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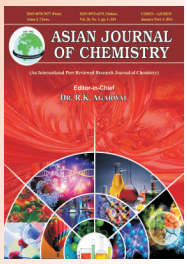

Purification of Bioethanol by Ionic Liquid Additives in Distillation System

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This study examined the potential use of ionic liquid (IL) as additives for the distillation of bioethanol from bioethanol-water mixture and applied an optimized distillation system to the purification of bioethanol from plant fermentation broths. Among the 9 ionic liquids added to the distillation system, [OMIM][BF_4] has the greatest effect on the purification of ethanol from aqueous solutions. In addition, the amount of [OMIM][BF_4], the initial concentration of ethanol in the mixture and the distillate fractions in the distillation system were studied systematically. Under the optimization distillation system using 2 g of [OMIM][BF_4], 20 mL of a 99.4 % (ethanol, v:v) aqueous solution was distilled from 100 mL of a 20 % (bioethanol, v:v) bioethanol-water mixture and the boiling point (71 °C) was lower than that of the bioethanol-water azeotrope.

Keywords: Bioethanol, Distillation, Ionic liquid, Purification.

INTRODUCTION

The global reserves of fossil fuels are decreasing, highlighting the need for a substitute. Bioethanol is an attractive alternative and renewable biofuel that can be produced from several different biomass feedstocks, such as corn grain and sugar cane[1,2]. Corn, however, is also a major human food resource, raising major ethical and moral issues when used for the production of bioethanol[3].

Water and ethanol are azeotrope compounds. Azeotrope is an ancient Greek word that translates to "to boil unchanged," and means that the emitted vapor and liquid have the same composition[4]. Azeotropic compounds have an azeotropic point, which prevents separation by simple distillation. For this reason, an azeotrope is called a fired point in nonlinear dynamics[5]. Therefore, extractive distillation is the most widely used process for separating azeotropic compounds. This method involves the addition of new solvents (entrainer) to interact with the components of the original mixture and alter their relative volatilities. On the other hand, this separation process has an environmental impact due to the use of volatile organic solvents as entrainers to break the binary azeotrope. This problem can be solved using ionic liquids[6,7]. Ionic liquids are ionic salts that exist in the liquid-state at temperatures less than 100 °C. Ionic liquids have attractive physical properties, such as low volatility, non-flammability, liquid-phase stability at high temperatures, high ability to solvate organic, inorganic or polymeric materials and high ionic conductivity. Ionic liquids can be synthesized easily by adjusting the combination of cations and anions, making them a so called "designer solvent"[8,9]. The properties of ionic liquids are determined by the structure and interaction of ions. The ionic liquids was composed of large cations and anions. The ionic liquids most commonly considered for synthesis are those with cations based on an imidazolium or pyridinium ring with one or more alkyl groups attached to the nitrogen or carbon atoms. The anions include halide ions, tetrafluoroborate $[BF_4]^-$, tetrachloroaluminate $[AlCl_4]^-$, hexafluorophosphate $[PF_6]^-$ and bis(perfluoromethyl-sulfonyl)imide anion $[CF_3SO_2]_2N^-$ (also known as bistriflate imide $[Tf_2N]^-$). In addition to the inter-actions in conventional organic solvents (hydrogen bonding, dipole-dipole and van der Waals interactions), ionic liquids also have ionic interactions (mutual electrostatic attraction or repulsion of charged particles)[10]. In addition, ionic liquids are recognized as new green media to substitute for volatile organic solvents, which have been widely used in the chemical, energy, material and electronic industries[11]. In recent years, ionic liquids has attracted considerable attention for their potential use as entrainers for the separation of azeotropic or close boiling mixtures[12].

