ASEAN Journal of Chemical Engineering 2023, Vol. 23, No. 3, 270 – 281

Extractive Distillation of Ethanol/Water with 1-Butyl-3-Methylimidazolium Bromide Ionic Liquid as a Separating Agent: Process Simulation

Dhoni Hartanto [*,1]
Prima Astuti Handayani [1]
Widi Astuti [1]
Ratna Dewi Kusumaningtyas [1]
Yulian Candra Purwana [1]
Maftukhaturrizqiyah [1]
Reni Titis Wijayanti [1]
Durroti Zuhriah Wulansari [1]
Ria Wulansarie [1]
Irene Nindita Pradnya [1]
Danang Subarkah Hadikawuryan [1]
Agung Ari Wibowo [2]
Riza Mazidu Sholihin [3,4]
Achmad Chafidz [5,6]
Ianatul Khoiroh [7]
[1]*Department of Chemical Engineering, Faculty of Engineering, Universitas Negeri Semarang, Kampus Sekaran, Gunungpati, Semarang, 50229, Indonesia*
[2] *Department of Chemical Engineering, Politeknik Negeri Malang, Jl. Soekarno-Hatta No. 9, 64415, Indonesia.*
[3]*RSUD Dr. Harjono, Pakunden, Ponorogo, 63419, Indonesia*
[4]*Akafarma Sunan Giri Ponorogo, Jalan Batoro Katong, Ponorogo 63411, Indonesia*
[5]*Department of Chemical Engineering, Universitas Islam Indonesia, Yogyakarta, 55584, Indonesia*
[6]*Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan*
[7]*Department of Chemical and Environmental Engineering, Faculty of Science and Engineering, University of Nottingham Malaysia, Jalan Broga, Semenyih, 43500 Selangor Darul Ehsan, Malaysia*
[*]e-mail: dhoni.hartanto@mail.unnes.ac.id

Submitted 14 January 2022 *Revised* 10 August 2023 *Accepted* 14 August 2023

Abstract. Ethanol purification has become of great interest recently because ethanol can be used as renewable energy, solvent in many industries, and for medicinal purposes. The separation of ethanol from water is challenging because the azeotropic point has appeared in this binary mixture. Extractive distillation technology is one of the most interesting methods to separate ethanol from water due to the competitiveness of its energy consumption and capital investment costs. Ionic liquids such as 1-butyl-3-methylimidazolium bromide [BMIM] [Br], categorized as a green solvent, produce a significant salting-out effect in the ethanol-water system. This makes ionic liquid a promising solvent in ethanol-water separation. This study simulated the extractive distillation of an ethanol-water system with 1-butyl-3-methylimidazolium bromide as a solvent. The simulation and sensitivity analysis were performed on the Aspen Plus Process Simulator to

DOI: 10.22146/ajche.72250

obtain the optimum configuration. The NRTL thermodynamic model was used in this study. The effects of the number of stages (NS), binary feed stage (BFS), entrainer feed stage (EFS), and reflux ratio (RR) on the ethanol concentration with minimum energy requirements were studied. The most optimal configurations to produce a high ethanol concentration with less energy are NS 28, BFS 22, EFS 4, and RR 1.5.

Keywords: Dehydration, Ethanol, Extractive Distillation, [BMIM] [Br] Ionic Liquid, Process Simulation

INTRODUCTION

Ethanol is widely used as an industrial solvent, a renewable energy source, and a building block chemical for fuels and chemicals. In medicine, ethanol acts as an antidote for the overdoses of methanol and ethylene glycol (Strohm, 2014), an activating agent for granular aerogel adsorbent to remove the organic pollutant in hospital wastewater (Prasanna et al., 2020), a chemical treatment for re-used N95 respirators and surgical masks (Grinshpun et al., 2020), and chemical treatment for benign prostatic hypertrophy (BPH) (Cheung et al., 2018), and testosterone-induced BPH (Ekeyi et al., 2021).

Ethanol sustainability sources, available in large quantities with a competitive price and the feasibility of converting ethanol into several derivative chemicals, make ethanol more attractive (Manochio et al., 2017; Dagle et al., 2020). The minimum concentration requirement of ethanol for many chemical industries as well as pharmaceutical or specific medical purposes and fuel purposes is 99.5 wt% (Zhu et al., 2016a) or 99.0–99.8 wt% according to international standards (EN 15376, ASTM D 4806). On the other hand, ethanol easily forms an azeotropic point at a purity of 95.6 wt%, requiring special separation methods to produce higher ethanol purity (Kiss and Suszwalak, 2012). The maximum purity obtained by conventional distillation can only be achieved up to the azeotrope point (95.6 wt%), and therefore simple distillation cannot be used to produce high-purity ethanol.

