



Design of biogas upgrading processes based on ionic liquids

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ABSTRACT

Biogas stands out as an alternative to traditional sources of energy since it presents a high methane content, and it is mainly produced by anaerobic digestions of organic wastes. Typical biogas streams do not only consist of biomethane but also carbon dioxide, water, ammonia, hydrogen sulfide or siloxanes, depending on the source of the organic waste. Therefore, it is important to remove all these contaminants to obtain a high-quality stream in a process known as biogas upgrading. Currently, there is not a predominant technology, all of them presenting advantages and drawbacks to be solved. In this work, we test a biogas upgrading process based on CO₂ chemical absorption by ionic liquids (ILs). The complete process was evaluated involving absorber and stripping columns in a wide range of operating temperatures and pressures to reach biomethane of 97% purity from an industrial biogas stream. Best specific energy consumptions are found at 50 °C in the absorber and 95 °C in the stripper at atmospheric pressure. Increasing the operating pressure of the absorber to 6 bar reduces the energy consumption from 0.8 kWh/Nm³ to 0.2 kWh/Nm³. This is mainly because of the reduction in IL flow (almost a half) and that the thermal energy needed is provided by the exothermic reaction and no external requirements are needed. IL-based proposal for biogas upgrading was found able to efficiently retain CO₂ but also other main impurities (H₂S, H₂O, siloxanes) producing biomethane with quality standards. Results from IL-based process reveal savings in operating cost and nearly the same equipment investment costs than available technologies (PSA, water and amine scrubbing, and membranes) for biogas upgrading process.

1. Introduction

Biogas is a renewable source of energy characterized by its high methane (CH₄) content [1,2]. It can be an alternative solution to satisfy the world energy demands and reduce greenhouse gases emissions. It is produced mainly from anaerobic digestion of biomass, commercial composting, landfills, etc. [3]. Raw biogas composition depends greatly on the nature of the substrate (source biomass). In general, typical biogas streams are composed of methane (55–70%) and carbon dioxide (30–45%) [4]. Several other gases and contaminants are usually present in minor proportions such nitrogen (0–15%), oxygen (0–3%), water (1–5%), light hydrocarbons (0–200 mg/m³), H₂S (0–10000 ppm), ammonia (0–100 ppm), and siloxanes (0–50 mg/m³) [5]. The presence of these contaminants does not allow the use of raw biogas as an alternative energy source [6]. For instance, H₂S reacts with water forming sulfuric acid and causing corrosion in the combustion chamber [7]; Siloxanes may form deposits of SiO₂ that would drastically damage the process equipment [8]. Therefore, the upgrading process has two objectives: first, the removal of harmful compounds (H₂S, Si, NH₃, VOCs...)

[9]; and second, the removal of CO₂ present in the stream to enhance the quality of the biomethane product [10]. Therefore, the final goal is to adjust the biomethane concentration to an optimum level to maximize the calorific content of the mixture, usually around 95–99% of methane to be injected in the existing gas grid or be used as fuel in automotive [11].

Biomethane market has experienced an exponential growth over the last years. Annual report from European biogas association (EBA) [12] calculates that in 2018 there was 483 active plants with a total production of 22,787 GWh/year. At the end of 2020 there were 729 biomethane-producing plants in Europe (51% increase from 2018) being the mayor producers Germany and France [12]. In addition, the actual European network (>14,000 anaerobic digesters) is expected to increase trying to supply 18–20 million m³ by 2030 [13].

In recent years, several upgrading technologies have been developed to produce high-quality biomethane, none of them is predominant in biogas market [2]: i) High pressure physical scrubbing: one of the most extended methods, it uses water as physical absorbent, consisting of washing the biogas stream with countercurrent water at mid-high

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pressure (6–10 bar). At these conditions, CO₂ shows higher solubility in water, resulting in an enrichment of biomethane product. However, water selectivity is limited, incurring in CH₄ losses (up to 8–10%). Additional limitations are the high-water consumption and the biomethane contamination by N₂ and O₂ desorbed from water; ii) Chemical scrubbing: a chemical absorbent (usually an amine aqueous solution) is used to capture the CO₂ present in biogas stream, allowing to obtain high biomethane purity (>99%), and reducing the required pressure to near atmospheric conditions. [2,14]. However, the regeneration of the solvent in this process implies high thermal requirements (0.40–0.75 kWh/Nm³). Additional disadvantages are related to the amine high volatility, which produces reactant loss and corrosive vapors that need to be controlled; iii) Membrane technology: An effective biomethane separation is achieved through a selective membrane barrier, obtaining high product purity and low methane loss. As main limitation, this process normally requires high operating pressures (>10 bar) and several steps (≥3) [15]. In addition, membranes are quite sensible to some impurities present in biogas (such H₂S, NH₃ or siloxanes), needing previous operations to be removed before membrane purification; iv) Adsorption: this technology uses a solid adsorbent, generally a molecular sieve based on activated carbon, to retain the CO₂ and other components of biogas by using two or more beds (some in capture, other in regeneration) for the continuous production of biomethane [16]. As in membrane technology, high pressures are needed to reach high separation efficiency; also requiring a pretreatment to avoid some impurities that can be irreversible adsorbed in the material [17]. Therefore, it exists a clear interest on the development of cost-effective and innovative biogas upgrading technology for the growing biomethane market.

