

Assessment of Deep Eutectic Solvents for Alcohol-Water Separations by Extractive Distillation

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Abstract. Deep eutectic solvents (DESs) have been considered as potential natural solvents. This work investigated extractive distillation with DESs for the separation of ethanol-water and isopropanol-water using Aspen Plus as process simulator. Based on the effect of the DESs on the vapour-liquid equilibrium (VLE), choline chloride:urea [ChCl:Ur] (1:2) and choline chloride:triethylene glycol [ChCl:TEG] (1:3) were evaluated for the ethanol system and isopropanol system, respectively. For both systems, the results show that a series of two evaporators is the most economical entrainer regeneration option. Compared to conventional organic solvent-based processes, introducing the DESs improves the process performance by at least 20% from an energy perspective and by a minimum of 16% from a total annual cost (TAC) perspective. Moreover, replacing ionic liquids with evaluated DESs also reduces energy consumption by a minimum of 6%. Therefore, it is concluded that extractive distillation using DESs outperforms conventional organic solvents and ionic liquids for both separations; ethanol-water and isopropanol-water.

Keywords extractive distillation, deep eutectic solvents, ethanol-water, isopropanol-water, energy-saving, cost-saving

Introduction

High purity ethanol and isopropanol (IPA) are used in a wide range of applications in the chemical industry. However, ethanol-water and IPA-water form a minimum boiling point azeotrope, which is difficult to separate. Extractive distillation (ED) has been widely applied throughout the chemical process industry as one of the main techniques for close-boiling or azeotropic mixture separation. Conventional organic solvents such as ethylene glycol (EG) for ethanol-water separation and dimethyl sulfoxide (DMSO) for IPA-water separation are common entrainers [1,2]. Unfortunately, application of organic entrainers poses some drawbacks, such as high volatility, accumulation in the atmosphere, non-biodegradability, secondary pollution problems, flammability, and high energy consumption [3,4]. Introducing alternative entrainers has received much attention to improve the sustainability by reducing energy requirements and addressing the environmental issues associated with using organic solvents. Recently, the use of ionic liquids (ILs) such as [Emim]⁺[BF₄]⁻ and [Emim]⁺[N(CN)₂]⁻ has gained attention as a new class of entrainers for anhydrous ethanol and anhydrous isopropanol production, respectively [5,6]. However, the use of ILs as entrainers has potential limitations e.g expensive, low biodegradability, complex synthesis, and possible toxicity [7]. Therefore, this study investigated a new class of green entrainers named DESs of [ChCl:Ur] (1:2) and [ChCl:TEG] (1:3) for ethanol-water and IPA-water, respectively. Most current research focuses on vapour-liquid equilibrium measurements, but process performance comparisons with conventional organic solvents and other entrainer alternatives are largely missing. In this study, the different entrainer recycle alternatives and a sensitivity analysis of the design variables were evaluated. Subsequently, a consistent performance evaluation for the costs and energy requirements of the final DESs-based processes against the processes employing conventional organic solvents and ionic liquids was carried out.

Design Methodology

Data collection.

Thermophysical properties of the components such as molecular weight (M_w), melting temperature (T_m), normal boiling point (T_b), and density (ρ) were obtained from Aspen Plus. For the DESs, the properties such as M_w , T_m , critical temperature (T_c), critical pressure (P_c), critical volume (V_c), the acentric factor (ω), vapor pressure (p_{vap}), ρ , viscosity

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(η), and heat capacity (c_p) in various temperatures were obtained from literature [8–15], as well as the VLE data for ethanol-water-ChCl:Ur (1:2) and IPA-water- ChCl:TEG (1:3) [16,17].

Thermodynamics

The nonrandom two-liquid (NRTL) thermodynamic model was used to describe the VLE behavior. Aspen Plus was used to regress the optimal binary interaction parameters for the NRTL model and the temperature-dependent properties.

