Simulation study of deep eutectic solvent-based biogas upgrading process integrated with single mixed refrigerant biomethane liquefaction

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ABSTRACT

Deep eutectic solvents (DESs) comprise ChCl/urea, in combination with water, have been considered in removing acid gases (CO₂ and H₂S) from biogas. The evaluation of DES for biogas upgrading at relatively high pressure (i.e., >8.0 bar) has not been reported before. The aqueous DES performance has also not been analyzed compared to conventional amines-based solvent (MEA) and ionic liquid (IL). To the best of our knowledge, this is the first study that presents the integration of DES-based biogas upgrading with a mixed refrigerant liquefaction process to facilitate the safe and economical transportation of biomethane over long distances. The biogas considered in this study consisted of 60% CH₄, 39% CO₂, and 1% H₂S. The aqueous ChCl/urea (70 wt%) results in biomethane with ≥99.0 wt% purity and ≥97.0 wt% recovery. Then, this biomethane was liquefied through a single mixed refrigerant process. Biomethane liquefaction process consumed 0.43 kW/hg-biomethane.
1. Introduction

Fossil fuels account for a significant proportion of global energy, delivering around 80% of the energy worldwide (Qyyum et al., 2020). Fossil fuels are also major contributors to air pollution and greenhouse gas (GHG) emissions. Greenhouse gases (GHGs), especially CO$_2$, play a primary role in climate change, and it is projected that the concentration of CO$_2$ will increase by 478–1100 ppm by the year 2100 (IPCC, 2018), which will lead to an increase in the overall environmental temperature of 2–5 °C. Global concerns about addressing climate change were highlighted in the Paris Agreement (UNFCCC, 2015), where it was proposed that the signatories should make efforts to limit the increase in the average global temperature to less than 2 °C, similar to the pre-industrial age, and take measures to restrict the increase in the temperature to 1.5 °C above that of the industrial era (Zain and Mohamed, 2018). Hence, there is an imperative need to find green, cost-effective, alternative energy sources such as biomethane to tackle global warming issues following the Paris Agreement (UNFCCC, 2015).

Biomethane is obtained from biogas upgrading. Biogas comprises CH$_4$ (50–75%), CO$_2$ (15–25%), H$_2$S (<2%), and traces of H$_2$, H$_2$O, and O$_2$, depending on the feedstock and operating conditions used (Cucchiella et al., 2018; Sciarlat et al., 2018; Tabatabaei et al., 2020). Biogas should be cleaned and upgraded efficiently to obtain biomethane with a purity of ≥97% to overcome the dependency on conventional natural gas (Carnevale and Lombardi, 2015). Therefore, biogas upgrading is one of the major components of the biomethane value chain. The end use of biomethane is critically affected by the efficiency of the upgrading technology. Biogas upgrading through the absorption approach is considered a well-established technology (Hashemi et al., 2019). High biomethane purity with low methane loss is the major feature of the absorption-based biogas upgrading approach and depends on the solvent, and the operating conditions utilized (Qyyum et al., 2020). Considering the environmental, operational, and economic factors, selecting an appropriate solvent is critical for optimizing the absorption-based biogas upgrading process.

Conventionally, amine-based solvents are known to remove acid gases from biogas and natural gas. Monoethanolamine (MEA) is the most well-known first-generation amine-based solvent. The major advantages of MEA are its ideal kinetics, reasonable stability, low capital cost, and high chemical reactivity with acid gases, especially CO$_2$ (Vega et al., 2018; Augelletti et al., 2020). Although MEA has shown promising performance for acid gas capture in different process plants (including biomethane production plants), many critical issues such as low absorption capacity, high enthalpy of reaction, thermal degradation, highly corrosive degradation products, and high operating costs for solvent regeneration are associated with the use of MEA (Vega et al., 2018; Haider et al., 2020).