Alternative processes have been developed for ethanol-water separation. Solar distillation technology was applied to purify the ethanol only up to 80% v/v (Vorayos et al., 2006). Membrane-based purification, i.e., conventional pervaporation and pervaporation with a dynamic control technology, generated anhydrous ethanol (Meireles et al., 2016; Luyben, 2009). However, membrane-based technology has drawbacks, such as the complex preparation of good-quality membranes, the low separation efficiency induced by plasticization, and the limitation of operating in large-scale ethanol production. Adsorption-based technology can also be implemented in ethanol purification (Zheng et al., 2023). But this technology faces a great challenge when implemented in large-scale processes. Moreover, a complex adsorber-desorber should be provided in this process.

Extractive and azeotrope distillation are dominant technologies for ethanol dehydration in industrial practice (Kiss and Suszwalak, 2012). Extractive distillation performs better than azeotrope distillation as it requires less energy, up to 30.3% (Arifin and Chien, 2008). Therefore, extractive distillation is preferred.

Entrainer selection is one of the most important factors in extractive distillation

(Pan et al., 2019). Ethylene glycol was used as a conventional entrainers in extractive distillation (Hartanto et al., 2020; Li et al., 2021). Unfortunately, ethylene glycol poses toxicity that causes depression in the central nervous system and failure of the cardio-pulmonary and renal systems (Leth and Gregersen, 2005). Inorganic salts were also considered potential entrainers, even though they cause corrosion and incrustation problems (Hernández-Hernández et al., 2022). Currently, greener entrainers are greatly interested in being used in extractive distillation technology. Ionic liquids have become a rising star chemical that can be used as an entrainer to substitute conventional solvents. The advantages of using ionic liquids are high-temperature stability, the ability to be used in various mixtures, a wide temperature range, and no vapor pressure (Tsanas et al., 2014). In addition, ionic liquids (ILs) are considered a green solvent and have been applied in extractive distillation technology as one of the promising entrainers (Malik et al., 2023). Some recent studies evaluated the use of ILs for the ethanol-water separation (Fadia et al., 2022; Graczová and Steltenpohl, 2022; Ma et al., 2019; Momeni and Shekaari, 2022). One of the ILs that is considered a green solvent is 1-butyl-3-methylimidazolium bromide [BMIM] [Br] (Sudhan et al., 2018; Ghorbani et al., 2021). Tsanas et al. (2019) measured the effect of 1-butyl-3-methylimidazolium bromide [BMIM] [Br] ionic liquid in ethanol/water vapor-liquid equilibrium. The results indicate that the [BMIM] [Br] ionic liquid can break the azeotrope point in the ethanol/water system. However, the simulation study of this system and the performance comparison of ionic liquid with conventional entrainers are not available in the open literature. Therefore, further study needs to be conducted to understand the process design and its optimum configuration. In this work, the simulation of the extractive distillation of ethanol/water with [BMIM] [Br] ionic liquid has been studied to understand the effect of the number of stages, binary feed stages, entrainer feed stages, and reflux ratio on the purity of ethanol, total annual cost, and the energy requirement in the condenser and reboiler. Moreover, the performance of the ionic liquid has been compared with that of the conventional entrainer.

METHOD

Thermodynamic Model

The software package Aspen Plus V.11 was used in this study. The rigorous method was applied to simulate extractive distillation. The nonideality condition of the liquid phase was calculated using the Non-Random Two-Liquid (NRTL), assuming that the vapor phase is in the ideal condition. The NRTL is one of the most common thermodynamic models used in liquid phase calculations because of its capability to produce good calculation results. The provided optimum binary interaction parameters are listed in Table 1. The optimum binary interaction parameters are important as they quantify the molecular interaction behavior and predict the vapor-liquid equilibrium properties. Hence, these properties will affect the whole process simulation's accuracy. Furthermore, the non-randomness factor (Cij) of NRTL has an optimum range of 0.2–0.5. However, the effect of the randomness factor of this range on the curve of excess Gibbs energy is not strong. Therefore, the founders of the NRTL model recommend 0.3 as the most optimal one (Renon and Prausnitz, 1968).

The extended Antoine equation evaluated the total and partial pressures (eq.1).

$$\ln(P^s) = A_1 + \frac{A_2}{T+A_3} + A_4 T + A_5 \ln T + A_6 T^{A_7}, for\ A_8 < T < A_9 \quad (1)$$

Where P^s in kPa and T in K.

The extended Antoine constants were taken from the Aspen Plus physical property databank, as provided in Table 2. The Antoine constant for ionic liquid has been fixed at A_1 = -1000, and A_2 to A_7 as 0 represents the non-vapor behavior, ensuring that the ionic liquid will have a zero-vapor pressure.

Ionic liquid databases are only partially available in Aspen Plus due to relatively novel compounds, limited experimental data, and a shortage of predictive methods to provide proper thermo-physical properties as basic data for the process simulation. Therefore, it is required to provide user-defined ionic liquids, which can be used as components in a process simulation. User-defined ionic liquids can be approached by drawing or importing the molecular structures as mol files into Aspen Plus. Aspen Plus will estimate some of its thermo-physical properties. The other method may also be used to approach the ionic liquid with a compound with a similar chemical structure and properties. In addition, the ionic liquid can be well defined by inputting some known thermo-physical properties, such as molecular weight, boiling point, critical properties, and acentric factor. For the 1-butyl-3-methylimidazolium bromide, the thermo-physical properties were obtained from Valderrama and Rojas (2009).

