



Cite this: *Green Chem.*, 2021, **23**, 6076

Biogas upgrading through blends of deep eutectic solvents and monoethanol amine: 4 E analysis (energy, exergy, environmental, and economic)[†]

Junaid Haider,^{‡a} Bilal Kazmi,^{‡b} Ahmad Naquash,^{id} ^{‡c} Muhammad Abdul Qyyum,^c Imran Ali,^b Moonyong Lee^c and Hankwon Lim^{id} ^{*a,d}

Blends of monoethanol amine (MEA) with an aqueous deep eutectic solvent (DES), with MEA present in various proportions of 5, 10, and 15 wt%, are used in process design for biogas upgrading. To the best of our knowledge, this is the first study that presents process analysis based on 4 major performance indicators, namely energy, exergy, environmental, and economic analysis, for biogas upgrading using a hybrid solvent. The process is modeled in Aspen Plus V10 commercial software. MEA and DES based configurations were considered as the base cases for the sake of performance comparison with the proposed configurations. Process evaluation determined that the addition of MEA to ChCl/urea not only reduces the amount of DES ($\geq 40\%$), but also improves the functionality of MEA itself together with overall solvent characteristics. As a result, the reduction in energy consumption in each proposed case is $\geq 72\%$ compared to the MEA-based base case. While the process efficiency in terms of exergy destruction is the highest in the 15 wt% MEA case, the 5 wt% MEA case exhibits more potential in terms of environmental aspects. However, the economic factor is in favor of the 10 wt% MEA case with TAC savings of up to 27.8%. The overall process evaluation based on performance indicators revealed that the choice of hybrid solvent improves the efficiency of the process and the hybrid solvent has the potential to replace conventional solvents.

Received 24th February 2021,
 Accepted 3rd July 2021
 DOI: 10.1039/d1gc00714a
rsc.li/greenchem

1. Introduction

Greenhouse gas emissions (GHGs), especially the anthropogenic CO₂ release from the combustion of fossil fuels, transportation, and process industries are the major factors responsible for the increase of global warming.¹ In this context, the Paris Agreement on climate change^{2,3} has highlighted the concerns that an increase in the average global environment temperature by 2 °C will pose a greater risk which could be mitigated by suppressing CO₂ emissions from large point sources; hence efforts should be made to limit the temperature rise below 1.5 °C. Consequently, conventional energy resources are depleting day by day and the energy demand is increasing rapidly.

Considering the environmental impact and scarcity of existing fossil resources, alternative fuels with the specialty of green and clean properties are in high demand for the accomplishment of long-term continuous energy demands. This is the reason that over the past few decades, intensive research has been directed towards renewable energy resources due to their green nature and as a result, some of the biofuels have been successfully commercialized, biogas is one among them.⁴

Raw biogas comprises mainly biomethane (CH₄ 50–80%) and carbon dioxide (CO₂ 20–50%) with some trace elements, depending on the feedstock material.⁵ Trace elements and associated impurities are removed in the cleaning step involved in the biogas value chain. Owing to the high concentration of CO₂, upgrading of biogas is considered as the mandatory step needed to be taken in order to enhance the biomethane concentration in the final product ($\geq 97\%$). In this regard, existing techniques for CO₂ removal are chemical absorption,⁶ water-based absorption,⁷ physical absorption,⁸ membrane technology,⁹ and adsorption.¹⁰ However, each technology has certain challenges and limitations for successful scale up. Considering the current status of commercialized plants, absorption is a well-established and widely used technique for biogas upgrading.¹¹ Among absorption techniques,

^aSchool of Energy and Chemical Engineering, UNIST, South Korea.

E-mail: hklim@unist.ac.kr; Tel: +82-52-217-2935

^bDepartment of Applied Chemistry and Chemical Technology, University of Karachi, Pakistan

^cSchool of Chemical Engineering, Yeungnam University, Gyeongsan 712-749, Republic of Korea

^dDepartment of Energy Engineering, UNIST, South Korea

[†]Electronic supplementary information (ESI) available. See DOI: 10.1039/d1gc00714a

^{*}These authors contributed equally to this work

solvent selection is one of the most crucial steps and decides the type of carbon capture method either chemical or physical absorption. Water scrubbing shares 41% of the world's biogas upgrading market; however, operational issues associated with this method such as high energy consumption, high water consumption even in regeneration, foaming, and low process efficiency are the major challenges.¹² On the other hand, amine-based chemical absorption is commercially used for carbon capture as it results in highly selective removal of CO₂ from biogas with lower solvent cost but amines are prone to degradation, toxic in nature, corrosive, and volatile, and the process requires an excessive amount of energy in the solvent regeneration step to recycle them back into the process.¹³

Therefore, it is pivotal to work towards a more sustainable and flexible process approach to specifically remove the CO₂ through an energy and cost efficient solvent. Ionic liquids (ILs) provide this edge over commercial solvents as a promising green solvent with their unique properties of less thermal degradation, lower flammability, non-volatility, and non-corrosiveness.¹⁴ However, the high cost of ILs and their toxicity-related issues are limiting their applications in CO₂ removal from biogas.¹⁵ Considering the superior properties of ILs and their derivatives, huge efforts are made to develop such solvents with at least low production cost while the corresponding viscosity issue was proposed to be solved by blending them with a certain amount of water, experimentally proved in numerous studies.^{16,17} A new generation of sustainable solvents known as Deep Eutectic Solvents (DESs) are gaining particular interest, consist of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) with engineered selection of a HBA and HBD. DESs are flexible and can be tuned as per desired thermodynamic characteristics.¹⁸ Among all the desirable properties of DESs as solvents, they possess high selectivity to absorb acid gases especially choline-based salts. Also, DESs show biodegradability and lower toxicity in comparison to ILs, indicating that they can be utilized as eco-friendly solvents for sequestration of CO₂ from biogas.^{19,20}

In this context, many researchers have examined the solubility of the CH₄/CO₂/H₂O/H₂S system in pure and aqueous ChCl/urea at various temperatures (30–80 °C) and pressures (0.105–45.04 bar), for example Liu *et al.*²¹ determined the CO₂, CH₄ and H₂S solubility up to 2 bar. Moreover, selectivities and the DES-based absorption mechanism were presented. Xie *et al.*,²² Leron *et al.*,²³ Li *et al.*,²⁴ and Mirza *et al.*²⁵ provided the solubility data of gas mixtures in wide ranges of pressure and temperature. Consequently, Hsu *et al.*¹⁶ provided the experimental solubility data of an aqueous mixture of ChCl/urea. The study claimed that the overall viscosity of the solvent was largely reduced with the addition of a certain amount of water. Recently, Haider *et al.*²⁶ and Ma *et al.*,^{27,28} presented the process design of biogas upgrading by utilizing an aqueous DES as an absorption solvent. The results revealed that the energy consumption in the overall process is largely reduced with the minimization of total cost factor. In addition, the selectivity towards CO₂ is slightly increased with the presence of water and the viscosity of pure ChCl/urea was reduced from

335 cP to around 6 cP.²⁸ However, it was observed that the total flow of solvent is increased due to addition of water which results in a high pumping power, large size of absorber, and high energy required in solvent recovery column.²⁶ Therefore, reduction of the overall flow rate of the co-solvent with minimum energy requirement is still an open issue. In this regard, Hsu *et al.*¹⁶ have highlighted that if an aqueous DES is blended with alkanol amines such as monoethanolamine (MEA) in various proportions of 5, 10, and 15 wt%, a hybrid solvent is formed which shows an enhanced CO₂ solubility in comparison to aqueous ChCl/urea and subsequently the volatility issue of the aqueous MEA is suppressed. Considering the experimentally claimed results, process design of the hybrid solvent (aqueous DES-MEA) is needed to determine the overall energy efficiency of the process. In addition, process system engineering (PSE) aspects have not been reported for the novel solvent mixture, so far.