To solve the issues related to typical amine-based solvents, ionic liquids (ILs) are emerging as a new class of solvents for acid gas removal applications. As their dominant advantages, ILs are non-toxic, non-flammable, biodegradable, recyclable, environmentally-friendly, have high chemical and thermal stability, are accessible, and favorably absorb various species for a wide range of applications (Lei et al., 2014; Xu et al., 2017; Nematollahi and Carvalho, 2019). The reaction enthalpy of ILs can be tuned by varying the anion group, and such flexibility in the structure of ILs can diversify their applications. However, ILs are costly, and this is a significant hurdle for their large-scale commercial applications. Deep eutectic solvents (DESs) have been introduced and considered as another class of ILs (Alkhathlawi et al., 2020; Slupek et al., 2020). Although DESs have the same characteristics as ILs, the price is significantly lower than ILs (Pena-Pereira and Namiešnik, 2014; Kamgar et al., 2017), making them more attractive for large-scale applications. Among the various available DESs, choline chloride/urea (ChCl/Urea; 1:2 by mole) is one of the most suitable candidates for commercial-scale biogas upgrading (Ma et al., 2018a) for its relatively low toxicity and highly biodegradable nature. The fundamental parameters for the selection of the aqueous DES (ChCl/Urea + water) are compared with those of pure DES, aqueous MEA, and a pure IL, i.e., [Bmim][PF$_6$] (recently studied (Haider et al., 2019) for biogas upgrading), in Table 1.

Ma et al. (2018a) surveyed and evaluated the thermophysical properties of pure and aqueous ChCl/Urea for large-scale biogas upgrading. By implementing a database for pure and aqueous ChCl/Urea in Aspen Plus, they compared the performance of aqueous ChCl/Urea vs. pure water for biogas upgrading. In another study, Ma et al. (2018b) compared the performance of aqueous (ChCl/Urea) with those of three physical solvents (water, dimethyl ether of polyethylene glycol (DEPG), and propylene carbonate (PC)) for biogas upgrading, and highlighted the possible techno-economic benefits of using the DES. They used Aspen Plus to evaluate the biogas upgrading processes and concluded that when the biogas production capacity was higher, pure water and aqueous DES performed better than...
The purified biomethane gas (99 wt%) at a temperature of 30 °C and 36 bar pressure is fed to the liquefaction section parallel to the refrigerant stream (S26), which comprises a mixture of nitrogen, methane, ethane, propane, and i-propane at 40 °C in a cryogenic heat exchanger (CHX-1). The refrigerants are compressed in multistage compressors with an inter-stage cooling system to raise the pressure to 52.5 bar. Subsequently, the high-pressure mixed refrigerant (MR) is expanded using a Joule-Thomson valve (JTV-1), which expands the mixture to the optimal evaporating pressure of 3.74 bar, resulting in a temperature drop to -149.71 °C. This expanded MR is recycled (S12) into the cryogenic heat exchanger (CHX-1), which exchanges the latent heat of vaporization from the incoming biomethane (S3) and warm MR (S26) stream. Finally, the sub-cooled liquefied biomethane (LBM) stream (S13) at -159.47 °C and 1.209 bar are sent to the storage unit. The super-heated saturated vapor stream of MR (S27) at a temperature of 38 °C is recycled to the compression unit, where the MR is introduced into a series of multistage compression units. The system is equipped with inter-stage cooling at each stage, where the intercooler outlet temperature is set to 40 °C.

2.2. Process simulation

To analyze any processes through modeling and simulation, the thermodynamic properties, including the binary interaction parameters, enthalpy, and entropy, are critical factors that determine the process reliability. The Aspen Plus simulator has an extensive and wide-range database with versatile thermodynamic fluid packages. Therefore, the process proposed in the present study was simulated by using Aspen Plus® v10. However, the solubility data for the studied system is not available in Aspen's database so far. Thus, the solubility data for CO₂, H₂S, H₂O, and CH₄ in ChCl/Urea (given in Table 2) were validated by performing rigorous regression using the Peng Robinson (PR) equation of state (EOS). The selected EOS model is distinct from most other enhanced models in the Aspen database as it can handle a broader range of temperatures and pressures and has the largest database of binary interaction parameters for a wide range of components (Nawaz et al., 2019).

Hence, by correlating the vapor-liquid equilibrium data using PR, the obtained binary interaction parameters after regression have minimum deviation, which shows a good agreement with experimental results, as shown in Table 3. The estimated solubilities of the respective components achieved by regressing the vapor-liquid equilibrium (VLE) data are shown in Figures 2a, b, and c for CO₂, H₂S, and CH₄ in ChCl/Urea, respectively.

