.3113	38.1329	28.9028
25	25.2847	121.4489	38.9069	47.7784	36.1569

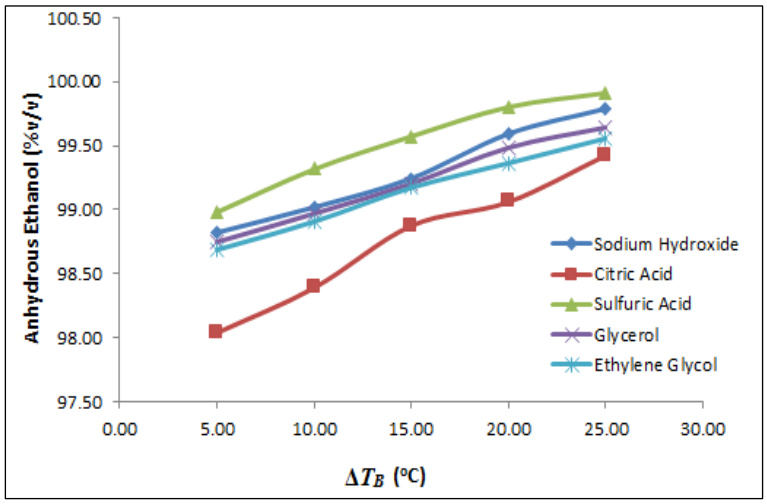

Figure 2. The anhydrous ethanol concentration as a function of the water boiling point elevation for different ternary systems

The increase in the anhydrous ethanol concentration because of extractive batch distillation exhibited a linear relationship with the boiling point elevation or the amount of solute ternary component added. The addition of sulfuric acid at a concentration of 22.148 mL to every 100 mL of 86% ethanol, corresponding to a ΔT_B of 15 °C, resulted in anhydrous ethanol with a concentration greater than 99.5%, which is equivalent to the ethanol concentration of standard fuel-grade ethanol, and achieved the desired ΔT_B. Meanwhile, sodium hydroxide was added at concentrations as low as 20.3156 g for every 100 mL of 86% ethanol (ΔT_B = 20 °C), and the addition of glycerol and ethylene glycol resulted in a ΔT_B = 25 °C. Thus, theoretically, if the separation achieved by extractive distillation continuously results in ethanol anhydrate with a concentration greater than 99.5% (standard fuel-grade ethanol) with an added ternary solute for higher boiling point elevation, then obtaining concentrations greater than 99.5% should be straightforward. However, the amount of ternary solute added should be optimized so that the ternary substance can be recovered and reused for efficient recycling. The highest anhydrous ethanol content was achieved using sulfuric acid as the ternary component, followed by those achieved using sodium hydroxide, glycerol, ethylene glycol and citric acid, with boiling point equivalents of 337, 318, 290, 197 and 175 °C, respectively. These results are clearly shown in Figure 3. These results show that the ternary solute phase, either solid or liquid, does not affect the concentration of the obtained anhydrous ethanol; rather, the ternary solute boiling point and its ternary solubility affect how it favors water/solvent. Result in this study is aligned with previous study reported [17, 23-24].

The relationship of ethanol concentration and boiling point elevation after adding each ternary solute can be determined by regression in equations 7-11 below:

$$C_{AE} = 0.0501\ \Delta T_B + 98.459 \text{ (sodium hydroxide)} \quad (7)$$

$$C_{AE} = 0.0687\ \Delta T_B + 97.725 \text{ (citric acid)} \quad (8)$$

$$C_{AE} = 0.0466\ \Delta T_B + 98.820 \text{ (sulfuric acid)} \quad (9)$$

$$C_{AE} = 0.0456\ \Delta T_B + 98.525 \text{ (glycerol)} \quad (10)$$

$$C_{AE} = 0.0436\ \Delta T_B + 98.482 \text{ (ethylene glycol)} \quad (11)$$

where C_{AE} is anhydrous ethanol concentration (% v/v).

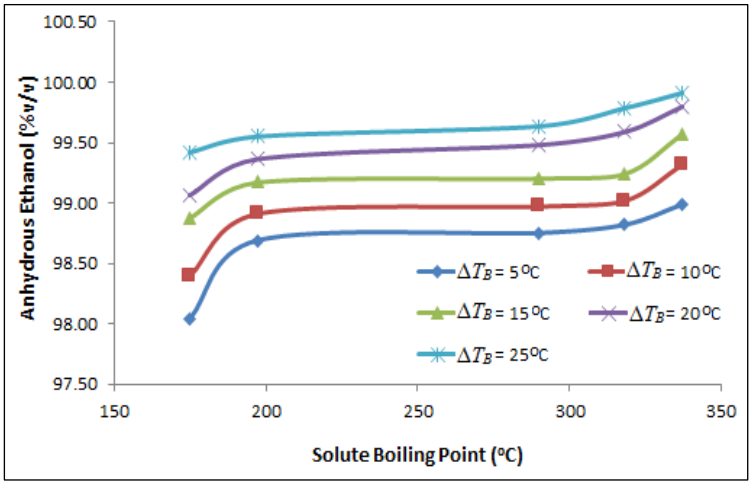

Figure 3. The effect of the anhydrous ethanol concentration on solute boiling point at ΔT_B values from 5 °C to 25 °C

Equations 7-11 are only valid for the addition of ternary solute. This shows that addition of ternary solute affects boiling point elevation and breaking of the azeotrope.

Conclusion

The colligative properties of a solution, particularly the boiling point elevation (ΔT_B), can be used to predict the amount of ternary substance that needs to be added. All the investigated ternary solutes (solid or liquid) could shift or break the ethanol-water azeotrope. The increase in the ethanol concentration from the extractive batch distillation was linear with the increase in the boiling point or the amount of ternary solute added as well as with the boiling point of the ternary solute. Meanwhile, the phase of the added ternary substance, either solid or liquid, had no effect. Therefore, anhydrous bioethanol can be produced by low cost and simple distillation process.

Acknowledgement

The authors would like to acknowledge the Universitas Pembangunan Nasional (UPN) "Veteran" Yogyakarta and The Directorate-General of New Renewable Energy and Energy Conservation (P3TKBTKE), Ministry of Energy and Mineral Resources of the Republic of Indonesia for sponsoring this project, and Universiti Kebangsaan Malaysia through GUP-2016-085 research grant.

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