Hence, this is the first study to provide the detailed design, overview, and investigation of the performance of a hybrid solvent (aq. ChCl/urea + MEA) based on 4E (energy, exergy, economic, and environmental) analysis for biogas upgrading. The performance of the hybrid solvent is compared with those of aqueous MEA (30 wt%) and ChCl/urea based process designs. For the sake of process design, the experimental CH₄/CO₂ solubility data were extracted, evaluated, and validated by performing rigorous regression for the determination of binary interaction parameters. Process simulation is then performed with the commercial software Aspen Plus V10. Later, sensitivity analysis was carried out for each proposed case for the determination of the optimum solvent flow required to upgrade biogas at given process constraints (≥97 wt% recovery and ≥99 wt% purity). Energy analysis and exergy destruction of the proposed processes are determined to estimate the thermodynamic performance. Consequently, emissions and the carbon capture rate are observed in environmental analysis and in the last step economic evaluation of the proposed cases was performed. Finally, conclusions are drawn about the feasibility of the process while choosing a hybrid solvent as a potential candidate for biogas upgrading.

2. Proposed process

2.1. Absorption-based production of biomethane

To date several techniques have been proposed for biogas upgrading in order to produce biomethane, namely adsorption (pressure swing adsorption, temperature swing adsorption),^{29,30} cryogenic based separation,^{31,32} membrane based separation,³³ physical solvent-based absorption (*i.e.* water,³⁴ organic solvents,³⁵ ionic liquids, deep eutectic solvents²⁶) and chemical solvent-based absorption.³⁶ However, absorption-based biogas upgrading is leading due to high energy efficiency compared to all available techniques. Absorption is categorized on the basis of the solvent used for the removal of CO₂. Table 1 presents the PSE aspects of the available absorption techniques used to upgrade biogas.

Table 1 Biogas upgrading based on various separation techniques from the process system engineering perspective

Absorption type	Solvent	Biogas composition	Capacity	Conditions	CH ₄ loss (%)	CH ₄ recovery & purity (%)	Energy consumption	Operating cost	Capital cost	Ref.
High pressure water-based scrubbing	Water	38.97 vol% CO ₂ , 60 vol% CH ₄ , 0.03 vol% H ₂ S, 0.05 vol% O ₂ , 0.05 vol% N ₂	1 Nm ³ h ⁻¹	30 °C, 10 bar	1.20	98.80 & 97.38%	0.34 kW h Nm ⁻³	—	—	38
		53.62 vol% CH ₄ , 45.2 vol% CO ₂ , 100 ppm H ₂ S, 0.93 vol% N ₂ , 0.19 vol% O ₂ , 0.05 vol% H ₂ O	500 Nm ³ h ⁻¹	20 °C, 8 bar	0.326	97 & 96.5%	0.55 kW h Nm ⁻³	—	—	34
		60 vol% CH ₄ , 37.5 vol% CO ₂ , 0.5 vol% N ₂ , 400 ppm H ₂ S, 0.2 vol% O ₂ , 0.0176 vol% H ₂ O	2000 Nm ³ h ⁻¹	20 °C, 8 bar	—	97 & 97%	0.2 kW h Nm ⁻³	11.45 × 10 ⁶ \$ per y	96.52 × 10 ⁶ \$	46
		55 vol% CH ₄ , 45 vol% CO ₂ , 68 mol% CH ₄ , 24 mol% CO ₂ , 3000 ppm H ₂ S, 5.6 mol% H ₂ O, 2 mol% N ₂ , 0.1 mol% O ₂	500 Nm ³ h ⁻¹	25 °C, 10 bar	0.92	99.08 & 98.7%	0.27 kW h Nm ⁻³	179 581 € per y	1 323 500 €	47
		60 mol% CH ₄ , 40 mol% CO ₂	500 m ³ h ⁻¹	35 °C, 0.102 MPa	1.3	98.7 & 98%	0.212 kW h m ⁻³	—	—	49
Physical solvent	DEPG	55% CH ₄ , 45% CO ₂	224 Nm ³ h ⁻¹	20 °C, 8 bar	<1	97 & 97%	0.21 kW h Nm ⁻³	287 k\$ per y	1004 k\$ per y	15
	PC	CH ₄ 65 vol%, CO ₂ 35 vol%	250 Nm ³ h ⁻¹	20 °C, 8 bar	4–7%	≤95 & 99%	0.426 kW h Nm ⁻³	0.375 k\$ per Nm ³ per CO ₂	>300 k\$	35
Chemical based	Aqueous solution of KOH	55 wt% CH ₄ , 45 wt% CO ₂	4.0 × 10 ⁷ kg h ⁻¹	30 °C, 5 bar	1%	99 & 99%	0.223 kW h Nm ⁻³	—	—	50
	Aqueous solution of NaOH	—	—	—	—	—	12 kW h (electrical) & 41 kW h (thermal)	—	—	—
	Aqueous solution of MEA	—	—	—	—	—	12 kW h (electrical) & 40 kW h (thermal)	—	—	—
	Hot potassium carbonate	55 vol% CH ₄ , 45 vol% CO ₂	500 Nm ³ h ⁻¹	70 °C, 8 bar	0.03	99.97 & 98.7%	51 kW h (thermal)	—	—	—
	MDEA (45 wt%)	60 mol% CH ₄ , 39.9 mol% CO ₂ , 0.1 mol% H ₂ S	1000 kmol h ⁻¹	30 °C, 35–55 bar	1.2	99.99 & 99%	1.54 kW h per kg per LBM (work) & 1.81 kW h per kg per LBM (heat)	279 094 € per y	1 057 400 €	47
Ionic liquid based	MEA (20 wt%)	65 vol% CH ₄ , 33.5 vol% CO ₂ , 10 ppmv H ₂ S, 0.2 vol% O ₂ , 1.3 vol% N ₂	10 000 Nm ³ day ⁻¹	35–40 °C, 20 mbar	0.1	>95 & ≥97%	—	—	—	36
	DEA (30 wt%)	68 mol% CH ₄ , 24 mol% CO ₂ , 3000 ppm H ₂ S, 5.6 mol% H ₂ O, 2 mol% N ₂ , 0.1 mol% O ₂	1743 kmol h ⁻¹	37 °C, 10.5 bar	—	95.2 & 96%	10 624 kW _e	—	—	48
	MEA	60 mol% CH ₄ , 40 mol% CO ₂	500 m ³ h ⁻¹	35 °C, 0.102 MPa	0.01	99.9 & 98%	0.426 kW h m ⁻³	—	—	49
	Aq. MEA (30 wt%)	60 wt% CH ₄ , 39 wt% CO ₂ , 1 wt% H ₂ S	0.58 MTPA	30 °C, 36 bar	<1%	≥96 & 99%	0.235 kW h kg ⁻¹ of biogas	13.14 (\$ × 10 ⁶) per y	34.96 (\$ × 10 ⁶)	26
	[Bnmim][Ntf ₂]	60 mol% CH ₄ , 40 mol% CO ₂	500 m ³ h ⁻¹	35 °C, 0.102 MPa	4.77	95.3 & 98%	0.218 kW h m ⁻³	—	—	49

Table 1 (Contd.)