The proposed process and base cases were simulated based on the following fundamental assumptions:

- Heat loss to surroundings was assumed to be zero
- Minimum pressure drop of 0.1 bar across inter-stage coolers
- 75% isentropic efficiency was maintained for each compressor and pump
- Minimum internal temperature approach (MITA) is fixed at 2.0 °C for efficient heat exchange through a multistage biomethane liquefaction cryogenic heat exchanger.
Table 2. Vapor-liquid equilibrium (VLE) data for CO$_2$, CH$_4$, and H$_2$S and H$_2$O in ChCl/Urea.

| DES            | System         | T (°C) | P (bar)         | Solubility range         | No. of points | Reference        |
|----------------|----------------|--------|-----------------|--------------------------|---------------|-----------------|
| ChCl/Urea (1:2)| CO$_2$         | 35.05-55.05 | 6.51-45.04     | 0.042-0.195              | 15            | Xie et al. (2016) |
|                | CH$_4$         | 35.05-55.05 | 5.48-36.18     | 0.012-0.089              | 15            |                 |
|                | CO$_2$         | 40.05-80.05 | 0.105-2.022    | 0.00038-0.01624           | 20            |                 |
|                | CH$_4$         | 40.05-80.06 | 0.106-2.028    | 0.00004-0.00110           | 20            |                 |
|                | HS$_2$         | 40.05-80.07 | 0.101-2.021    | 0.00151-0.04640           | 20            |                 |
|                | CO$_2$         | 38.85-55.85 | 0.405-1.535    | 0.000906-0.0035           | 21            | Mirza et al. (2015) |
|                | CO$_2$         | 30.70       | 2.99-59.11     | 0.1562-3.5592             | 34            | Leron et al. (2013) |

Fig. 1. Biogas liquefaction followed by DES-based biogas upgrading. LBM: Liquefied biomethane.
3. Results and Discussion

3.1. Process analysis: optimal design variables and parameters

The proposed integrated process was investigated and analyzed by varying the concentration of the DES solvent, as shown in Figure 3. Table 4 tabulates the design variables, parameters, constraints, and overall energy consumption for all the investigated cases compared to MEA- and IL-based biogas upgrading.

The effect of varying the concentration of the aqueous solutions of DES on biogas upgrading was analyzed using the proposed configurations. It was reported that the addition of 30% water to DES lowered its viscosity by 90% (Zhang et al., 2012; Kalhor and Ghandi, 2019). Therefore, the analysis included six cases in which the solvent's composition was varied; the data were compared with those of alkanol amine- and IL-based solvents.
### Table 4
Design variables and parameters for biomethane liquefaction followed by DES-, MEA-, and IL-based biogas upgrading.