Configuration of Process Simulation

The process designs consisting of an extractive distillation column (EDC) and an entrainer regeneration were simulated using Aspen Plus V.8.8. Evaporation or evaporation combined with stripping for entrainer regeneration were selected as the first two base case designs. The RadFrac model was used to simulate the EDC, and the stripping column. A pressure drop of 20 kPa was applied in EDC as base case design. Two-outlet Flash vessels were used to simulate the evaporators and the Newton algorithm was applied for the simulation of the EDC and the entrainer regeneration column. Subsequently, a total condenser was used when only evaporation was applied, while for the stripping column a partial condenser was taken. As follow-up to the base case designs, the feed flowrates and purity constraints of the simulation were taken from literature, as summarised in Table 1. These constraints were used to compare the DESs-based processes with the processes using conventional organic solvents and ionic liquids.

Table 1. Simulation constraints of ethanol and water separation, and IPA and water separation

Parameter	Ethanol and water separation		IPA and water separation
	Process using EG [1]	Process using IL [Emim] ⁺ [BF ₄] ⁻ [5]	Process using IL [Emim] ⁺ [N(CN) ₂] ⁻ [6]
Feed (kmol/h)	245	100	100
Alcohol feed composition (mol%)	88.5	85	50
Alcohol product purity (mol%)	99.7	99.9	99.9
Alcohol recovery (%)	99.9	99.9	99.9
Entrainer recovery (%)	99	99	99

For both DESs systems, a sensitivity analysis was performed to define the optimized design parameters, such as EDC pressure (P_{EDC}), entrainer purity (x_E), EDC number of stages (N_{th}), feed stage (N_F), entrainer feed stage (N_E), entrainer-to-feed ratio (E/F), reflux ratio (RR), feed temperature (T_F), and entrainer feed temperature (T_E). Additionally, a sensitivity analysis on the entrainer regeneration was used to determine the best regeneration configuration. For both systems, the extractive distillation process designs were evaluated with and without heat integration, both from an energy and economic perspective.

Results and Discussion

DES selection and its feasibility

For the ethanol-water system, the DESs of ChCl:Ur (1:2), choline chloride:ethylene glycol [ChCl:EG] (1:2), and choline chloride:glycolic acid [ChCl:GA] (1:3) were compared to find the most feasible DES. For the IPA-water system, the DES with the highest selectivity and capacity was taken from literature [17]. A residue curve map analysis revealed that there are no azeotropes or miscibility gaps for ternary compositions, which confirms the feasibility of the selected DES as entrainer. For the ethanol-water system, ChCl:Ur (1:2) is the smallest molecule resulting in the highest polarity, which leads to the highest selectivity of the three investigated DESs. Apparently, ChCl:Ur (1:2) is the best hydrogen bond donor (HBD) for selective interaction with water over ethanol because water is the strongest hydrogen bond acceptor (HBA) [7]. In contrast to the ethanol-water system, it seems that an effective entrainer for IPA-water system is preferred to have a strong HBA capacity. ChCl:TEG (1:3) shows the strongest HBA ability to interact with IPA rather than water because IPA acts as the strongest HBD, making ChCl:TEG (1:3) the most suitable entrainer for the IPA-water system [17].

EDC Sensitivity analysis

a. Effect of pressure on energy requirements

An important design variable is the pressure of the EDC column. Four different pressures were evaluated in terms of total energy requirement. Fig. 1 illustrates that for each pressure decrease of approximately 30 kPa, the total energy requirement decreases by approximately 100 kW, but a pressure below 14 kPa requires more expensive condensing

utilities instead of cooling water. Therefore, a pressure of 14 kPa was taken for further evaluation and economic comparison with the EDC at atmospheric pressure.