Absorption type	Solvent	Biogas composition	Capacity	Conditions	CH ₄ loss (%)	CH ₄ recovery & purity (%)	Energy consumption	Operating cost	Capital cost	Ref.
Deep eutectic solvents	[Bmim][Ntf ₂]	55 vol% CH ₄ , 45 vol% CO ₂	224 Nm ³ h ⁻¹	20 °C, 8 bar	<1	0.99 & 97%	41.082 kW (power), -28.135 kW (heat)	—	—	52
	[Hmim][Ntf ₂]						45.348 kW (power), -30.687 kW (heat)	—	—	
	[Bmim][PF ₆]						44.512 kW (power), -28.042 kW (heat)	—	—	
	[Emim][Ntf ₂]	65 vol% CH ₄ , 35 vol% CO ₂	3775 kg h ⁻¹	15 °C, 30 bar	—	95%	545 kW	3.10 M\$	15.18 M\$	53
	[Hmim][Ntf ₂]						575 kW	3.18 M\$	15.28 M\$	
	[P ₆₆₆₁₄][Ntf ₂]						595 kW	3.23 M\$	15.10 M\$	
	[Bmim][Ntf ₂]	55% CH ₄ , 45% CO ₂	224 Nm ³ h ⁻¹	20 °C, 8 bar	1–3%	97 & 97%	0.18 kW h Nm ⁻³	—	—	15
	[Bmim][PF ₆]	62.6 mol% CH ₄ , 37.4 mol% CO ₂	0.6 MTPA	30 °C, 40 bar	<1	>96 & >99%	1.1048 kW h kmol ⁻¹	\$ 192.78 × 10 ⁵	\$ 594.10 × 10 ⁵	13
	[Bmim][PF ₆]	60 wt% CH ₄ , 39 wt% CO ₂ , 1% H ₂ S	0.58 MTPA	30 °C, 36 bar	<1%	0.99% & 99%	0.235 kW h kg ⁻¹ of biogas	10.93 (\$ × 10 ⁶) per y	33.5 (\$ × 10 ⁶)	26
	Aqueous [Amim][HCOO] 90%	55% CH ₄ , 45% CO ₂	224 Nm ³ h ⁻¹	20 °C, 8 bar	<1	97 & 97%	0.13 kW h Nm ⁻³	260 k\$ per y	932 k\$	15
Deep eutectic solvents	Aqueous ChCl/urea (30%, 50%, 70%)	45 vol% CH ₄ , 55 vol% CO ₂	243.14 Nm ³ h ⁻¹	20 °C, 8 bar	0.415–0.838	97 & 96.7%	0.21–0.22 kW h Nm ⁻³	—	—	28, 52
	Aqueous ChCl/urea	60 wt% CH ₄ , 39 wt% CO ₂ , 1% H ₂ S	0.58 MTPA	30 °C, 36 bar	<1%	0.99% 99%	5.76–6.369 kW h kg ⁻¹ of biogas	7.85–16.57 (\$ × 10 ⁶) per y	32.06–44.87 (\$ × 10 ⁶)	26

Physical absorption using water and organic solvents (dimethyl ether) is commonly used as a physical scrubbing method at high pressure ranges.³⁷ Water-based scrubbing proceeds with the introduction of compressed biogas in the absorption column where it interacts counter-currently with the trickling solvent, which selectively removes CO₂ and thus provides wet biomethane.³⁸ The process of using an organic solvent (DEPG) offers higher selectivity for CO₂.³⁹ However, DEPG as a solvent requires a higher thermal energy load of 0.456 kW h Nm⁻³ for its regeneration compared to water, which requires around 0.2–0.3 kW h Nm⁻³.³⁵ Around 2% CH₄ loss occurs in the water-based process, and 4.5% CH₄ loss occurs in the DEPG based process due to a distinct pressure drop between the absorber and desorber.

Chemical based absorption is another commercialized process for upgrading biogas, which utilizes alkanol amines such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), and monodiethanolamine (MDEA) in combination with water and piperazine as the solvent. In this process amines selectively react with CO₂ in the absorber and regeneration of the solvent is carried out in a regenerator where the rich stream is heated to temperatures >100 °C, resulting in a very high thermal energy requirement.⁴⁰ Also, amines have relatively high vapor pressure and cause significant vaporization losses, particularly in low-pressure operation which in turn raise the overall economics of the process, while corrosivity and toxicity are the other major concerns which undermine the performance of amines.³⁹

Another type of absorption process is based on physical solvents such as ionic liquids, which overcome the issues of conventional solvents with their favorable solvent properties.⁴¹ ILs show efficient removal of CO₂ with lower to negligible solvent loss in the system due to their high thermal stability and low vapor pressure. However, high viscosity and synthesis cost are the major issues associated with ILs.^{14,42} In recent times derivatives of ILs known as deep eutectic solvents (DESs) based on choline based salts have overcome this issue of toxicity and biodegradability and are comparatively cheap as they are synthesized using common organic chemicals.^{43–45} DESs show a high rate of CO₂ separation with almost negligible CH₄ loss, making them a potential choice for physical solvent-based absorption as shown in Table 1.

2.2. Solvent features

The choice of solvent is the most important step in biogas upgrading. Certain parameters such as selectivity, viscosity, toxicity, and biodegradability have significant importance in the solvent selection step for an effectual biogas upgrading process.

The key features of conventional amines (MEA) and the proposed solvents are enlisted in Table 2. To pick out the potential solvent, energy consumption throughout the process is regarded as a major factor which is associated with the enthalpy of absorption (ΔH_{abs}). It needs to be lower as it allows the absorption column to be operated at a milder temperature with enhanced CO₂ removal capability that ultimately results

Table 2 Potential solvent properties

Solvents	ΔH_{abs} (J per mol CO_2)	C_p (J $\text{mol}^{-1} \text{K}^{-1}$)	(Q_s)	$\Delta \text{SCF}_{\text{CO}_2}$	SSED (kJ per kg of CO_2 captured)	Selectivity			Viscosity (cP)	Ecotoxicity & biodegradability	Corrosivity (m/y)	Price (\$ per kg)	Ref.
						$(\text{CO}_2/\text{CH}_4)$	$(\text{H}_2\text{S}/\text{CH}_4)$	$(\text{H}_2\text{S}/\text{CO}_2)$					
Amine (aq. MEA)	−84	121.9	3.657 kJ mol^{-1}	0.0939 ^a	38.9184 ^a	156.72	—	2.6–4.0	2.48	7100 mg l^{-1}	2.43	5.8	60–62
DES (ChCl/urea)	−16.1	181.4–190.8	0.26 GJ per ton per CO_2	$7.86 \times 10^{-3 a}$	15.2617 ^a	5.5–4.76	60.8–42.8	11.1–9.1	1372–11.2	>100 mg l^{-1} & 60–98% degradation/month	Negligible	6.3	21, 54, 56, 63 and 64
DES (aq. ChCl/urea)	−15 to −12.5	81.5–177.8	—	—	—	15.2–12.4	43.7–35.4	2.9–3.1	0.6–436.1	>100 mg l^{-1}	1×10^{-5}	6.3	54–56, 63 and 64

^a Calculated based on the equation described in the manuscript and the results of the simulation.

in lower energy requirements in solvent regeneration. As can be seen from Table 2, ChCl/urea has a lower ΔH_{abs} compared to MEA.

Heat capacity (C_p) and sensible heat (Q_s) also relate to energy consumption as a lower heat capacity of the absorption solvent results in a lower energy requirement for CO_2 and H_2S removal. As described by Leron *et al.*⁵⁴ addition of water changes the heat capacity of ChCl/urea from 178 to 81 J mol⁻¹ K⁻¹, resulting in the enhancement in selectivity and reduction in viscosity.⁵⁵ Xie *et al.*⁵⁶ also confirmed that the water content has a significant impact on the viscosity of ChCl/urea.