Configuration and Sensitivity analysis

Initial process design parameters were fixed on a simulation basis. The parameters and their values are listed in Table 3. The concentration of aqueous ethanol solution was set at 0.7 mole fraction due to below the azeotrope point of the ethanol/water mixture. The pressure was set in atmospheric conditions (101.3 kPa).

Sensitivity analysis was studied to understand the effect of several parameters, such as a number of stages, binary feed stages, entrainer feed stages, and reflux ratio to ethanol purity and condenser-reboiler duty.

Table 1. Optimum binary interaction parameters for the NRTL model (Tsanas et al., 2014)

Component *i*	Component *j*	A_{ij}	A_{ji}	B_{ij} (K)	B_{ji} (K)	C_{ij}
Ethanol	Water	0	0	-34.59	621.73	0.3
Ethanol	[BMIM][Br]	0	0	1089.56	-961.22	0.3
Water	[BMIM][Br]	0	0	2361.08	-1146.1	0.3

where A_{ij}, A_{ji}, B_{ij}, and B_{ji} are the adjustable parameters, and C_{ij} is the non-randomness factor fixed to be 0.3 in this work.

Table 2. The extended Antoine equation constant.

Components	A_1	A_2	A_3	A_4	A_5	A_6 10^{-6}	A_7	A_8	A_9
Etanol	61.7911	-7122.3	0	0	-7.1412	2.88	2	-114	240.85
Water	62.1361	-7258.2	0	0	-7.3037	4.16	2	0.01	373.95
[BMIM] [Br]	-1000	0	0	0	0	0	0	-	-

Table 3. Initial process design parameter

Parameters	Value
Ethanol feed mole-fraction	0.7
Theoritical stage numbers	30
Entrainer mole fraction	0.5
Feed temperature (°C)	25
Entrainer temperature (°C)	70
Binary feed stage	21
Entrainer feed stage	3
Pressure (kPa)	101.3

RESULTS AND DISCUSSION

Conceptual Process Design and Preliminary Simulation

The conceptual process design for the separation of ethanol from water using [BMIM] [Br] ionic liquid as an entrainer through extractive distillation consists of two main columns, which are the extractive distillation column (EDC) as a first column and the entrainer recovery column (ERC) as a second column. The RadFrac block, as a rigorous calculation model, was used to simulate EDC and ERC. The main parameters in EDC that can be used to optimize the separation performance consist of the number of stages (NS), binary feed stage (BFS), entrainer feed stage (EFS), and reflux ratio (RR). The details of the process flow diagram are provided in Figure 1. The aqueous ethanol solution (FEED stream) and [BMIM] [Br] ionic liquid (SOLVENT stream) enter the EDC. In the first column, ethanol was separated from the water using the entrainer. Higher purity of ethanol (ETHA stream) was obtained in the top column, and a mixture of water/[BMIM] [Br] ionic liquid was achieved in the bottom column. The mixture of water/[BMIM] [Br] ionic liquid (RICH-SOL) enters the second column, followed by the separation process. [BMIM] [Br] ionic liquid was collected in the bottom column, and water was obtained in the top column. [BMIM] [Br] ionic liquid (IL-1 stream) was cooled to meet the desired temperature. The cooler [BMIM] [Br] ionic liquid (IL-2) was recycled to the EDC and mixed with the make-up entrainer to keep a sufficient amount of entrainer in the EDC. In addition, the preliminary simulation was studied in our previous work to validate the simulation method (Hartanto et al., 2021). The simulation indicates satisfactory results with a small deviation compared to the literature. The simulation results for extractive distillation, recovery column, and stream are provided in Tables 4 and 5, respectively.

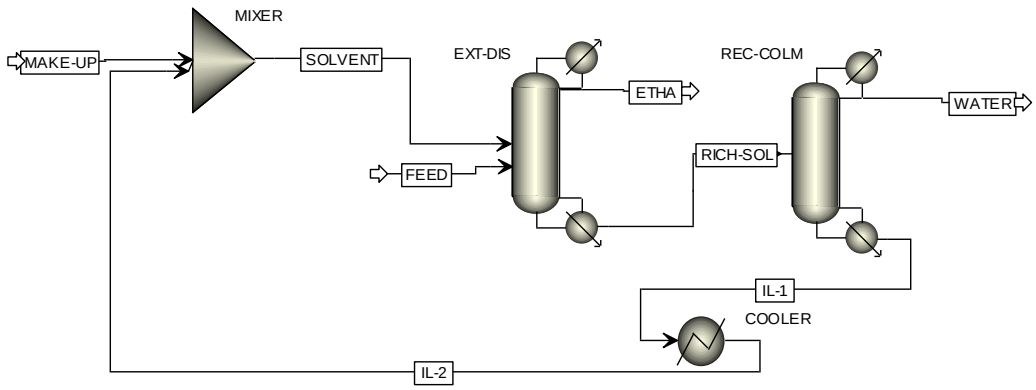


Fig. 1: Extractive distillation process flow diagram for ethanol and water separation using [BMIM] [Br] ionic liquid as an entrainer.