This study examined the optimal conditions for separating azeotropic mixtures (water + ethanol) using ionic liquids. The separation of these mixtures is often required in industry. The ionic liquids studied were composed of a cation ($[EMIM]^+$, $[BMIM]^+$, $[HMIM]^+$, $[OMIM]^+$ or $[DMIM]^+$) and an anion ($[Br]^-$, $[Cl]^-$, $[BF_4]^-$, $[PF_6]^-$ or $[Tf_2N]^-$). The effect of different amounts of ionic liquids and different factions were analyzed.

EXPERIMENTAL

Ethanol, ethyl acetate and methylene chloride were obtained from Duksan Pure Chemical Co., Ltd. (Ansan, Korea). 1-Methylimidazole, bromoethane, bromobutane, bromohexane, bromooctane, bromodecane, chlorooctane, hexafluorophosphoric acid, sodium tetrafluoroborate and lithium were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Distilled water was filtered through a vacuum pump (Division of Millipore, Waters, USA) and filter (HA 0.45, Division of Millipore, USA) prior to use.

Synthesis of ionic liquid polymers: All the ionic liquids were synthesized according to the following process. 1-Methylimidazole was reacted with an excess of bromoethane, bromobutane, bromohexane, bromooctane, bromodecane and chlorooctane in a round-bottom flask under a 70 °C for 6 h and washed with ethyl acetate to produce [EMIM][Br], [BMIM][Br], [HMIM][Br], [OMIM][Br], [DMIM][Br] and [OMIM][Cl]. [OMIM][BF_4] was synthesized by a substitution reaction of the corresponding bromide[13]. [OMIM][Br] was mixed with sodium trafluoroborate in methylene chloried solution at room temperature for 0.5 h. After this time, two phases separated. The upper liquid phase containing the ionic liquids was dissolved in methylene chloride. For remove the remaining methylene chloride, the mixture was placed in a rotary evaporator and heated. Only [OMIM][BF_4] remained after evaporation. [OMIM][PF_6] and [OMIM][Tf_2N] were synthesized using the following process: [OMIM][Br] was mixed with aqueous solution of hexafluorophosphoric and lithium at room temperature for 0.5 h. After this time, two phases separated. The upper aqueous phase was decanted off leaving the [OMIM][PF_6] and [OMIM][Tf_2N] ionic liquids phase decant in the bottle.

Distillation process: Distillation was performed using the following process: A heating mantle was used to slowly increase the temperature of the water + ethanol +ionic liquid mixture in a round bottom flask. Different ionic liquids ([EMIM][Br], [BMIM][Br], [HMIM][Br], [OMIM][Br], [DMIM][Br], [OMIM][Cl], [OMIM][BF_4], [OMIM][PF_6] and [OMIM][Tf_2N]) were used to determine which could distill the highest concentration of ethanol. After distillation, the effects of different amounts of ionic liquids (0.2, 0.5, 1.0, 1.5 and 2.0 g), different initial concentrations of ethanol and different fractions of ethanol were assessed to optimize the process.

Gas chromatography conditions (GC): Gas chromatography was performed using a Younglin 6100 GC system and Younglin thermal conductivity detector (Younlin Co. Ltd., Korea). Data analysis was performed using Autochro-3000 software. GC consisted of a thermal conductivity detector (TCD) and DB-1701 capillary column (30 × 0.23 mm × 1.00 μm I.D). The injector, detector and oven temperatures were 220, 220 and 170 °C, respectively. Nitrogen, hydrogen and air were used as the carrier gases.

Standard solutions of ethanol (20, 50, 80 and 100 %) in water were prepared. As a result, linear regression equations (Y = aX + b) of the five compounds were obtained within the concentration range studied. X and Y represent the peak areas and concentrations of the analyte, respectively. The linear regression equation of ethanol was Y = 3.3485X + 37.731. The high correlation coefficients ($r^2 > 0.9981$) indicated good linearity between their peak areas (X) and the compound concentrations (Y) over a relatively wide concentration range.