Another important parameter, solvent capturing factor ($\Delta \text{SCF}_{\text{CO}_2}$), indicates the process efficiency using the desorption ability of the solvent.⁵⁷ $\Delta \text{SCF}_{\text{CO}_2}$ is quantified using eqn (1) which depends on the CO_2 mole fraction in the rich stream from the absorber (X_{CO_2} in the rich stream) and the mole fraction of CO_2 in the lean stream from the stripper (X_{CO_2} in the lean stream).

$$\text{Solvent separation factor}(\Delta \text{SCF}_{\text{CO}_2}) = \left[\left(\frac{X_{\text{CO}_2 \text{ in rich stream}}}{1 - X_{\text{CO}_2 \text{ in rich stream}}} \right)_{\text{absorber}} - \left(\frac{X_{\text{CO}_2 \text{ in lean stream}}}{1 - X_{\text{CO}_2 \text{ in lean stream}}} \right)_{\text{stripper}} \right] \times \frac{m_{\text{CO}_2}}{m_{\text{solvent}}} \quad (1)$$

$\Delta \text{SCF}_{\text{CO}_2}$ is an indicator of the solvent requirement for removal of CO_2 ; a higher value of $\Delta \text{SCF}_{\text{CO}_2}$ for amines means that a lower amount of solvent is required for recirculation. As can be seen from Table 2, aq. ChCl/urea in comparison to amines has a lower value. However, amines face other severe problems due to their high volatility and degradation rate in the regeneration column. Alternatively, DESs show relatively low toxicity and highly biodegradable nature. Further on, $\Delta \text{SCF}_{\text{CO}_2}$ and Q_s were correlated for the calculation of the solvent specific energy demand (SSED) as shown in eqn (2) which provides an overview of the heat requirement in each system.⁵⁷

$$\text{Solvent specific energy demand (SSED)} = \frac{\text{sensible heat } (Q_{\text{sensible}})}{\text{solvent capturing factor}(\Delta \text{SCF}_{\text{CO}_2})} \quad (2)$$

Since DESs are composed of organic components, their price is significantly lower than conventional ILs, making them suitable candidates for biogas upgrading.^{58,59} Nevertheless, the low absorption power of DESs makes them less attractive for large scale adaptation due to their low mass transfer operation, high flow rate requirement in the absorption column, and slow operation. In this context, Hsu *et al.*¹⁶ proposed a hybrid solvent, a mixture of an aqueous DES and MEA, that not only overcomes the volatility and energy requirement issues of MEA, but also improves the solvent characteristics of the DES with the slight addition of MEA. Hence, blends of an aqueous DES with MEA (5, 10, and 15 wt%) are

used to develop a process design and estimate the process feasibility.

2.3. Thermodynamic model analysis and data regression

For the modeling of the biogas upgrading process, a database of non-conventional components such as ILs (ChCl/urea) is necessary for incorporation in the Aspen Plus library by introducing their basic properties. In recent studies, property analysis, estimation, and thermodynamic modeling of user-defined components have been introduced by many researchers.^{26,35} Since ILs/DESSs are non-conventional components, their properties are not readily available in the simulator's library. Therefore, in order to make them ready for process simulation and analysis, their introduction in the Aspen plus library is the first step where the basic properties are incorporated based on available experimental data as provided in Tables S-1 to S-8 in the ESI.[†] Later vapor liquid equilibrium data (VLE) were used for rigorous regression and were validated on the basis of the in-built Aspen tool to perform process simulation and analysis. Detailed information on the critical and temperature dependent properties utilized to define it as a component in the Aspen plus interface is presented in the ESI (Tables S-9 to S-11[†]). The Peng Robinson (PR) model is used to perform rigorous regression. The PR model is based on the standard equation of state (EOS) and works well with hydrocarbons due to handling of the wide

ranges of temperature and pressure. The physical property system of Aspen Plus is based on the binary interaction parameters (k_{ij}) and data for a large number of organic and inorganic components are readily available in the database of Aspen Plus. However, interaction parameters between ChCl/urea and CO_2 , H_2S , H_2O , CH_4 , and MEA generated from vapor-liquid equilibrium (VLE) solubility data between the components are presented in Table 3. In addition, the obtained regression results show agreement between the experimental and estimated data as represented by the VLE in Fig. 1. Furthermore, to show that the estimated data fit well the experimental data detailed information is available in the supplementary sheet (Fig. S-1 and S-2[†]).

2.4. Process design and simulation

The proposed process consists of biogas upgrading using a hybrid absorption solvent mixture to obtain purified bio-methane as a product. Modeling of the process was performed with the commercial software Aspen plus® V10. All the proposed processes and base cases were simulated based on the following fundamental assumptions:

- There was zero heat loss to the surroundings
- The pressure drop across coolers is kept at 25 kPa
- The isentropic efficiency for compressors and pumps is maintained at 75%

Table 3 Binary interaction parameters for the Peng Robinson model using rigorous regression

Peng Robinson-based binary parameters					
<i>i</i>	<i>j</i>	KA_{ij}	KB_{ij}	Deviation	Ref.
ChCl/urea	CH_4	0.030768859	2.28×10^{-5}	0.030892042	26
	CO_2	0.058406364	7.27×10^{-6}	0.028740977	
	H_2S	-0.13458251	0.000568031	0.132269889	
	H_2O	-0.024105302	0.002267954	0.027514354	
	MEA	0.300415	0	0.0602555955	
Average deviation				0.05593	This work

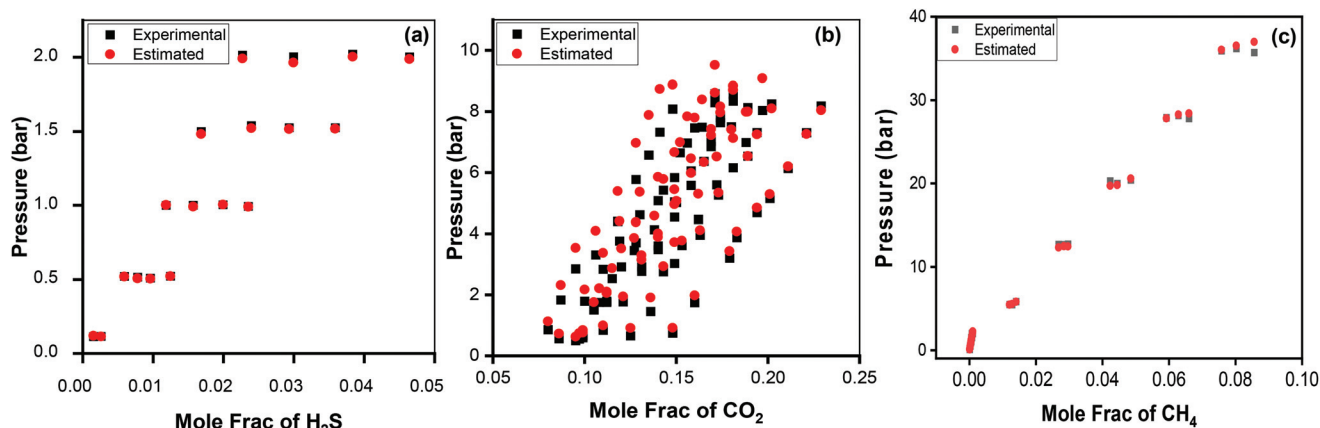


Fig. 1 Experimental and estimated vapor liquid equilibrium between (a) H_2S and aq. ChCl/urea + MEA⁶⁵ (b) CO_2 and aq. ChCl/urea + MEA^{16,21} (c) CH_4 and aq. ChCl/urea + MEA.²¹