Table 4. The extractive distillation and recovery column simulation results

Parameters	Distillation Column	
	Extractive	Recovery
Pressure (kPa)	101.3	101.3
Condenser temperature (°C)	78.4	143.5
Condenser heat duty (kW)	-1669.15	-3052.02
Reboiler temperature (°C)	144.2	159.3
Reboiler heat duty (kW)	2513.54	3051.75
Distillate rate (kmol/hr)	60	140
Bottom rate (kmol/h)	145	5
Boil up rate (kmol/h)	174.25	266.28
Molar boil up ratio	1.207	53.255

Table 5. The extractive distillation stream results

Parameters	Distilate	Bottom
Flowrate (kmol/h)	60	145
Ethanol mole fraction	0.9956	0.007
Water mole fraction	5.7×10^{-5}	0.206
Ionic liquid mole fraction	0.004	0.722

Sensitivity Analysis

The initial simulation of extractive distillation uses BFS 21, EFS 3, feed molar flow, and entrainer molar flow of 100 kmole/hr and 105 kmole/hr, respectively. The simulation shows the ethanol purity of the top product was 0.9956 of mole fraction. The sensitivity analysis results for the effect of the NS and reflux ratio on the ethanol purity are shown in Figure 2.

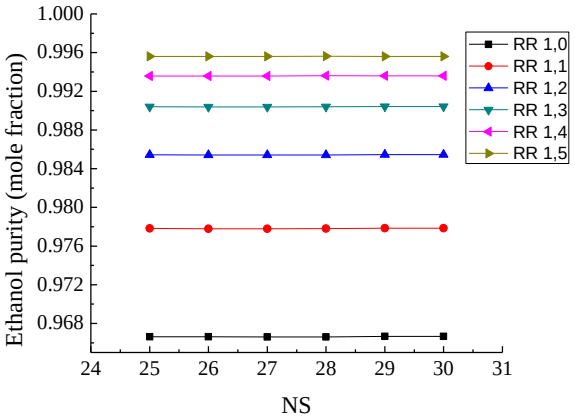


Fig. 2: Effect of NS and RR on Ethanol Purity (BFS 21, EFS 3).

As shown in Figure 2, ethanol purity remains constant as the stage number increases from 25 to 30. The contact between liquid and vapor remains constant in these stages, so adding more stages will not significantly change the ethanol's purity. Stage 28 was selected as an optimum condition, with the safety design consideration between 25 and 30. On the other hand, ethanol purity has increased with the reflux ratio. Reflux ratios significantly affect ethanol purity more than stage numbers from 25 to 30 because a higher reflux ratio will increase the liquid-vapor contact and mass transfer rates in the extractive distillation column. This work evaluated reflux ratios of 1, 1.1, 1.2, 1.3, 1.4, and 1.5.

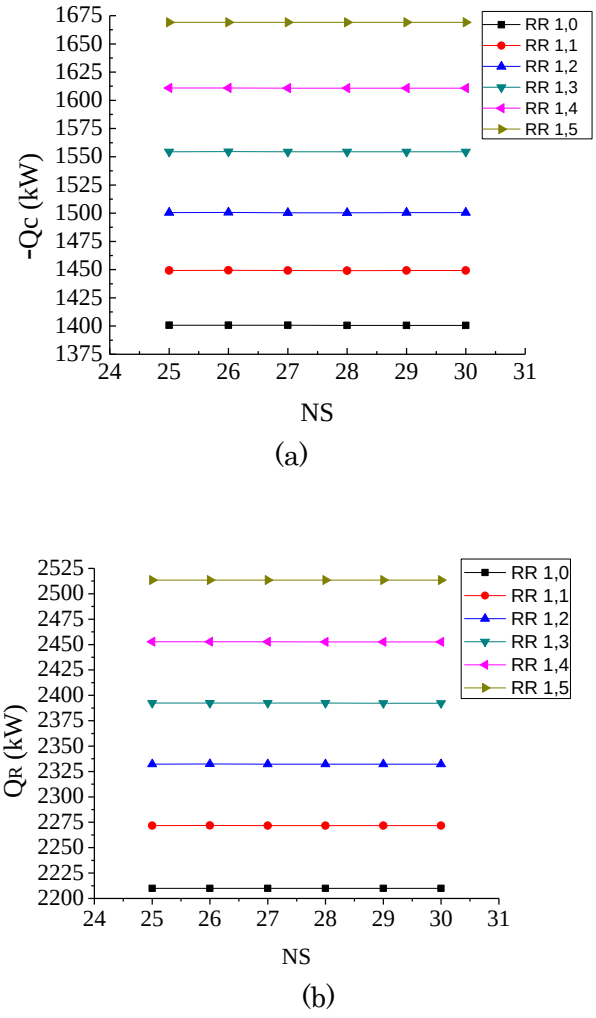


Fig. 3: Effect of NS and RR on: (a) Condenser heat duty (QC) and (b) Reboiler heat duty (QR).