| Variables/Parameters | Base case-I | Base case-II | Case-I | Case-II | Case-III | Case-IV | Case-V | Case-VI |
|----------------------|-------------|-------------|--------|---------|----------|---------|--------|--------|
| **Biogas upgrading** |             |             |        |         |          |         |        |        |
| Solvent composition (wt%) | MEA (30), H₂O (70) | [Bmim][PF₆] (100) | ChCl/urea (100) | ChCl/urea (30), H₂O (70) | ChCl/urea (40), H₂O (60) | ChCl/urea (50), H₂O (60) | ChCl/urea (60), H₂O (60) | ChCl/urea (70), H₂O (60) |
| Purity of biomethane (wt%) | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 |
| Recovery of biomethane (wt%) | 0.99 | 0.96 | 0.97 | 0.97 | 0.97 | 0.97 | 0.97 | 0.97 |
| H₂S reduction (ppm) | ≤ 10 | ≤ 10 | ≤ 10 | ≤ 10 | ≤ 10 | ≤ 10 | ≤ 10 | ≤ 10 |
| CO₂ removal (%) | 0.99 | 0.985 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 |
| **Absorber** |             |             |        |         |          |         |        |        |
| Flowrate of biogas (kg/h) | 58000.0 | 58000.0 | 58000.0 | 58000.0 | 58000.0 | 58000.0 | 58000.0 | 58000.0 |
| Flowrate of biogas (m³/h) | 66759 | 66759 | 66759 | 66759 | 66759 | 66759 | 66759 | 66759 |
| Flowrate of solvent (m³/h) | 1181.63 | 909.463 | 1168.282 | 12083.379 | 5888.14 | 3137.673 | 1902.631 | 1134.903 |
| Solvent/Feed ratio (m³/m³) | 0.0177 | 0.01362 | 0.0175 | 0.181 | 0.0882 | 0.047 | 0.0285 | 0.0166 |
| Absorber stages | 20 | 14 | 10 | 12 | 10 | 8 | 8 | 8 |
| Absorber pressure (bar) | 36 | 36 | 36 | 36 | 36 | 36 | 36 | 36 |
| Absorber temperature (°C) | 40 | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
| Flash drum pressure (bar) | 6.8 | 14.7 | 14.7 | 14 | 14 | 12.8 | 13.2 | 12.8 |
| **Regenerator** |             |             |        |         |          |         |        |        |
| Regenerator stages | 19 | 1 | 8 | 8 | 8 | 8 | 8 | 8 |
| Regenerator temperature (°C) | 40 | 80 | 40 | 40 | 40 | 40 | 40 | 40 |
| Regenerator pressure (bar) | 1.1 | 0.1 | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 |
| Reflux ratio | 2 | - | - | - | - | - | - | - |
| Duty of regenerator (kW) | 26718 | 4594.41 | - | - | - | - | - | - |
| Airflow rate (m³/h) | - | - | 18777.8 | 55429 | 40893.6 | 31055.8 | 24952.9 | 17482.4 |
| Air/DES rich ratio (m³/m³) | - | - | 0.282 | 0.825 | 0.615 | 0.469 | 0.377 | 0.257 |
| Power of pump for recycling (kW) | 26718 | 4594.41 | - | - | - | - | - | - |
| Power of air compressor (kW) | 5.067 | 5.067 | 6.369 | 6.146 | 5.244 | 5.24 | 5.29 | 5.76 |
| Specific thermal load (kWh/kmol biogas) | 0.235 | 0.235 | 0.296 | 0.286 | 0.244 | 0.244 | 0.246 | 0.245 |
| **Biomethane liquefaction** |             |             |        |         |          |         |        |        |
| LNG product (liquid fraction) | 0.91 | 0.91 | 0.91 | 0.91 | 0.91 | 0.91 | 0.91 | 0.91 |
| MITA (°C) | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 |
| **Design variables** |             |             |        |         |          |         |        |        |
| Mass flow rate of nitrogen, m_N₂ (kg/h) | 9357.5 | 9357.5 | 9357.5 | 9357.5 | 9357.5 | 9357.5 | 9357.5 | 9357.5 |
| Mass flow rate of methane, m_C₁ (kg/h) | 39561.5 | 39561.5 | 39561.5 | 39561.5 | 39561.5 | 39561.5 | 39561.5 | 39561.5 |
| Mass flow rate of ethane, m_C₂ (kg/h) | 17464.4 | 17464.4 | 17464.4 | 17464.4 | 17464.4 | 17464.4 | 17464.4 | 17464.4 |
| Mass flow rate of propane, m_C₃ (kg/h) | 50397.2 | 50397.2 | 50397.2 | 50397.2 | 50397.2 | 50397.2 | 50397.2 | 50397.2 |
| Mass flow rate of i-pentane, m_C₅ (kg/h) | 44315.6 | 44315.6 | 44315.6 | 44315.6 | 44315.6 | 44315.6 | 44315.6 | 44315.6 |
| Refrigerant low pressure (bar) | 9.3 | 9.3 | 9.3 | 9.3 | 9.3 | 9.3 | 9.3 | 9.3 |
| Refrigerant discharge pressure (bar) | 2.74 | 2.74 | 2.74 | 2.74 | 2.74 | 2.74 | 2.74 | 2.74 |
| Pressure ratio | 2.1 | 2.1 | 2.1 | 2.1 | 2.1 | 2.1 | 2.1 | 2.1 |
| **Objectives** |             |             |        |         |          |         |        |        |
| Total compression power (kW) | 14563 | 14563 | 14563 | 14563 | 14563 | 14563 | 14563 | 14563 |
| Specific (molar) compression power requirement (kW/kmol biomethane) | 6.89 | 6.89 | 6.89 | 6.89 | 6.89 | 6.89 | 6.89 | 6.89 |
| Specific (mass) compression power requirement (kW/kg biomethane) | 0.43 | 0.43 | 0.43 | 0.43 | 0.43 | 0.43 | 0.43 | 0.43 |

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Consequently, a sensitivity analysis was carried out for the upgrading section to evaluate the required solvent/feed ratio when the number of stages was varied to achieve constraint satisfaction. The optimum solvent flow rate associated with the absorber stages is pivotal as it is directly associated with the solvent recovery unit. Notably, a high solvent flow rate during the absorption process leads to cost-intensive recovery in the solvent regeneration step for the high power required to pump back the solvent and the high flow of air required to regenerate the solvent. Figure 4 shows the DES’s estimated flow regarding the absorber stages for the required purity and recovery of biomethane. The analysis was performed for aqueous DES with various compositions, and the deep eutectic solvent to feed (DES/F) ratio was calculated to estimate the number of stages in the absorber. The addition of water reduces the solvent's viscosity but increases the overall flow of the DES in the absorber to meet the process constraints. It was predicted that after a certain stage number, the DES/F ratio would become constant in each case. Hence, the process configurations proposed at the stages required for certain stage number, the DES/F ratio would become constant in each case. Notably, the compressor power needed to recover the DES from acid gas. Therefore, for 70% DES, eight stages were selected for the regenerator for solvent recovery. Similarly, for the other cases, the Air/DES ratio became constant at the 8th stage. Nevertheless, the airflow was comparatively high compared to that required for 70% DES, where the former ultimately requires greater compression power and causes the overall cost of the process to increase.