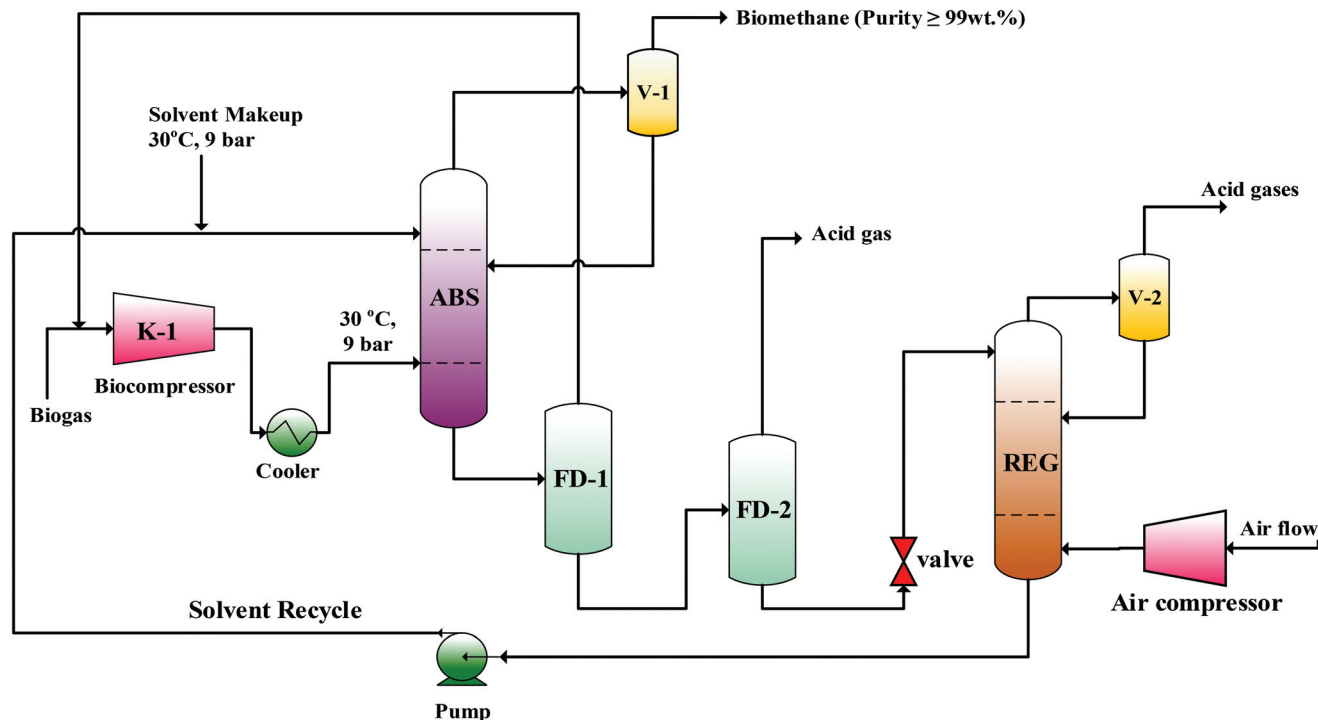


Fig. 2 Process flow diagram for the biogas upgrading process using a mixture of DES and MEA.

• The purity and recovery of the biomethane (CH_4) content in the final product stream are ≥ 99 wt% and ≥ 97 wt%, respectively

Fig. 2 shows the flow diagram of the proposed process. A typical feed of biogas is obtained from the open literature,²⁶ 60 wt% of CH_4 , 39 wt% CO_2 and 1 wt% of H_2S at 30 °C and 1 bar pressure with a flow rate of $58\,000\text{ kg h}^{-1}$ (0.4 MTPA of biogas). The biogas stream was charged to the upgrading unit where it was compressed to 9 bar pressure through a series of multi-stage compressors and the interstage cooling system. Compressed gas is then introduced into a sixteen-stage absorption column (ABS). An aqueous solvent stream containing a mixture of ChCl /urea and MEA was introduced from the top of the column (ABS) at 30 °C and 9 bar pressure; the solvent drifts downwards and interacts counter-currently with the upward flowing biogas. The solvent selectively absorbs CO_2 and H_2S , resulting in biomethane with a recovery of ≥ 97 wt% and 99 wt% purity from the top of the absorption column. At the top of the absorption column, a reflux drum is installed to restrict the amine loss and to ensure the purity of biomethane at specified process constraints. The rich bottom stream is routed towards the flash columns (FD-1) and (FD-2), which operate at reduced pressures of 4.02–2.75 bar to further recover the CH_4 content, and recycled back to the absorption column. The pressure of the bottom stream from FD-2 is further reduced to 1 bar through a valve and it is introduced into the stripping column (REG) while the compressed air stream is simultaneously introduced from the bottom of the column using a blower. Both streams interact counter-cur-

rently to recover and purify the solvent mixture from acid gas contents. A recovered hybrid mixture of solvents is then recycled back to the absorber through a pump. The stripping column top is provided with a reflux vessel to recycle the carry-over amine solvent back into the REG to avoid excessive solvent loss in the process. Additionally, a solvent makeup stream is also provided to compensate for the loss of MEA and water during the process.

3. Results and discussion

3.1. Process energy analysis: optimal design variables and results

The proposed process schemes were investigated and analyzed by varying the concentration of MEA from 5–15 wt% in the aqueous solution of DES, as shown in Fig. 3. For the sake of comparison, 30 wt% of MEA with water and DES-based biogas upgrading schemes were chosen as base case-I and II, respectively. It was claimed that the volatility of MEA is reduced when added to the DES + water mixture, which results in the improvement of the selectivity of the hybrid solvent and is expected to reduce the required flow rate of DES with the slight addition of MEA in an aqueous solution of ChCl /urea.¹⁶ Therefore, process analysis based on PSE aspects was carried out to evaluate the outcomes of the proposed configurations. Table 4 lists the constraints, parameters, and energy requirements for all the investigated cases in comparison with MEA-based biogas upgrading.

Process analysis-proposed solvents

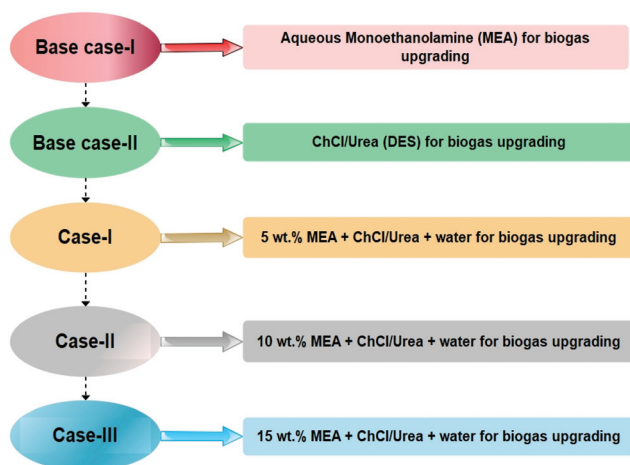


Fig. 3 Process analysis cases for the DES + MEA-based biogas upgrading process.

As mentioned earlier, the analysis includes three cases in which the composition of the solvent was varied; sensitivity analysis was performed to point out the minimum requirement of the solvent/feed (S/F) ratio against the absorber stages

with the agreement of constraint satisfaction (biomethane purity 99 wt% and recovery $\geq 97\%$). The determination of the optimum flow rate of the solvent charging into the absorber is one of the most crucial factors as it directly depends on the energy requirement in the regeneration section; a high flow rate requires a high energy in the regenerator for the recovery of the solvent and consequently a high power is required to pump back the regenerated solvent in an absorber. Moreover, the size of the equipment increases which tends to increase the investment cost. Based on the proposed cases, the S/F ratio was calculated to estimate the number of stages in the absorber as shown in Fig. 4. It was observed that the addition of MEA reduces the overall flow of the solvent due to the improvement in mass transfer operation compared to base case-II. The corresponding reductions in solvent flow were recorded as 40%, 43.8%, and 42.7% in case-I, case-II, and case-III, respectively. In Fig. 4, it can be seen that after a certain stage number, the S/F ratio becomes constant in each case. Hence, the process configurations proposed at the stages required for cases I–III were 16, 18, and 18, respectively; the corresponding S/F ratios were 0.0513, 0.0620, and 0.0759, respectively.