An alternative for the biogas upgrading is the use of ionic liquids (ILs) [18], which are liquid salts formed by a cation and an anion with melting points below 100 °C [19]. Their excellent solvent properties such as low vapor pressure, high thermal and chemical stability, high solvation capacity, among others, make ILs being investigated as physical and chemical absorbents [20]. The possibility of tuning the cation and the anion to specific applications makes them being considered “designer solvents” [21]. In last years, ILs are being widely studied as CO₂ absorbents [22]. The first type of ILs tested were those based on physical absorption. Thus, it was demonstrated that the suitable selection of the cation and the anion maximizes CO₂ physical absorption [23], revealing that ILs based on long alkyl chain cations and fluorinated anions exhibit the higher CO₂ solubility in molar terms [22,23]. However, it was proved that ILs with high molar weights do not present competitive mass absorption capacities compared with traditional organic solvents [24]. Moreover, it is stated that mass transfer kinetics is the controlling stage in CO₂ physical absorption operation based on ILs, being those with lower viscosities, the ones that exhibit the best performance [25]. The other type of ILs reported are those presenting CO₂ chemical absorption that exhibit higher CO₂ solubility than physical absorbents, specially at low partial pressures [26]. ILs based on different anion families present CO₂ chemical absorption such as carboxylate-based [27,28], amino acid-based [29,30] or aprotic heterocyclic anions (AHA) [31,32]. The first two families share their high CO₂ absorption capacities and huge viscosity values, especially when they react with CO₂, which limits the mass transfer kinetics. AHA-IL family presents some advantages against other CO₂ chemical absorbents such as 1:1 stoichiometry, relatively low viscosity value (100 cP at 323 K for cyanopyrrolide-based ILs) and tunable reaction enthalpy [32]. It has been demonstrated that AHA-ILs can be successfully designed to obtain a compromise exothermic reaction enthalpy to promote high CO₂ uptake at low regeneration cost [33]. Process analysis revealed that using AHA-IL triethyl(octyl)phosphonium 2-cyanopyrrole ([P₂₂₂₈][CNPyrr]) in different CO₂ capture systems (post-combustion, biogas, pre-combustion) implies lower solvent and energy consumptions than amino acid- and carboxylate-based ILs [34], minimizing operating and investment costs of CO₂ capture process [35].

On the other hand, recent studies have evidenced the outstanding absorbent properties of ILs to retain other relevant impurities present in

the biogas, such as H₂S [36–38], ammonia [39,40], water [41] or siloxanes [8]. In addition, ILs present very high CO₂/CH₄ selectivity, what ensures minimizing CH₄ losses in absorption process [34]. For these reasons, ILs seem to be ideal absorbents for biogas upgrading applications. The first works that report biogas upgrading using ILs were centered in CO₂ physical absorption. García-Gutiérrez et al., reported the techno-economic feasibility of biogas upgrading with ILs as physical absorbents (using bis[(trifluoromethyl)sulfonyl] imide [NTf₂]⁺) based on Aspen Plus process simulator and COSMO-SAC model. They reported production costs 40–51% higher than the same-scale process using MEA absorbent [42]. Xie et al., published a work regarding biogas upgrading using imidazolium-based ILs presenting CO₂ physical absorption ([NTf₂]⁺ and [PF₆]⁺) by means of process simulations. The energy consumptions are lower than water scrubbing (typically used as benchmark), but higher than urea/water solutions [43,44]. Orloff et al., presented the results of [NTf₂], [DCA] and [TCM] anions doped with a small amount of chemical absorption anions such aminoacids for physical/chemical CO₂ absorption on biogas upgrading process. They carried out experimental (thermal stability, viscosity, CO₂/CH₄ selectivity, etc.) and theoretical analysis (energy consumptions, process costs). The results revealed that the process is able to work at isothermal conditions with lower energy demands than MEA solutions but at the cost of very high solvent demands [45]. Recently, Hospital-Benito et al., proposed a process analysis overview of ILs presenting CO₂ chemical absorption (amino acid-based, carboxylate-based and AHA-based ILs) in different capture systems, including biogas streams [34]. The results revealed the technical viability of the CO₂ capture in biogas upgrading operation using ([P₂₂₂₈][CNPyrr]) AHA-IL, obtaining lower solvent and energy consumptions than with other ILs [34] and minimizing operating and investment costs of CO₂ capture process in biomethane purification respect to conventional technology [35]. Although these previous results revealed a great process optimization margin by selecting proper operating conditions to improve the cyclic absorption capacity, lower energy consumption is required [35].