These results also agree with a recent study indicating that a higher distillate will be achieved at a higher reflux ratio (Zhu et al., 2016). The highest ethanol purity of 0.9956 mole fraction can be achieved when the reflux ratio is 1.5. A higher reflux ratio means the energy required will increase because the reboiler and condenser duty will also increase. Therefore, maintaining the reflux ratio as low as possible should be considered. However, a low reflux ratio will only produce ethanol with a purity of less than 99%. Hence, this work selected the reflux ratio of 1.5 as the optimum one.

Figure 3 indicates that increasing the stage number did not affect the condenser and reboiler duties. However, the reflux ratio can affect the duties of the equipment. More vapor flow will be produced in the column with an increased reflux ratio. Thus, the energy duties of the reboiler and condenser will also increase due to the product vaporization and distillate condensation requirements. The results align with the previous study, which indicated that an increasing reflux ratio would significantly increase reboiler and condenser duties (Zhu et al., 2016; Stewart, 2014). The highest energy duties for the reboiler and condenser occurred in the highest reflux ratio of 1.5.

The effect of BFS and EFS on ethanol purity was studied. Figure 4 shows that the ethanol purity remains constant for the BFS 20 until 29. On the other hand, EFS caused a significant change in ethanol purity. As the solvent is supplied to the top stages, it is possible to confirm that the entrainer in the liquid phase is present in all the tower's trays below the EFS. Therefore, this condition results in less contact between vapor and liquid in a binary mixture, resulting in a less effective separation process. The highest ethanol purity was achieved at EFS 4. However, the ethanol purity decreased after BFS 29 because, as the BFS goes to the lower part of the column, the bottom part will contain more volatile compounds and therefore less ethanol purity than the top part, the resulting increase in condenser and reboiler duty, as depicted in Figure 5. In this work, the BFS has the maximum number in stage 29. BFS 22 was selected as the optimum number because the binary mixture can be fed near the bottom column, which has longer contact with the entrainer, while maintaining the purity of the ethanol in the top product. Moreover, too low a feed stage

can cause excessive reboiler and condenser duty.

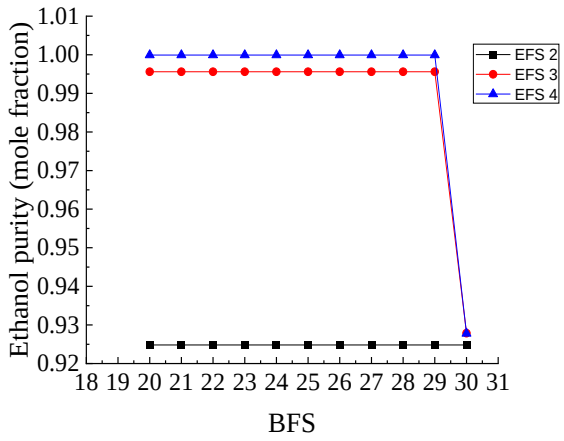
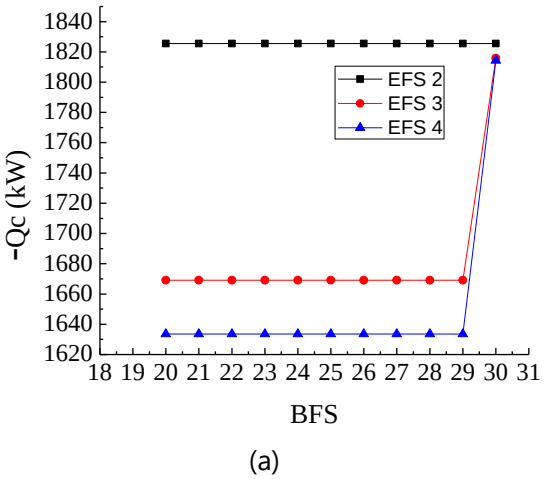
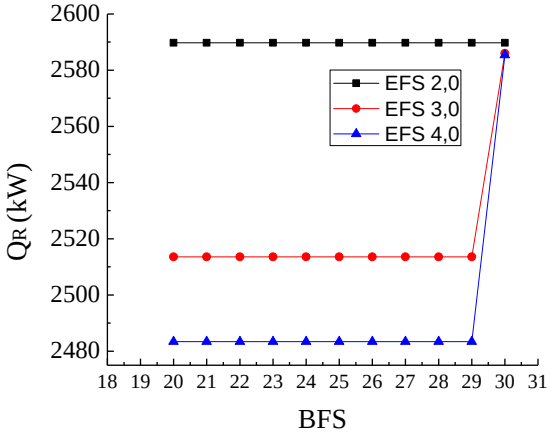


Fig. 4: Effect of BFS and EFS on Ethanol Purity on stage number 28.