The flash column coupled with the bottom stream of the absorber helps in improving the purity and recovery of biomethane by adjusting its pressure. Notably, the flow at the top of the absorber fluctuates as the pressure inside FD-1 is

Table 4 Design constraints and parameters for biomethane production using biogas upgrading

Variables/parameters	Base case-I	Base case-II	Case-I	Case-II	Case-III
Biogas upgrading					
Solvent composition (wt%)	MEA (30), H ₂ O (70)	ChCl/urea	ChCl/urea (70), H ₂ O (25), MEA (5)	ChCl/urea (60), H ₂ O (30), MEA (10)	ChCl/urea (50), H ₂ O (35), MEA (15)
Constraints					
Purity of biomethane (wt%)	0.99	0.99	0.9927	0.9927	0.9927
Recovery of biomethane (wt%)	0.99	0.97	0.9726	0.97	0.97
H ₂ S (ppm)	≤ 10	≤ 10	≤ 10	≤ 10	≤ 10
CO ₂ removal (%)	0.99	0.99	0.99	0.99	0.99
Absorber					
Flow rate of biogas (kg h ⁻¹)	58 000.0	58 000	58 000.0	58 000.0	58 000.0
Flow rate of biogas (m ³ h ⁻¹)	65 629	65 629	65 629	65 629	65 629
Flow rate of solvent (m ³ h ⁻¹)	234.6	3530	3367	4071.35	4985.25
Solvent/feed ratio (m ³ m ⁻³)	0.00357	0.054	0.051	0.0620	0.0759
Absorber stages	20	16	16	18	18
Absorber pressure (bar)	9	9	9	9	9
Absorber temperature (°C)	30	30	30	30	30
Flash drum 1 pressure (bar)	2.8	2.45	3.8	4.03	4.02
Flash drum 2 pressure (bar)	—	—	3.65	3	2.75
Power of the biogas compressor (kW)	6958	8104	7306	7271	7292
Regenerator					
Regenerator stages	20	14	16	14	14
Regenerator temperature (°C)	132.2	30	30	30	30
Regenerator pressure (bar)	1.1	1.1	1.1	1.1	1.1
Reflux ratio	1	—	—	—	—
Duty of the regenerator (kW)	24 913.88	—	—	—	—
Air flow rate (m ³ h ⁻¹)	—	42 400	39 219	41 025	51 024
Air/DES rich ratio (m ³ m ⁻³)	—	11.87	4.24	4.65	5.48
Power of the pump for recycling (kW)	57.72	1047	856	949	1180
Power of the air compressor (kW)	—	151	150	171	207
Specific thermal load (kW h kmol ⁻¹ of biogas)	11.826	3.445	3.08	3.11	3.21
Specific thermal load (kW h kg ⁻¹ of biogas)	0.55	0.1604	0.143	0.145	0.15

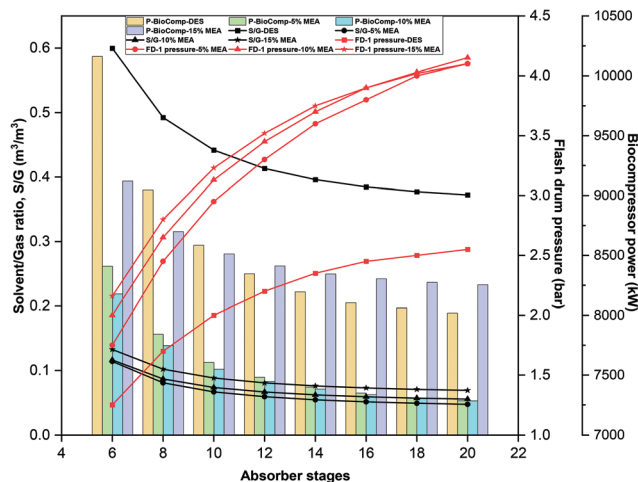


Fig. 4 Absorber analysis based on stages for selection of the solvent flow and flash drum pressure.

reduced. This effect is certainly crucial when determining bio-methane in the absorber's top stream with strict process constraints. Besides, it is important to note that the recycle flow from FD-1 enters the compressor which means that the load on the compressor increases when entering the flash stream, so an optimum pressure drop in FD-1 with respect to S/G ratio is the factor of concern for the specified number of absorber stages as shown in Fig. 1. The compression power required to recycle the vapor stream of the flash column was the highest in case-I, while it was the least in case-II as the pressure reduction in the flash columns was about 3.8 and >4 bar, respectively.

A solvent-rich stream is brought to the air stripping unit for solvent regeneration. Compressed air is used to remove the captured CO₂ from the solvent in the regenerator. The flow of air and regenerator stages are selected in such a way that the energy consumption tends to decrease as much as possible while a high recovery (99.99 wt%) and purity of the solvent are kept as the main objectives in the solvent regeneration section. As shown in Fig. 5, the power required for the air blower depends on the flow rate of air corresponding to the regenerator stages. From the analysis, it can be seen that the airflow becomes constant after a certain number of stages. Therefore, at those pinch points, the air/S ratio corresponding to regenerator stages has been chosen for process design in each case such as the air/S ratio of 4.24 with sixteen (16) stages in case-I. Similarly, for the other proposed cases (II and III), the air/S ratio became constant at the 14th stage. Nevertheless, the flow of air was comparatively higher than that required for case-I (70% DES + 25 H₂O + 5% MEA) due to the increased concentration of water in the hybrid solvent mixture where the former ultimately requires a greater compression power and tends to increase the overall cost of the process. A simplified optimization methodology is presented in Fig. S-3 in the ESI.†

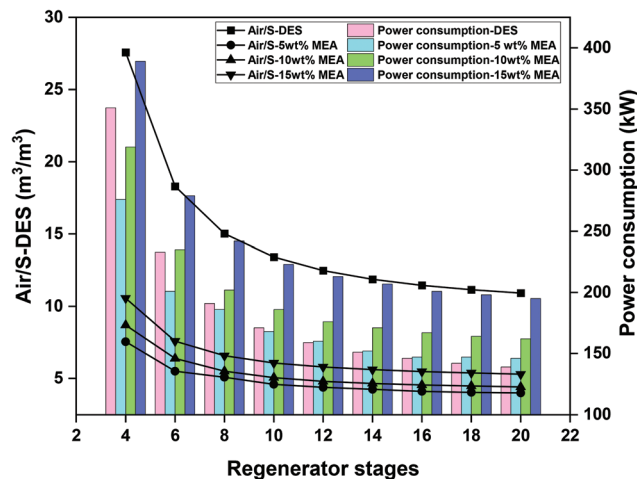


Fig. 5 Regenerator analysis to choose the airflow rate based on regenerator stages and power required in an air blower.

3.2. Exergy analysis

Exergy analysis is a useful thermodynamic tool, derived from the second law of thermodynamics, to provide an in-depth assessment of process inefficiencies. Unlike energy analysis, exergy can identify and locate the source of inefficiencies which helps in improving the performance of the process. Exergy can be physical, chemical, kinetic, and potential. Considering the process at rest and in the steady state, the kinetic and potential exergies were neglected. To calculate chemical exergy, the standard chemical exergy of ChCl/urea is required which is not available in the open literature, to the best of the author's knowledge. Therefore, only physical exergy is considered in this study. Physical exergy can be calculated from eqn (3).⁶⁶

$$Ex_{ph,i} = (h_i - h_o) - T_o(s_i - s_o) \quad (3)$$

where h_o and s_o are the enthalpy and entropy of a component under ambient conditions (25 °C and 1 atm), T_o is the ambient temperature (25 °C) and h_i and s_i are enthalpy and entropy under the given conditions. Table 5 provides the list of equations to calculate the equipment exergy destruction, where m is the mass flow rate of a stream, Ex is the exergy value of a stream taken from Aspen Plus, Q is the heat and W is the work done on the system. The calculated exergy destruc-

Table 5 Exergy destruction equations⁶⁷ for equipment

Equipment	Exergy destruction equations
Compressor/pump	$Ex = \dot{m}(Ex_{in} - Ex_{out}) - \dot{W}$
Coolers	$Ex = \dot{m}(Ex_{in} - Ex_{out})$
Heat exchanger	$Ex = \sum(\dot{m})Ex_{in} - \sum(\dot{m})Ex_{out}$
Valve	$Ex = \dot{m}(Ex_{in} - Ex_{out})$
Absorber	$Ex = \dot{m}(Ex_{in} - Ex_{out}) + Q$
Stripper	$Ex = \dot{m}(Ex_{in} - Ex_{out}) + Q$
Separator	$Ex = \dot{m}(Ex_{in} - Ex_{out})$

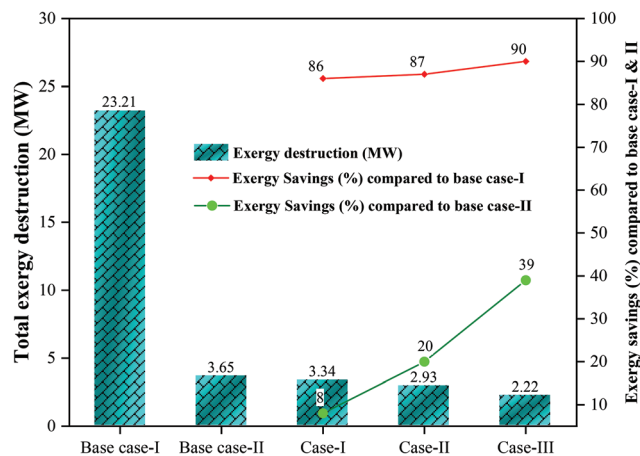


Fig. 6 Total equipment exergy destruction and exergy savings.

tion of base case-I, base case-II, and the proposed cases is shown in Fig. 6.