Figure 4 shows the solvents’ estimated flow regarding the absorber stages for the required purity and recovery of biomethane. The analysis was performed for aqueous DES with various compositions, and the deep eutectic solvent to feed (DES/F) ratio was calculated to estimate the number of stages in the absorber. The addition of water reduces the solvent’s viscosity but increases the overall flow of the DES in the absorber to meet the process constraints. It was predicted that after a certain stage number, the DES/F ratio would become constant in each case. Hence, the process configurations proposed at the stages required for certain stage number, the DES/F ratio would become constant in each case.

The flash column connected to the absorber enhances the purity and recovery of biomethane in the top stream. Nevertheless, optimizing the pressure in the flash column is a crucial factor. The flow of the recycle stream changes as the pressure of the flash column varies. Thus, reducing the flash column pressure directly affects the power of the biogas compressor required to accelerate the ejection of the gas from the flash drum. Notably, the compressor power needed to recycle the vapor stream of the flash column was the lowest with the use of 70% DES as the pressure reduction in the flash column was about 13.5 bar. Whereas the pressure in the flash column was lower in the other cases, as shown in Figure 4. The top stream from the absorber containing biomethane is sent to the separate section where liquefaction takes place. In contrast, the bottom stream from the absorber is rich in DES that must be recovered in the solvent recovery column.

Air stripping was used to recover and purify the solvent by separation from the acid gases in the solvent regeneration column. The air was compressed at 1.1 bar through the mechanical blower and introduced into the regenerator, where the acid gas components were separated from the DES through air stripping. The flow of air for each selected stage was set such that DES was recovered with 99.99% purity and recycled to the absorption column by stripping. The flow of air for each selected stage was set such that DES was recovered with 99.99% purity and recycled to the absorption column by stripping. The flow of air for each selected stage was set such that DES was recovered with 99.99% purity and recycled to the absorption column by stripping. The flow of air for each selected stage was set such that DES was recovered with 99.99% purity and recycled to the absorption column by stripping.
Table 5. Capacity parameters and values of constants for equipment used in this study (Turton et al., 2008).

| Equipment category | \( K_1 \) | \( K_2 \) | \( K_3 \) | Capacity, Unit |
|--------------------|---------|---------|---------|---------------|
| Absorber           | 3.4974  | 0.4485  | 0.1074  | Volume, m\(^3\) |
| Packing            | 2.4493  | 0.9744  | 0.0055  | Volume, m\(^3\) |
| Regenerator        | 3.4974  | 0.4485  | 0.1074  | Volume, m\(^3\) |
| Air cooler         | 4.0336  | 0.2341  | 0.0497  | Area, m\(^2\) |

The TOC of the process was calculated by considering the electricity cost for power generation required to compress the biogas, air compression

\[
\log_{10} (C_{\text{p},i}) = K_1 + K_2 \log_{10}(A) + K_3 (\log_{10}(A))^2
\]

where, \( K_1, K_2, \) and \( K_3 \) denote the selective equipment-based constant parameters, and \( A \) is the capacity measure. The parametric relations and constant values were taken from the literature (Turton et al., 2008) and are listed in Table 5. The volume of the column was calculated as \( \pi D^2 L/4 \), and that of the packing as \( \pi D^2/4 \). In the case of the cryogenic heat exchanger, the plate-fin heat exchanger type was used for the capacity-based small-scale liquefaction plant. However, the value of \( F_{\text{BM}} \) for this specific heat exchanger is not documented in the open literature. Therefore, the Aspen economic analyzer was used to estimate the capital cost of the cryogenic heat exchanger. Similarly, "UA" was determined from the simulation results, where "U" is the heat transfer coefficient, and "A" is the area with the air cooler. Nevertheless, "A" is the capacity factor for calculation of the capital cost, which was estimated by considering "U" as 568 W m\(^{-1}\)K\(^{-1}\) for the air-cooler based on the literature (The Basics of AIR-COOLED HEAT EXCHANGERS. HUDSON Products Corporation, 2007).