RESULTS AND DISCUSSION

The azeotrope of ethanol-water does not allow the separation of two compounds by simple distillation. In this study, the methodology used for optimal process design first consists of the development of alternative ionic liquids for the optimal additive of a distillation system. The second step examined the effect of the optimal ionic liquids with different factors, such as the amount of ionic liquid, different concentrations of ethanol in the mixtures and different distillate fraction.

Effect of ionic liquids: Water/ethanol is a well know azeotrope, which can sometimes be broken by the addition of anther compound. Ionic liquids is normally quite hygroscopic materials with a strong affinity to water. Therefore, ionic liquids as additives in the distillation of ethanol-water systems are a good choice. Table-1 lists the structure of ionic liquids as additives. The selected ionic liquids is an important process for increasing the separation of ethanol. In this study, nine different ionic liquids were selected as additives. Table-1 and Fig. 1 (or Table-2.) shows that ionic liquid distillation involves a lower boiling temperature than distillation with on ionic liquid. The boiling point of the ethanol-water mixtures of including the ionic liquid system was lower more than that without the ionic liquid. In additions, the concentration of ethanol after distillation was obviously higher. The interactions between the ionic liquids and water are much stronger than between water and ethanol. The ionic liquids literally hold the water and release ethanol, which is distilled off as a pure material in the distillation system. In particular, [OMIM][BF_4] as an additive in the ethanol-water distillation system decreased the boiling point of the ethanol-water mixture and increased the concentration of ethanol in the distillate. Therefore, with [OMIM][BF_4] as an additive, the production of high purify bioethanol with high energy efficiency is expected. These ionic liquids have relatively low melting points and viscosities. These results highlight the effect of the ionic liquids in enhancing the relative volatility of the azeotropic mixture. The effects of the ionic liquids on the relative volatility are associated with their influences on the activity coefficients and their structure.

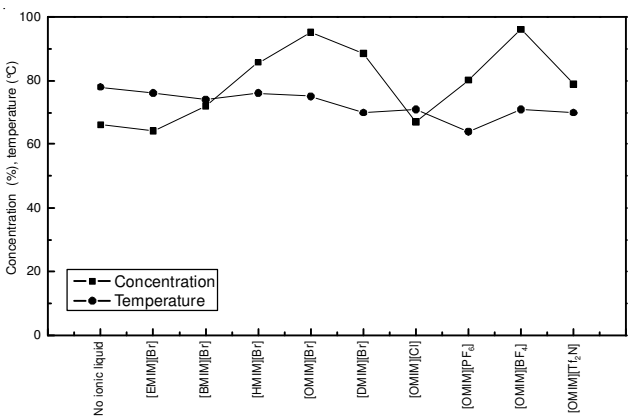


Fig. 1. Effect of the ionic liquids on the distillation of ethanol from ethanol-water mixtures (mixture concentration: ethanol-water (20:80 v/v), amount of ionic liquid: 1 g)

TABLE-1
STRUCTURES OF THE IONIC LIQUIDS

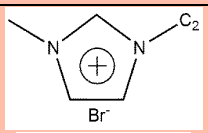
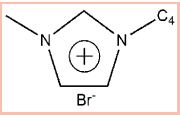
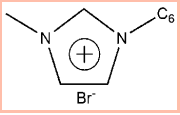
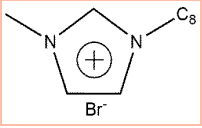
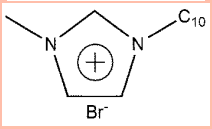
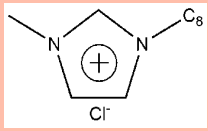
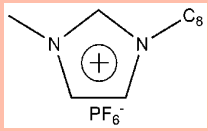
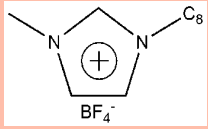
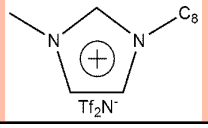
No	Cations	Anions	Structure
1	[EMIM]	[Br]	
2	[BMIM]	[Br]	
3	[HMIM]	[Br]	
4	[OMIM]	[Br]	
5	[DMIM]	[Br]	
6	[OMIM]	[Cl]	
7	[OMIM]	[PF_6]	
8	[OMIM]	[BF_4]	
9	[OMIM]	[Tf_2N]	