Figure 5 displays the effect of the BFS and EFS on the energy required in the condenser and reboiler. As shown in Figure 5, the increase in the BFS did not show a significant change in the condenser and reboiler duties, while the increase in the EFS gave a significant change in the condenser and reboiler duties. EFS 2 shows the highest energy requirement for the condenser and reboiler compared with EFS 3 and 4. As entrainer is fed at the top of the column, the liquid entrainer will cover all the trays below the entrainer, which makes less contact between the vapor and liquid phases of the binary mixture. Therefore, a harder separation will take place. Harder separation needs to be adjusted by the increase of reflux ratio, followed by the increase of reboiler and condenser duty, to meet the required ethanol purity. These results match earlier studies, which show that reboiler duty will increase when the entrainer is fed in the upper part (Gómez and Gil, 2007). The entrainer feed stage of 4 was selected as an optimum condition because it needs less energy than the EFS of 2 and 3 but can produce the highest ethanol concentration.



(a)



(b)

Fig. 5: Effect of BFS and EFS on: (a) Condenser heat duty (QC) and (b) Reboiler heat duty (QR).

Table 6 compares several best possibilities for the entrained feed stage at the binary feed stage of 22 with an NS of 28 and a reflux ratio of 1.5. The results performed at EFS 4 at BFS 22 give the best results with the highest ethanol purity and the lowest energy, which are 0.9999 mole fraction and 4116.96 kW, respectively. The optimum configuration is listed in Table 7. The optimum configuration was obtained by iterative analysis. BFS and EFS trial values were used to provide suitable NS and RR to obtain a high purity of ethanol. The selected NS and RR were used to evaluate the

optimum BFS and EFS based on the ethanol purity obtained and the energy requirements.

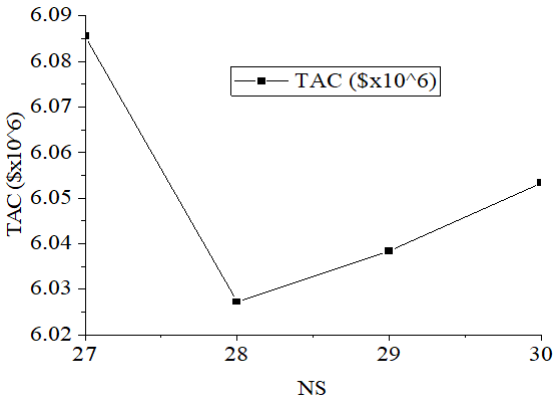


Fig. 6: Total annual cost of extractive distillation process using 1-butyl-3-methylimidazolium bromide as an entrainer.

Table 6. The comparison for the combination of entrainer feed stage to the ethanol purity and total heat duties

BFS	EFS	Ethanol purity (mole fraction)	Total of Energy (kW)
22	2	0.9248	4415.33
22	3	0.9956	4182.7
22	4	0.9999	4116.96

Table 7. Optimum configuration

Parameters	Value
Number of stages	28
BFS	22
EFS	4
Reflux ratio	1.5
Ethanol purity (mole fraction)	0.9999
Reboiler duty (kW)	2513.47
Condensor duty (kW)	-1669.04

Moreover, the selection of number of stages 28 also supported by the cost analysis. NS 28 produces a high ethanol purity of ethanol with the lowest total annual cost (TAC) compared to the other stages, as seen in Figure 6. The TAC using NS 28 was 6.02 x 10^6 USD, lower than the TAC when glycerol is used as an entrainer, as simulated by Novita et al. (2018), with a TAC of 6.56 x 10^6 USD.

CONCLUSIONS

In this work, extractive distillation for the azeotropic mixture of ethanol/water with [BMIM] [Br] ionic liquid as an entrainer, has been studied. The Aspen Plus V11, as process simulation software, has been equipped. The NRTL thermodynamics model was used to calculate the nonideality of the liquid phase. A sensitivity analysis has been performed to determine the effect of stage number, reflux ratio, binary feed stage, and entrainer feed stage on ethanol purity and condenser and reboiler duties. The selected stage number was 28, which produces high purity ethanol and is a safety design consideration. The reflux ratio of 1.5 was chosen due to its capability to produce high purity ethanol. BFS did not significantly affect the ethanol purity or condenser-reboiler duty, but BFS 22 was selected to prevent excessive reboiler and condenser duties. On the contrary, the change in EFS number can affect ethanol purity and condenser-reboiler duty. EFS 4 was selected because it can produce high-purity ethanol with less energy. The optimum configuration can reach an ethanol purity of 0.9999 moles fraction. Furthermore, the ionic liquid performs better in total annual cost than glycerol entrainers.