The capacity range for pumps documented by Turton (Turton et al., 2008) was up to 300 kW, while in the current study, even a higher power was required for the pumps to operate on the viscous DES. Therefore, the capital cost relations for the high pressure and high capacity data were taken from the Engineering design book by Douglas (Erwin, 2015). The cost relation is presented as Equation 5, in which \( F_p \) denotes the pressure factor, and \( F_M \) represents the material factor. Similarly, the compressors' capital cost was estimated by applying Equation 6, in which \( M & S \) represents the Marshall and Swift Index; \( W \) is the power of the compressor in hp; and \( F_c \) is the correction factor, where the value is unity.

\[
\text{Base module unit cost} = \text{Base cost} \times (F_p + F_M) \times \text{Cost Index} \quad \text{Eq. 5}
\]

\[
C_{\text{p},i} = 517.5 \times \left( \frac{M & S}{280} \right) \times W^{0.82} \times F_c \quad \text{Eq. 6}
\]

The TOC of the process was calculated by considering the electricity cost for power generation required to compress the biogas, air compression.
for regeneration of the solvent, pumping cost for solvent recycling in the upgrading section, and compression of the refrigerants for liquefaction. The major portion of the power required in each section was due to the compression of the biogas and refrigerants. The cost of electricity was assumed to be $16 GJ⁻¹, leading to a cost of $504.5 kWh⁻¹ (Turton et al., 2008). Table 6 lists the equipment for the upgrading and liquefaction section and the corresponding power consumption.

### Table 6.

Power required in unit operations.

| Equipment                  | Power (kW) |
|----------------------------|------------|
| Biogas upgrading           |            |
| Biogas compressor          | 14183      |
| Air blower                 | 69         |
| DES pump                   | 1307       |
| Biomethane liquefaction    |            |
| K-1                        | 4001       |
| K-2                        | 3941       |
| K-3                        | 3626       |
| K-4                        | 2926       |
| P-1                        | 69         |
|                                 |            |

Table 7 presents the cost estimate for all the proposed DES-based integrated processes, compared with the MEA- and IL-based integrated processes. The TAC for each case mainly depends on the compressors. However, economic comparison of the MEA-based process with the proposed configurations reveals that for the former, a high cost is incurred for the energy-intensive solvent regeneration, i.e., around USD 6.69 ×10⁶. Similarly, the overall operating cost for the amine-based biogas upgrading and subsequent liquefaction was estimated at USD 20.487 ×10⁶, which is far greater than that of the DES-based upgrading process. Unlike the amine-based process, the capital cost for the absorber in IL-based biogas upgrading is very high (USD 6.06 ×10⁶) because of the viscous and heavy solvent. The prolonged mass transfer rate means that a high flow rate of the IL is required to absorb CO₂. Nevertheless, regeneration is much easier and more energy-efficient for the high thermal stability of ILs, which makes them stable at high temperatures; the total operating cost was calculated at USD 4.03 ×10⁶.

Hence, based on the process analysis and cost estimation, the 70% DES process was chosen for integration with the liquefaction process. The proposed SMR liquefaction process is cost-intensive in terms of its capital investment as it requires multistage compression of the refrigerants, while a cryogenic heat exchanger is used to liquefy the biomethane. As an added advantage, the proposed scheme provides an overall potential TAC savings of 14.26% and 8.71% compared to the amine- and IL-based configurations. The calculated TCC was USD 68.42 ×10⁶, while the operating cost was even lower than that of the upgrading process as biogas is compressed at high pressure (36 bar) before entering the absorber. However, based on the TAC, the unit cost for the upgrading and liquefaction processes was USD 0.6 kmol⁻¹ of biogas and $1.14 kmol⁻¹ of biomethane, respectively.