TABLE-2
EFFECT OF THE IONIC LIQUIDS ON THE DISTILLATION OF ETHANOL FROM THE ETHANOL-WATER MIXTURES (MIXTURE CONCENTRATION: ETHANOL-WATER (20:80 v/v), AMOUNT OF IONIC LIQUID: 1 g)

Ionic liquid	Boil temp. (°C)	Concentration of ethanol of distillation (%)
[EMIM] [Br]	76	64.1881
[BMIM] [Br]	74	72.0418
[HMIM] [Br]	76	85.6889
[OMIM] [Br]	75	95.2373
[DMIM] [Br]	70	88.4934
[OMIM] [Cl]	71	66.9320
[OMIM] [PF_6]	64	80.1785
[OMIM] [BF_4]	71	96.1282
[OMIM] [Tf_2N]	70	78.9803
Blank	78	64.1881

Effect of the amounts of ionic liquid: The amount of ionic liquids in the ethanol-water mixtures has a direct effect on the distillate purity. Therefore, this study first considered the effect of the amounts of ionic liquids without affecting the energy consumption significantly.

Water has a stronger affinity with an ionic liquid than ethanol. Therefore, the volatilization of water decreased and the two components (water + ethanol) could be separated. The effect of the amount of ionic liquid (0.2, 0.5, 1.0, 1.5 and 2.0 g) was examined. In this experiment, the concentration of ethanol was fixed and the amount of ionic liquid was increased. As shown in Fig. 2, the ethanol concentration in the distillate increased with increasing amount of ionic liquid. On the other hand, with more than 1 g of ionic liquid, the concentration of ethanol increased slowly because there was no interaction between the ionic liquid and water. An ionic liquid is an expensive solvent, meaning that large amounts of ionic liquids will increase the cost of the process. The non-volatility of the mixture (water + ethanol) is increased by adding an ionic liquid with a higher boiling point than the mixture (water + ethanol). Consequently, the amount of ionic liquids used must be as low as possible. Therefore, the amount can be manipulated to reach the distillate composition without high energy consumption. A large amount of ionic liquids increases the energy consumption in the distillation system. Accordingly, 2 g of ionic liquid was considered to be the optimal amount.

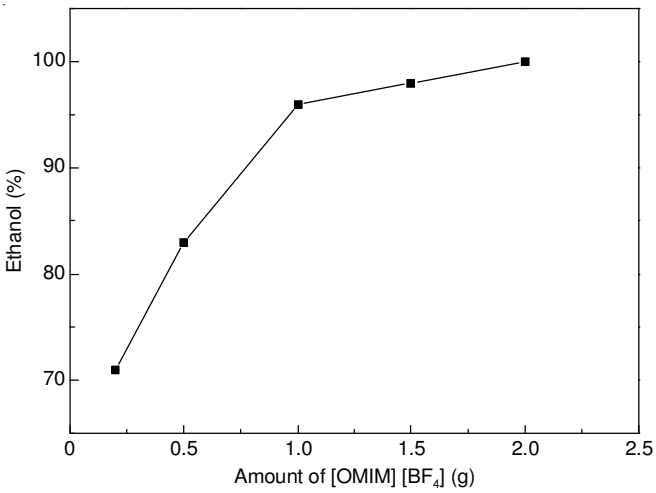


Fig. 2. Effect of the amounts of [OMIM][BF_4] on the distillation of ethanol from ethanol-water mixture (mixture concentration: ethanol-water (20:80 v/v))

Effect of the initial ethanol concentration: The effect of the initial ethanol concentration in the ethanol-water mixtures in a distillation system on the distillate composition was examined (Fig. 3). The distillation ethanol concentration was relatively unchanged regardless of the initial ethanol concentration. Only small variations in ethanol purity were observed over a wide range of initial concentrations. This experiment was carried out with a fixed amount of ionic liquid (2 g) and volume of mixtures (200 mL). Because a sufficient amount of ionic liquid was present in the small volume of the mixtures, which can interaction with water, a constant ethanol concentration can be obtained regardless of the initial concentrations of ethanol, suggesting that this process can be made commercially available.