According to Fig. 6, all the proposed processes show considerably lower exergy destruction than base case-I and II. The main reason for this low exergy destruction is the lower energy load on the stripper compared to base case-I and II. Due to the high energy load on the stripper in base case-I, additional energy is required to cool down the recycle stream. This additional energy load contributes largely to the overall energy consumption and exergy destruction. Among the proposed cases, MEA-DES (15 wt%) shows the lowest exergy destruction (2.22 MW), whereas MEA-DES (5 wt%) shows the highest exergy destruction (3.34 MW) mainly due to its high-power consumption by compressors. This high exergy destruction can be reduced by optimizing the energy load on compressors and strippers. Moreover, as demonstrated in Fig. 6, due to the lowest exergy destruction in case-III, 90 and 39% exergy savings are observed compared to base case-I and II respectively. Similarly, MEA-DES (5 wt% and 10 wt%) also shows considerable savings in exergy destruction.

3.3. Environmental analysis

Environmental analysis is another useful strategic tool, utilizing certain key performance indicators (KPIs), to evaluate the potential impact of a chemical process on the environment. KPIs for the evaluation of CO₂ capture are defined in terms of carbon capture rate (%), specific CO₂ emissions, and specific energy consumption for CO₂ avoided (SPECCA).⁶⁸ Carbon capture rate is defined as the ratio of sequestered CO₂ to total CO₂ in the feed, as shown in eqn (4).⁶⁸

$$\text{Carbon capture rate (\%)} = \frac{\text{sequestered CO}_2}{\text{total CO}_2 \text{ in feed}} \quad (4)$$

Specific CO₂ emissions are the total CO₂ emissions corresponding to the feed flow rate. Total CO₂ emissions are determined based on the total process energy consumption including the energy required for the production of steam

delivered to the reboiler, which can be calculated using eqn (5).⁶⁹

$$\text{CO}_2 = \left(\frac{Q_{\text{fuel}}}{\text{NHV}} \right) \left(\frac{C\%}{100} \right) \alpha \quad (5)$$

where NHV denotes the net heating value of a fuel, C% is the carbon content of a fuel, α is the ratio of CO₂ mass to C mass, and Q_{fuel} is the energy from the burnt fuel calculated from eqn (6).⁶⁹

$$Q_{\text{fuel}} = \frac{Q_{\text{process}}}{\lambda_{\text{process}}} (h_{\text{process}} - 419) \left(\frac{T_{\text{FTB}} - T_0}{T_{\text{FTB}} - T_{\text{stack}}} \right) \quad (6)$$

Q_{process} is the energy required by the process, λ_{process} is the latent heat of steam, h_{process} is the enthalpy of steam, T_{FTB} is the flame temperature of boiler flue gases, T_0 is ambient temperature, and T_{stack} is the stack temperature.

SPECCA is defined as the energy required to mitigate CO₂ emissions, calculated from eqn (7).⁶⁸ The obtained values of carbon capture rate (%), specific CO₂ emissions, and SPECCA for base case-I, base case-II, and the proposed cases are shown in Fig. 7.

SPECCA =

$$\frac{\text{base case energy consumption} - \text{proposed case energy consumption}}{\text{base case CO}_2 \text{ emissions} - \text{proposed case CO}_2 \text{ emissions}} \quad (7)$$

As presented in Fig. 7, the proposed cases have very low CO₂ emissions compared to the base cases. The process outcome in terms of the environmental aspect shows that the hybrid solvent is beneficial for reducing the carbon emissions ($\leq 45\%$) with an improved energy efficiency of the biogas upgrading process. However, increasing the concentration of MEA in the hybrid solvent mixture results in a slight increment in carbon emissions as reported in case-III (15 wt% MEA-DES) and shows specific CO₂ emissions as 1.78 kg CO₂ per kmol of biogas, mainly because of its highest power consumption in the regeneration section *i.e.*, 8.67 MW which leads to higher fuel burning. Nevertheless, base case-I has

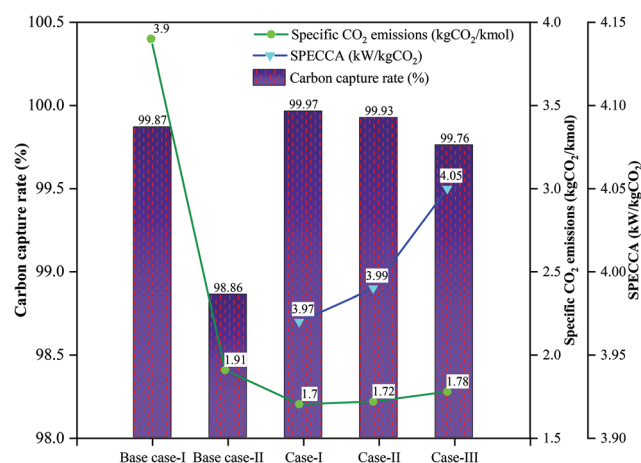


Fig. 7 Carbon capture rate (%), specific CO₂ emissions and SPECCA of the base cases and proposed cases.

shown the highest CO₂ emissions (3.90 kg CO₂ per kmol). Similarly, the CO₂ capture rate has been observed to be very high in the proposed cases as case-I (5 wt% MEA-DES) is the most efficient with 99.97% CO₂ capture rate followed by case-II (99.93%). Notably, as MEA-DES % increases, CO₂ emissions and energy consumption by pumps and compressors increase.

On the other hand, SPECCA compares the processes in terms of energy required to capture CO₂ and relative emissions; lower SPECCA means higher process efficacy and *vice versa*. In this study, base case-I is considered as a reference case for the calculation of SPECCA in the proposed cases. The MEA-DES (5 wt%) case has the lowest SPECCA value (3.97 kW per kg per CO₂) because of lower energy consumption and CO₂ emissions, whereas the MEA-DES (15 wt%) case shows the highest SPECCA value *i.e.*, 4.05 kW per kg CO₂ mainly influenced by higher energy consumption. Moreover, as the proposed cases utilize air for stripping, the energy consumption by the reboiler is not required which greatly reduces CO₂ emissions and the overall energy consumption is largely reduced compared to the MEA-based base case. Conclusively, based on environmental analysis, the MEA-DES (5 wt%) case is the most efficient.

3.4. Economic evaluation

An economic evaluation of the process is one of the powerful tools to estimate the feasibility of the process. The economic factor mainly depends on fixed capital investment and variable expenses incurred on an annual basis, where the annual expenditure in a certain project is estimated by the calculation of total annualized cost (TAC). TAC is a function of total capital investment (TCI) and total operating cost (TOI) as shown in eqn (8). A payback period of 5 years is kept for each proposed configuration.

$$\text{TAC} = \left(\frac{\text{Capital cost}}{\text{Payback period}} \right) + \text{Operating cost} \quad (8)$$

TCI is a function of bare module cost and calculated on the basis of the Guthrie method.⁷⁰ Cost relations for the calculation of TCI are presented in Table 6. Since ILs are viscous

and a high power is required to pump them for recycling and the cost relation provided by R. Turton is not valid for high capacity pumps, the cost relation for pumps was taken from the process engineering design book.⁷¹ Similarly, the cost of high-pressure compressors was calculated through the equation provided in Table 6. The operating cost of the proposed schemes was calculated with the main consideration of the cost of electricity \$16/GJ used to operate compressors and pumps.⁷⁰ Other utilities are cooling water used in the inter-stage-cooling system between compressors and the steam used in the regenerator.