### 5. Conclusions and future directions

This study investigated the potential of DES for biogas upgrading at 36.0 bar. Different concentrations of DES were investigated for the simultaneous removal of CO₂ and H₂S from biogas. The upgraded biogas (biomethane) was further liquefied by using a single mixed refrigerant comprising nitrogen, methane, ethane, propane, and iso-pentane. The following major conclusions could be drawn from the proposed analysis:

- The process of employing DES with 70 wt% concentration could efficiently and economically remove acid gases from biogas.
- DES-based biogas upgrading integrated with SMR-LBM affords 14.26 and 8.71% TAC savings compared to the MEA and IL-based integrated processes, respectively.
• It cannot decisively be concluded that DES is an economical option for biogas upgrading. The economic feasibility depends on the concentration of DES, feed biogas composition, and conditions. For example, the TCC for case-I (pure DES) was 9.58% and 11.15% higher (negative savings) than base case-I and II, respectively. Similarly, case-II (30% DES) was totally infeasible based on the TCC, TOC, and TAC, compared to base case-I and II.
• Because biomethane liquefaction is a cryogenic operation, the methane content should be >99.99%, with 99.99% recovery. Nevertheless, the proposed schemes failed to yield such high purity and recovery. Therefore, 0.2% CO₂ (by mole) remains in the upgraded biogas, which can lead to undesirable CO₂ freezing in the liquefaction section.

Future works should be focused on determining the TAC savings opportunities in the studied integrated cases, including the base cases, through heat integration of the biogas upgrading and liquefaction section.