Concentration of ethanol in different fractions: Fig. 4 shows the concentration of ethanol in different distillate fractions. The distillation condition was 20:80 v/v ethanol-water, 2 g of the ionic liquids and 5 mL of each distillate

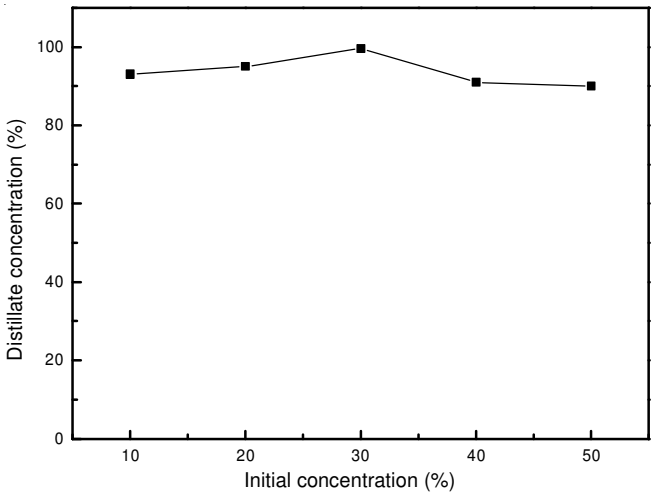


Fig. 3. Effect of the initial concentration of ethanol in mixtures in the distillation system (initial concentration: ethanol-water, v/v)

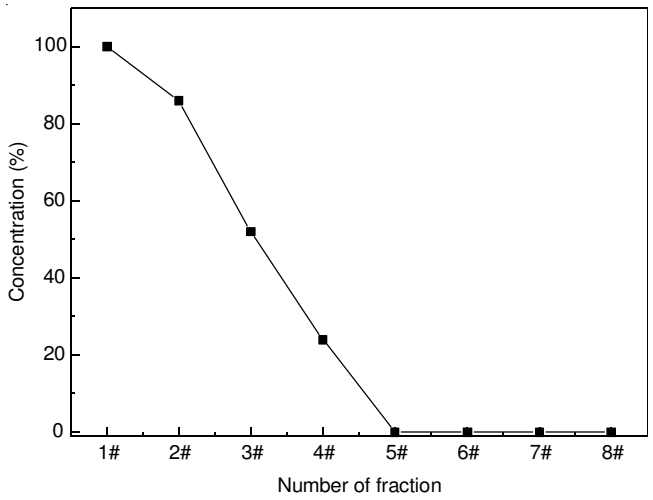


Fig. 4. Effect of the [OMIM][BF_4] fraction on the distillation of ethanol from an ethanol-water mixture (mixture concentration: ethanol-water (20:80 v/v)).

fraction obtained. As a result, the number of distillate fractions increases with decreasing ethanol concentration. Initially, high concentrations of ethanol were obtained in the distillate fraction because of the low boiling point of ethanol. With time, the amount of ethanol in the mixture (water + ethanol) decreased with a concomitant increase in the amount of water. Therefore, the concentration of ethanol decreased in the following distillate fractions.

Conclusion

The effects of nine ionic liquids in the ethanol-water distillation system were examined. The experimental data of the distillation systems were correlated with the different ionic liquids structures. [OMIM][BF_4] was found to have the best effect on distillation of the ionic liquids examined. Ionic liquids has potential use as an additive in the distillation system.

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