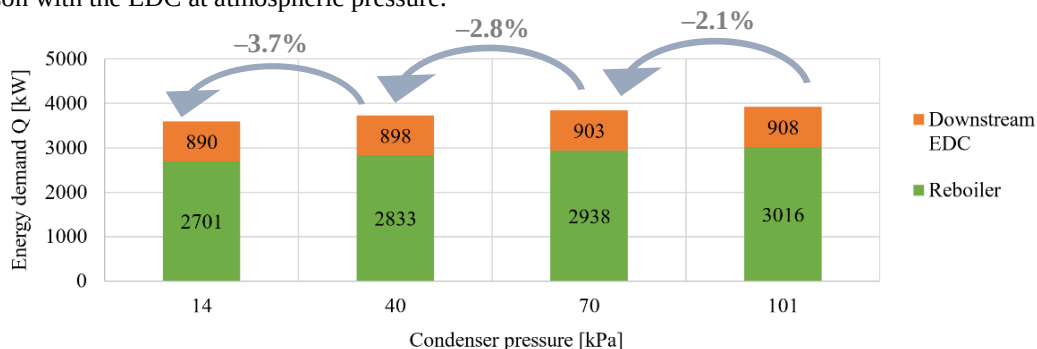


Fig. 1 Reboiler and downstream energy requirement for different EDC condenser pressures.

b. Effect of x_E on x_{1dist}

As can be seen from Fig. 2, an entrainer with a purity of 99.5 mol% can satisfy the distillate ethanol purity constraint, while an entrainer with a purity of 98.5 mol% cannot, even with increased RR and E/F (mol basis). Hence, entrainer impurities of 0.5 and 1 mol% were further evaluated.

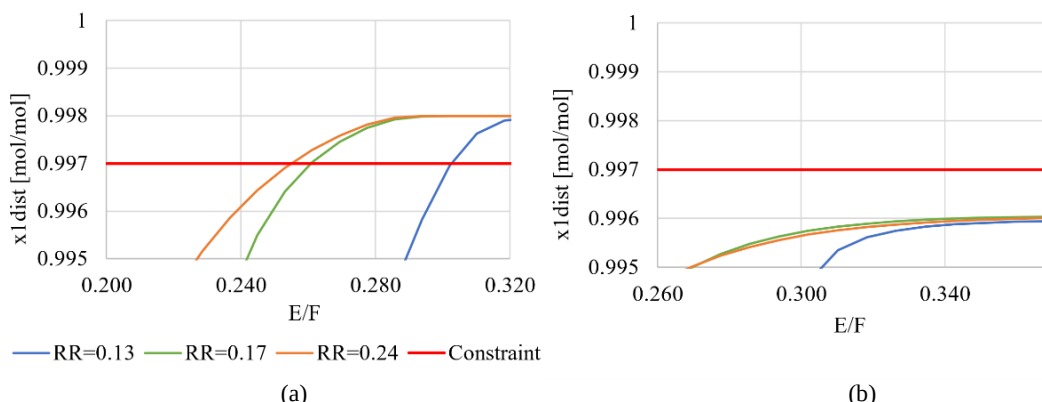


Fig. 2 Ethanol mole fraction in the distillate (x_{1dist}) as function of E/F for three different RR and two entrainer, ChCl:Ur (1:2), purities (a) 99.5 mol% ; (b) 98.5 mol% .

c. Effect of N_{th} on reboiler duty (Q_{reb})

The minimum number of stages (N_{min}) for the cases with $x_E = 99.5$ and 99 mol% equal 12, and 14 respectively. Fig. 3 shows the decrease of the reboiler duty for N_{th} of 15, 20, 25 and 30 at both entrainer purities. $N_{th}=30$ was selected because of the lowest energy demand and that a further 5 stage increase only reduces the reboiler duty by less than 1%.

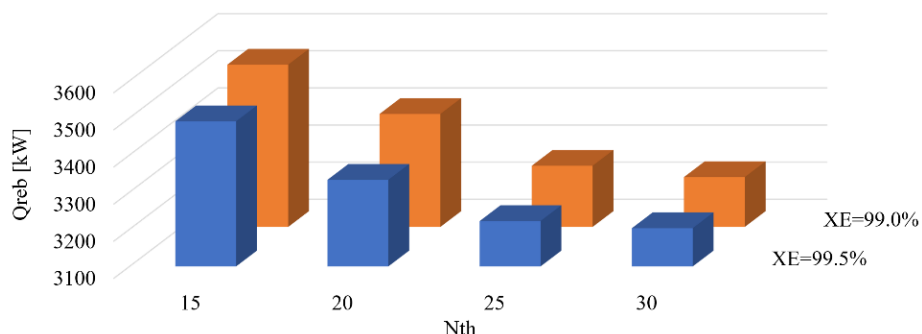


Fig. 3 Reboiler duty (Q_{reb}) as a function of N_{th} for two different entrainer purities (x_E).