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References

[1] Alkhatib, I.I., Ferreira, M.L., Alba, C.G., Bahamón, D., Llovel, F., Pereiro, A.B., Araújo, J.M., Abú-Zahr, M.R., Vega, L.F., 2020. Screening of ionic liquids and deep eutectic solvents for physical CO₂ absorption by Soft-SAFT using key performance indicators. J. Chem. Eng. Data.
[2] Amundsen, T.G., Øi, L.E., Eimer, D.A., 2009. Density and viscosity of monoethanolamine + water + carbon dioxide from 25 to 80 °C. J. Chem. Eng. Data. 54(11), 3096-3100.
[3] Angelliti, R., Galli, S., Cislon, P., Granati, M., Monteleone, G., Murrara, M.A., Annesini, M.C., 2020. Biogas upgrading through CO₂ removal by chemical absorption in an amine organic solution: physical and technical assessment, simulation and experimental validation. Biomass Bioenergy. 141, 105729.
[4] Azimova, M.A., Morton III, S.A., Frymier, P.D., 2009. Comparison of three bacterial toxicity assays for imidazolium-derived ionic liquids. J. Environ. Eng. 135(12), 1388-1392.
[5] Barbosa, L.C., Nascimento, M.V.D.C., Ofélia de Queiroz, F.A., de Medeiros, J.L., 2020. A cleaner and more sustainable decarbonation process via ionic-liquid absorption for natural gas with high carbon dioxide content. J. Clean. Prod. 242, 118421.
[6] Bernaconi, R., Panzeri, G., Accogli, A., Liberale, F., Nobili, L., Magagnin, L., 2017. Electrodéposition from deep eutectic solvents. Intech. Prog. Dev. Lon. Liq. 235-261.
[7] Carnevale, E., Lombardi, L., 2015. Comparison of different possibilities for biogas use by life cycle assessment. Energy Procedia. 81, 215-226.
[8] Cucchiella, F., D’Adamo, I., Gastaldi, M., Miliacca, M.A., 2018. Profitability analysis of small-scale plants for biomethane injection into the gas grid. J. Clean. Prod. 184, 179-187.
[9] Dubois, L., Thomas, D., 2010. Comparison of various alkaline solutions for H₂S/CO₂-selective absorption applied to biogas purification. Chem. Eng. Technol. 33(10), 1601-1609.
[10] Erwan, D., 2015. Industrial chemical process design. 2nd Edition.
[11] Hayd-Kali, M.K., Althuthuth, M., Mokraoui, S., Awaizer, I., Ali, E., Richon, D., 2020. Screening of ionic liquids for gas separation using COSMO-RS and comparison between performances of ionic liquids and aqueous alkalolamine solutions. Chem. Eng. Commun. 207(9), 1264-1277.
[12] Handy, H., Santoso, A., Guido, G., Pellegrini, L.A., Lee, M., 2020. Biogas to liquefied biomethane: assessment of 3P’s-production, Processing, and Prospects. J. Renew. Sust. Energy Rev. 119, 105501.
[13] Hsu, Y.H., Leron, R.B., Li, M.H., 2014. Solubility of carbon dioxide in aqueous mixtures of (reline + monoethanolamine) at T = (313.2 to 353.2) K. J. Chem Thermodyn. 72, 94-99.
[14] IPCC, 2018. Intergovernmental panel on climate change (IPCC).
[15] Juneidi, I., Hayyan, M., Ali, O.M., 2016. Toxicity profile of choline chloride-based deep eutectic solvents for fungi and Cyprinus carpio fish. Environ. Sci. Polihut. Res. 23(8), 7648-7657.
[16] Kaltho, P., Ghandi, K., 2019. Deep eutectic solvents for pretreatment, extraction, and catalysis of biomass and food waste. Molecules. 24(22), 4012.
[17] Kamgar, A., Mohsenpour, S., Esmaeilzadeh, F., 2017. Solubility prediction of CO₂, CH₄, H₂, CO and N₂ in choline chloride/urea as a eutectic solvent using NRTL and COSMO-RS models. J. Mol. Liq. 247, 70-74.
[18] Kazmi, B., Haider, J., Qyyum, M.A., Saeed, S., Kazmi, M.R., Lee, M., 2019. Heating load depreciation in the solvent-regeneration step of absorption-based acid gas removal using an ionic liquid with an imidazolium-based cation. Int. J. Greenhous Gas Control. 87, 89-99.
[19] Lei, Z., Dai, C., Chen, B., 2014. Gas solubility in ionic liquids. Chem. Rev. 114(2), 1289-1326.
[20] Leron, R.B., Carpana, A., Li, M.H., 2013. Carbon dioxide solubility in a deep eutectic solvent based on choline chloride and urea at T = 303.15-343.15K and moderate pressures. J. Taiwan Inst. Chem. Eng. 44(8), 879-885.
[21] Liu, F., Chen, W., Mi, J., Zhang, J.Y., Kan, X., Zhong, F.Y., Huang, K., Zheng, A.M., Jiang, L., 2019. Thermodynamic and molecular insights into the absorption of H₂S, CO₂, and CH₄ in choline chloride plus urea mixtures. AIChE J. 65(5), e16574.
[22] Liu, X., Hou, M., Han, B., Wang, X., Zou, L., 2008. Solubility of CO₂ in a choline chloride + urea eutectic mixture. J. Chem. Eng. Data. 53(2), 548-550.
[23] Ma, C., Xie, Y., Ji, X., Liu, C., Lu, X., 2018a. Modeling, simulation and evaluation of biogas upgrading using aqueous choline chloride/urea. Appl. Energy. 229, 1269-1283.
[24] Ma, C., Liu, C., Lu, X., Ji, X., 2018b. Techno-economic analysis and performance comparison of aqueous deep eutectic solvent and other physical absorbents for biogas upgrading. Appl. Energy. 225, 437-447.
[25] Mirza, N.R., Nichols, N.J., Wu, Y., Mumford, K.A., Kentish, S.E., Stevens, G.W., 2015. Experiments and thermodynamic modeling of the solubility of carbon dioxide in three different deep eutectic solvents (DESs). J. Chem. Eng. Data. 60(11), 3246-3252.
[26] Nawaz, A., Qyyum, M.A., Lee, M., Aslam, M., De Guido, G., Pellegrini, L.A., Lee, M., 2019. Optimization of mixed fluid cascade LNG process using a multivariate Coggins step-up approach: overall compression power reduction and exergy loss analysis. Int. J. Refrig. 104, 189-200.
[27] Nematollahi, M.H., Carvalho, P.J., 2019. Green solvents for CO₂ capture. Curr. Opin. Green Sust. Chem. 18, 25-30.
[28] Pena-Pereira, F., Namiesnik, J., 2014. Ionic liquids and deep eutectic mixtures: sustainable solvents for extraction processes. ChemSusChem. 7(7), 1784-1800.
[29] Qyyum, M.A., Haider, J., Qadeer, K., Valentina, V., Khan, A., Yasin, M., Aslam, M., De Guido, G., Pellegrini, L.A., Lee, M., 2020. Biogas to liquefied biomethane: assessment of 3P’s-production, Processing, and Prospects. J. Renew. Sust. Energy Rev. 119, 105601.
[30] Rehman, A., Qyyum, M.A., Qadeer, K., Zahir, F., Ding, Y., Lee, M., Wang, L., 2020. Integrated biomethane liquefaction using exergy from the discharging end of a liquid air energy storage system. Appl. Energy. 260, 114260.
[31] Scarlat, N., Dallemann, J.F., Fahl, F., 2018. Biogas: developments and perspectives in Europe. Renewable Energy. 129, 457-472.
[32] Slupek, E., Makoś, P., Gębiński, J., 2020. Theoretical and economic evaluation of low-cost deep eutectic solvents for effective biogas upgrading to bio-methane. Energies. 13(13), 3379.

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