A cost estimation of the proposed processes is presented in Fig. 8; the overall cost factor is presented in millions of dollars on the y-axis with the account of TCI, TOI, and TAC projected for each proposed case. It can be seen from Fig. 8 that the TCI is the least for base case-I ($\$22.35 \times 10^6$); however high energy consumption leads to a high TOI ($\$9.9 \times 10^6$) that ultimately increases the overall TAC ($\$14.37 \times 10^6$) of the biogas upgrad-

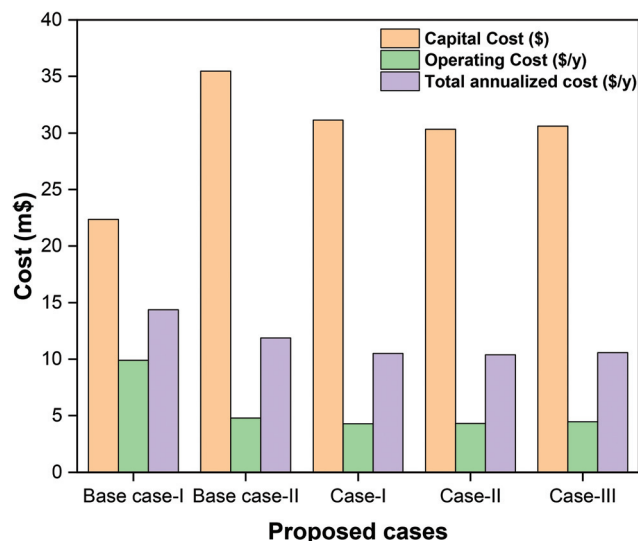


Fig. 8 Economic evaluation of each proposed case.

Table 6 Capital cost relations of the selected equipment⁷⁰

Cost relations	Parameter's description
$\text{FCI} = \sum_{i=1}^N C_{\text{BM},i}$	C_{BM} bare module cost
$C_{\text{BM},i} = C_{\text{p},i}^0 F_{\text{BM},i} = C_{\text{p}}^0 (B_1 + B_2 F_{\text{M}} F_{\text{p}})$	$F_{\text{BM},i}$ bare module factor B_1, B_2 equipment constant values for $F_{\text{BM},i}$ F_{M} material factor F_{p} pressure factor
$\log_{10}(C_{\text{p},i}^0) = K_1 + K_2 \log_{10}(A_i) + K_3 [\log_{10}(A_i)]^2$	$C_{\text{p},i}^0$ purchase cost of equipment K_1, K_2 , and K_3 constant parameters of specific equipment
$C_{\text{BM}} = \text{base cost} \times (F_{\text{p}} + F_{\text{M}}) \times \text{cost index (Pump capital cost relation, power >300 kW)}$	A capacity measure based on equipment F_{M} material factor F_{p} pressure factor
$\text{Compressor(CC)} = 517.5 \times \left(\frac{\text{cost index}}{280} \right) \times W^{0.82} \times F_{\text{c}} \quad (\text{Compressor cost relation, power >3000 kW})$	W is the power of the compressor in hp F_{c} is the correction factor

Table 7 Potential savings in operating and total annualized cost compared to base case-I and base case-II

Corresponding savings (%)	Case-I	Case-II	Case-III
TOI savings compared to base case-I	56.8	56.4	55
TOI savings compared to base case-II	10.7	9.8	6.8
TAC savings compared to base case-I	26.9	27.8	26.4
TAC savings compared to pure base case-II	11.6	12.6	10.9

ing process. Consequently, the DES-based configuration represented by base case-II is comparatively energy-efficient but the heavy solvent demands high initial capital investment ($\$35.47 \times 10^6$) compared to all proposed cases. However, the overall TAC ($\$11.87 \times 10^6$) required in the latter case is far less than that in base case-I. Among all proposed cases, it is important to note that the slight addition of MEA in aqueous DES solution reduces the amount of solvent by 40%, 43.8%, and 42.7% in case-I, case-II, and case-III, respectively. Reduction in solvent flow helps in improving the economy of the process as TCC in all three cases is observed to be lessened by 12–14% compared to base case-II. Moreover, the introduction of a hybrid solvent with an optimized flow rate in the absorber tends to reduce the operating expenses in the regeneration step. Thus, the TAC of all cases is as case-I ($\$10.5 \times 10^6$), case-II ($\10.38×10^6), and case-III ($\$10.58 \times 10^6$).

Table 7 presents the potential savings in terms of operating expenditure and TAC compared to the base cases. Since it is quite easy to regenerate the DES mixture due to high thermal efficiency and negligible vapor pressure, the energy consumption in regeneration is comparatively lower than in the MEA-based base case. It can be seen from Table 7 that the TOI savings are higher in case-I (56.8%), leading to other proposed cases. Similarly, the effect of the hybrid solvent is significant when the economics of the process were compared with those of base case-II as the addition of water reduces the viscosity of the solvent while the hybrid combination of water–MEA–DES produces a strong mixture that improves the efficiency of MEA as well. As a result, a highly selective hybrid solvent used in the proposed configurations simultaneously provides benefits in terms of TAC when compared with MEA and DES-based designs. It is important to note that the ratio of each constituent in the hybrid solvent mixture has significant importance; 5 wt% of MEA in DES solution shows the highest operating cost savings (56.8%), while 10 wt% of MEA in DES solution has the highest TAC savings (27.8%).

4. Conclusions

Removing the high amount of CO₂ from biogas is a key part in the biogas value chain where solvent selection is one of the most crucial steps. Conventional solvents such as amines fulfill the target recovery and purity of biomethane, however high energy consumption and environmental concerns are major challenges which need to be overcome. In this context, a hybrid solvent with a combination of various proportions of

MEA and aqueous ChCl/urea is selected to overcome the major challenges based on solvent characteristics and its functionality, energy efficiency, environmental hazards, and most importantly process economy are investigated. Process modeling and evaluation is carried out to check the feasibility of the proposed processes on the basis of the hybrid solvent. The results indicated that the hybrid solvent is advantageous as the amount of solvent flow for biogas upgrading is largely reduced when compared with the DES-based process. In addition, the major conclusions drawn from process evaluation are as follows;

- Compared to base case-I, hybrid solvent-based biogas upgrading is highly energy efficient as the specific energy saving in each proposed case is $\geq 72\%$.
- The exergy analysis results revealed that the exergy destruction in each proposed case is far less (85–90%) than that in base case-I. However, case-III is exergetically most powerful and efficient as compared to other cases.
- As high energy is required in each base case and compared to them, the proposed cases are energy efficient, lower emissions are recorded. Among the proposed cases, case-I is leading in terms of carbon capture rate (99.97%), specific CO₂ emissions (1.7 kg CO₂ per kmol), and SPECCA (3.97 kW per kg CO₂).
- Compared to both base cases, each proposed case is cost efficient and provides benefits in operating expenditure ($\geq 55\%$ savings) as well as TAC ($\geq 26.4\%$ savings). However, it is worth noting that the capital investment in the proposed cases is much higher as compared to base case-I which is due to the effect of the heavy solvent (DES) and the associated mixture. Nevertheless, the overall savings in terms of TAC are significant and confirm the potential suitability of the hybrid solvent for biogas upgrading.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

This work was supported by the Technology Development Program to Solve Climate Changes through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT (NRF-2018M1A2A2026257) and the National Research Foundation of Korea (NRF) grant funded by the Korea government (NRF-2019M1A2A2065614) as well as the 2021 Research Fund (1.210103.01) of UNIST (Ulsan National Institute of Science and Technology).

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