d. Effect of N_E and N_F on x_{1dist}

Fig. 4a shows that the ethanol purity constraint was met for a N_F range of 19-22 with N_E ranging from 2 to 4. N_E of 2 and 3 were further investigated in terms of energy requirement. As can be seen in Fig. 4b, feeding the entrainer at the

second stage yields a higher energy consumption compared to feeding at the third stage. This occurs because water vaporizes close to the condenser, which requires RR and E/F to be increased to meet the desired ethanol purity. Consequently, Q_{reb} is increasing. Thus, the selected N_E and N_F were determined from an iterative loop analysis with E/F, and RR.

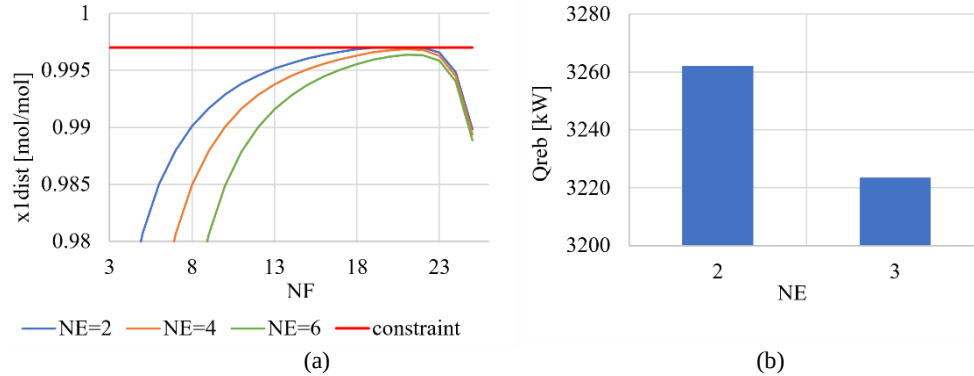


Fig. 4 (a) Ethanol mole fraction in distillate (x_{1dist}) as a function of N_F for three different N_E ; (b) Reboiler duty (Q_{reb}) for two different N_E .

e. Effect of E/F and RR on x_{1dist} and Q_{reb}

From Fig. 5a, it can be observed that only for small ranges of E/F and RR values the ethanol purity constraint is met. Furthermore, Fig. 5b illustrates that, although E/F and RR increase Q_{reb} , the sensitivity to increasing E/F is much less compared to an increase of RR. Based on the region where the ethanol purity constraint is met an E/F ranging from 0.25 to 0.31 and RR in the range of 0.1-0.5 were taken.

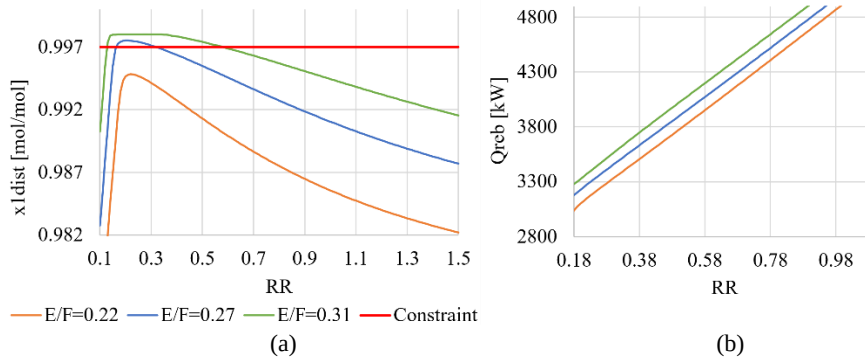


Fig. 5 (a) Ethanol mole fraction in distillate (x_{1dist}) and (b) reboiler duty (Q_{reb}) as a function of RR and E/F.

f. Effect of T_F and T_E on x_{1dist} and Q_{reb}

Fig. 6 shows that when T_F is above the boiling point, the ethanol purity constraint cannot be achieved. For a higher T_E , less energy is required in the reboiler to heat the entrainer. In order to achieve the best energy efficiency, T_F and T_E were chosen to be as close as possible to the stage temperature where the feed and entrainer enter the column.