ACKNOWLEDGEMENT

The authors acknowledge the Faculty of Engineering, Universitas Negeri Semarang for the financial support through Dana DIPA Fakultas Tahun 2021 Grant No. DIPA-

023.17.2.677507/2021. The authors also gratefully acknowledge the financial support through a doctoral scholarship for Dhoni Hartanto by Indonesia Endowment Fund for Education (LPDP), Ministry of Finance, the Republic of Indonesia

REFERENCES

Arifin, S., and Chien, I.-L., 2008). "Design and control of an isopropyl alcohol dehydration process via extractive distillation using dimethyl sulfoxide as an entrainer." *Industrial & Engineering Chemistry Research*, *47*(3), 790–803.

Cheung, D. C., Millman, A. L., Lenardis, M., and Elterman, D., 2018). *Chapter 21 - Ethanol Injection of the Prostate in Benign Prostatic Hypertrophy* (B. B. T.-A. C. G. to the P. Chughtai, Ed.; pp. 189–195. Academic Press.

Dagle, R. A., Winkelman, A. D., Ramasamy, K. K., Lebarbier Dagle, V., and Weber, R. S., 2020. "Ethanol as a renewable building block for fuels and chemicals." *Industrial & Engineering Chemistry Research*, *59*(11), 4843–4853.

Ekeyi, Y., Uchendu, N. O., Anaduaka, E. G., and Ezeanyika, L. U. S., 2021. "Ethanol extract of *Cassia sieberiana* leaves ameliorates deviances associated with benign prostatic hyperplasia in rats." *All Life*, *14*(1), 473–483.

Gil, I. D., Uyazán, A. M., Aguilar, J. L., Rodríguez, G., and Caicedo, L. A., 2008. "Separation of ethanol and water by extractive distillation with salt and solvent as entrainer: Process Simulation." *Brazilian Journal of Chemical Engineering*, *25*(1), 207–215.

Gómez, P., and Gil, I., 2007. Simulation of the tetrahydrofuran dehydration process by extractive distillation in Aspen Plus. *Proceedings of European Congress of Chemical Engineering (ECCE-6)*, 1–19.

Grinshpun, S. A., Yermakov, M., and Khodoun, M., 2020. "Autoclave sterilization and ethanol treatment of re-used surgical masks and N95 respirators during COVID-19: impact on their performance and integrity." *Journal of Hospital Infection*, *105*(4), 608–614.

Hartanto, D., Fardhyanti, D. S., Laela, N., Wulansarie, R., Harianingsih, Imani, N. A. C., Chafidz, A., Kusumaningtyas, R. D., and Khoiroh, I., 2021. "Anhydrous tert-butanol production via extractive distillation using glycerol as an entrainer: technical performances simulation." *IOP Conference Series: Earth and Environmental Science*, *700*(1), 12029.

Kiss, A. A., and Suszwalak, D. J.-. P. C., 2012. "Enhanced bioethanol dehydration by extractive and azeotropic distillation in dividing-wall columns." *Separation and Purification Technology*, *86*, 70–78.

Manochio, C., Andrade, B. R., Rodriguez, R. P., and Moraes, B. S., 2017. "Ethanol from biomass: A comparative overview." *Renewable and Sustainable Energy Reviews*, *80*, 743–755.

Pan, Q., Shang, X., Li, J., Ma, S., Li, L., and Sun, L., 2019. "Energy-efficient separation process and control scheme for extractive distillation of ethanol-water using deep eutectic solvent." *Separation and Purification Technology*, *219*, 113–126.

Prasanna, V. L., Mamane, H., Vadivel, V. K., and Avisar, D., 2020. "Ethanol-activated granular aerogel as efficient adsorbent for persistent organic pollutants from real leachate and hospital wastewater." *Journal of Hazardous Materials*, *384*, 121396.

Stewart, M. I., 2014. Chapter Nine - Gas Sweetening. In M. I. Stewart (Ed.), *Surface Production Operations (Third Edition)* (Vol. 2, pp. 433–539). Gulf Professional

Publishing.

Strohm, B., 2014. *Ethanol* (P. B. T.-E. of T. (Third E. Wexler, Ed.; pp. 488–491). Academic Press.

Tsanas, C., Tzani, A., Papadopoulos, A., Detsi, A., and Voutsas, E., 2014. "Ionic liquids as entrainers for the separation of the ethanol/water system." *Fluid Phase Equilibria*, *379*, 148–156.

Zhu, Z., Ri, Y., Li, M., Jia, H., Wang, Y., and Wang, Y., 2016a. "Extractive distillation for ethanol dehydration using imidazolium-based ionic liquids as solvents." *Chemical Engineering and Processing: Process Intensification*, *109*, 190–198.

Fadia, G., Hassiba, B., Weifeng, S., 2022. "Separation of ethanol – water mixture by extractive distillation using pyridinium-based ionic liquid 1-ethyl-3-methylpyridinium ethylsulfate." *Chem. Eng. Process. - Process Intensif.*, 173, 108815.