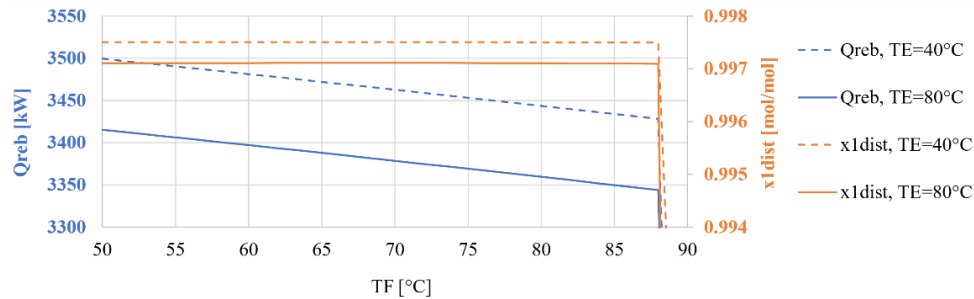


Fig. 6 Ethanol mole fraction in distillate (x_{1dist}) and reboiler duty (Q_{reb}) as function of the feed temperature for two different entrainer feed temperatures.

Entrainers regeneration

A minimum of two evaporators in series is required as regeneration unit to meet the desired entrainer purity and recovery. As illustrated in Fig.7, two evaporators in series yield lower cost compared to the option of an evaporator combined with stripping.

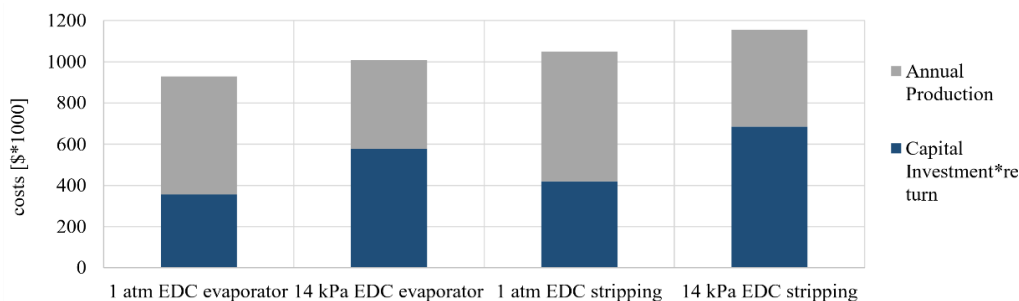


Fig. 7 Total annual cost of four entrainer regeneration base case designs.

Separation process design

The designed process for ethanol and water separation using DES through EDC operating at a pressure of 101 kPa using two evaporators and including heat integration is provided in Fig. 8. For IPA/water separation using DES, the same optimal conceptual process design was found, but with different design parameters. The selected design parameters of the ethanol-water system and the IPA-water system containing DESs as entrainer were determined according to the sensitivity analysis described in the previous section for the ethanol-water system. For comparability with the benchmark organic solvent and IL-based processes of the literature, the EDC pressure drop was changed to 0 kPa, which also changed the relative volatility of the mixtures. Table 2 lists the updated design parameters and main results for both systems.

Table 2. Optimized design parameters and main results of the EDC operating at 101 kPa with two evaporators with heat integration.

Design parameters	P (kPa)	x_E mol%	N_{th}	N_F	N_E	E/F	RR	T_F (°C)	T_E (°C)	Flow rate (kmol/h)	Duty (kW)	T (°C)
Ethanol-water system with ChCl:Ur (1:2)												
EDC	101	99.7	25	14	3	0.26	0.16	78	73	Top: 217.26	3088.6	-
Evaporator 1	2	-	-	-	-	-	-	-	-	Bottom: 68.28	53.63	106
Evaporator 2	0.3	-	-	-	-	-	-	-	-	Bottom: 63.69	111.6	121.5
IPA-water system with ChCl:TEG (1:3)												
EDC	101	99.9	25	16	2	0.16	0.99	73	70	Top: 50.0	1026.4	-
Evaporator 1	8	-	-	-	-	-	-	-	-	Bottom: 18.99	732.5	157
Evaporator 2	0.3	-	-	-	-	-	-	-	-	Bottom: 15.79	45.5	155

Energy and TAC

Along with the environmental benefits of DESs, evaluating the specific energy requirements and the TAC is an important part for industrial competitiveness. The specific energy requirements are not only crucial for the cost consideration but also for the sustainability of the process. TAC was calculated based on the equation taken from literature [18]. Table 3 provides the results based on the design parameters from Table 2 for each system.

Table 3. Comparison of possible savings in TAC and specific energy requirement for ED using DES and conventional solvent or IL as entrainer with and without heat integration.

System	Saving (%) for the non-heat integrated process using DES compared to:				Saving (%) for the heat integrated process using DES compared to:			
	Conventional solvent		IL		Conventional solvent		IL	
	TAC	Energy	TAC	Energy	TAC	Energy	TAC	Energy
Ethanol-water	17.4	27.6	15.9	32.0	20.2	35.1	18.2	38.9
IPA-water	16.6	20.1	1.5	6.3	19.1	26.9	4.4	14.2

For both systems, it can be seen that the specific energy requirement and the TAC are lower when the DES is applied compared to the conventional solvent and IL. With a lower specific energy requirement, the use of DESs can reduce

the CO₂ emissions. Applying the heat integration results in increased savings for the specific energy requirement as well as the TAC.

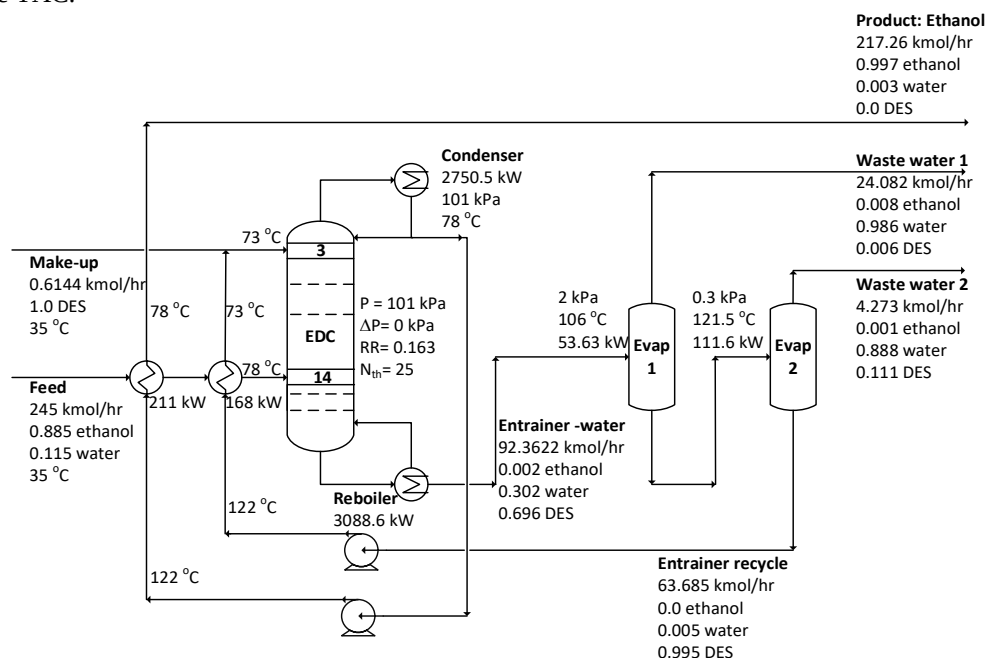


Fig. 8 Process flowsheet for ethanol and water separation through EDC operating at 101 kPa with two evaporators for entrainer regeneration and including heat integration.

Conclusions

To produce anhydrous ethanol and anhydrous IPA, extractive distillation with DESs entrainers operating at 101 kPa using two evaporators for entrainer regeneration was selected as the most feasible process design. The optimized design parameters were obtained from a sensitivity analysis. Applying DESs improves performance compared to the benchmark organic solvent-based processes by at least 20% in terms of energy and a minimum of 16% in terms of TAC. Additionally, replacing ionic liquids with DESs reduces energy usage by at least 6%.

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