Ghorbani, S.M., Housaindokht, M.R., Bozorgmehr, M.R., 2021. "Investigating the effect of 1-Butyl-3-methylimidazolium bromide and 1-Butyl-3-methylimidazolium methyl sulfate ionic liquids on structure and function of Chloroproxidase by molecular dynamics simulation." *J. Mol. Liq.,* 332, 115850.

Graczová, E., Steltenpohl, P., 2022. "VLE measurement of binary systems containing imidazolium ionic liquids and water or ethanol." *Fluid Phase Equilib.,* 556, 113400.

Hartanto, D., Sutrisno, A., Widya, V., Mustain, A., Handayani, P.A., Prasetiawan, H., Chafidz, A., Khoiroh, I., 2020. Simulation of the Extractive Distillation using Ethylene Glycol as an Entrainer in the Bioethanol Dehydration, in: Proceedings of the 7th Engineering International Conference on Education, Concept and Application on Green Technology (EIC 2018. SCITEPRESS – Science and Technology Publications, pp. 450–454.

Hernández-Hernández, E. de J., Cabrera-Ruiz, J., Hernández-Escoto, H., Gutiérrez-Antonio, C., Hernández, S., 2022. "Simulation study of the production of high purity ethanol using extractive distillation: Revisiting the use of inorganic salts." *Chem. Eng. Process. - Process Intensif.,* 170, 108670.

Kiss, A.A., Suszwalak, D.J.-. P.C., 2012. "Enhanced bioethanol dehydration by extractive and azeotropic distillation in dividing-wall columns." *Sep. Purif. Technol.*, 86, 70–78.

Leth, P.M., Gregersen, M., 2005. "Ethylene glycol poisoning." *Forensic Sci. Int.*, 155, 179–184.

Li, G., Liu, S., Yu, G., Dai, C., Lei, Z., 2021. "Extractive distillation using ionic liquids-based mixed solvents combined with dividing wall column." *Sep. Purif. Technol.*, 269, 118713.

Luyben, W.L., 2009. "Control of a column/pervaporation process for separating the ethanol/water azeotrope." *Ind. Eng. Chem. Res.*, 48, 3484–3495.

Ma, S., Shang, X., Li, L., Song, Y., Pan, Q., Sun, L., 2019. "Energy-saving thermally coupled ternary extractive distillation process using ionic liquids as entrainer for separating ethyl acetate-ethanol-water ternary mixture." *Sep. Purif. Technol.,* 226, 337–349.

Malik, H., Khan, H.W., Hassan Shah, M.U., Ahmad, M.I., Khan, I., Al-Kahtani, A.A., Sillanpää, M., 2023. "Screening of ionic liquids as green entrainers for ethanol water separation by extractive distillation: COSMO-RS prediction and

aspen plus simulation." *Chemosphere,* 311, 136901.

Meireles, I.T., Brazinha, C., Coelhoso, I.M., Crespo, J.G., 2016. 10 - Membranes for ethanol dehydration, in: Figoli, A., Cassano, A., Basile, A.B.T.-M.T. for B. (Eds.), Woodhead Publishing, pp. 241–262.

Momeni, P., Shekaari, H., 2022. "Effect of choline lactate ionic liquid as entrainer on the thermodynamic properties of alcohols + water azeotropic mixtures." *J. Mol. Liq.,* 366, 120138.

Novita, F.J., Lee, H.-Y., Lee, M., 2018. "Energy-efficient and ecologically friendly hybrid extractive distillation using a pervaporation system for azeotropic feed compositions in alcohol dehydration process." *J. Taiwan Inst. Chem. Eng.,* 91, 251–265.

Sudhan, S.P.N., Ahmed, R.N., Kiyani, H., Mansoor, S.S., 2018. "Ionic liquid 1-butyl-3-methylimidazolium bromide: A green reaction media for the efficient synthesis of 3-methyl-1,4-diphenyl-1,4,5,7-tetrahydro-pyrazolo[3,4-d]pyrimidine-6-ones/thiones using phthalimide-N-sulfonic acid as catalyst." *J. Saudi Chem. Soc*. 22, 269–278.

Valderrama, J.O., Rojas, R.E., 2009. "Critical Properties of ionic liquids. Revisited." *Ind. Eng. Chem. Res*,. 48, 6890–6900.

Vorayos, N., Kiatsiriroat, T., Vorayos, N., 2006. "Performance analysis of solar ethanol distillation." *Renew. Energy*, 31, 2543–2554.

Zheng, X., Chen, L., Zhang, H., Yao, Z., Yang, Y., Xiang, F., Li, Y., Xiang, S., Zhang, Z., Chen, B., 2023. "Optimized sieving effect for ethanol/water separation by ultramicroporous MOFs." *Angew. Chemie Int.* Ed. 62, e202216710.