In this work, a biogas upgrading process based on chemical capture by [P₂₂₂₈][CNPyrr] AHA-IL is developed to reach biomethane with a 97% purity from a synthetic raw biogas with CH₄ (60% in mol) and CO₂ (40 % mol), by means of COSMO-based/Aspen methodology [46], which has been successfully applied to design IL-based process to capture biogas impurities such as CO₂ [34,41], H₂S [36] and siloxanes [8]. As we noted, this AHA-IL is selected based on its outstanding CO₂ capture process performance compared to other ILs in previous works [34,35]. A process configuration based on an absorption column and an air stripping column to regenerate the IL is proposed. A flow of 300 Nm³/h was used, which is equivalent to a small-medium size scale plant, the most common case in the European union according to the European Biogas Association [12]. A delivery pressure of 6 bar is used, which can be applicable to a small local distribution grid. Two base cases at two different absorber pressures (1 and 6 bar) are evaluated at different working temperatures in the absorber (40–90 °C) and stripper (70–120 °C), in order to improve the process and minimize solvent and energy consumptions. Later, an economic analysis was performed to compare the proposed IL-based CO₂ capture to commercially available technologies. Finally, the best process configuration will be applied in the upgrading of a multicomponent biogas (presenting most common impurities) to evaluate the suitability of AHA-IL biogas upgrading, in terms of chemical and energy consumptions, process costs and biomethane quality standards.

2. Computational details

2.1. Component definition

The complete biogas process was modeled using Aspen Plus v11 commercial simulator using the multiscale COSMO/Aspen methodology [46]. A complete description of the methodology and the information

used to define the components in the simulations are described in detail in previous works [34,35]. As a brief summary, [P₂₂₂₈][CNPyr] and its reaction products were introduced as pseudo-components, using their density, molecular weight and normal boiling point. Quantum chemical structure optimizations in combination with COSMO-RS were used to fully specify COSMO-SAC property method in Aspen Plus introducing σ -profiles (SGPRF1-5) and COSMO volume (CSACVL). The CO₂ chemical absorption was modelled with experimental data, using a 1:1 stoichiometry between the IL and the CO₂ and it was introduced as an equilibrium reaction. Regarding the physical absorption, CO₂, CH₄, N₂ and O₂ were defined as Henry components. The viscosity of the IL is included using their temperature dependance:

$$\mu(cp) = \exp\left(-12.033 + \frac{5364.1}{T(K)}\right) \quad (1)$$

3. Process simulation

The inlet biogas stream used in this work is defined in Table 1. The initial composition was simplified to consider only their two mayor components, CO₂ and CH₄, being other typical impurities present in biogas streams such N₂, H₂S, water vapor or siloxanes not considered in the study.

The equipment configuration used in this study can be found in Fig. 1. First consideration is the compression step, where a delivery pressure of 6 bar is used, which can be applicable to a small local distribution grid. Further compression is not considered in this study as it would be independent of the upgrading process, and it is not usually considered in the technology evaluation. Thereby, two different configurations were evaluated, one in which the compression step up to 6 bar takes place after the absorption (configuration I), and the other alternative in which the biogas stream is pressurized up to 6 bar before the absorption process (configuration II). Apart from the compression step, the process configuration and specifications are the same in both cases.

In the upgrading process, the biogas stream enters the absorber, where comes into contact with the regenerated IL from the stripping column. The solvent flow is adjusted to achieve a purity of the resulting biomethane of 97%. The exhausted IL leaves the absorption column, and it is heated to the regeneration temperature ($T_{str} \sim 70\text{--}120\text{ }^{\circ}\text{C}$) before entering the stripping column. The maximum regeneration temperature of $120\text{ }^{\circ}\text{C}$ was selected for being considerably lower than the decomposition temperature of the IL ($294\text{ }^{\circ}\text{C}$) to avoid thermal decomposition [32]. In the stripper, the saturated IL is put in contact with an air flow ($300\text{ Nm}^3/\text{h}$) provided by a blower at a total pressure of 1 bar. This reduction in the CO₂ partial pressure provided by the air in combination with the heating achieves the regeneration of the IL. Once the IL regenerated, it is cooled up to the absorption temperature ($T_{abs} \sim 40\text{--}90\text{ }^{\circ}\text{C}$) and it is pumped to the absorption column.

Both absorption and stripper columns are incorporated using the rigorous RADFRAC column model implemented in Aspen Plus, with the Rate-based mode to account the mass transfer kinetic process of the different species. The column was discretized by 15 stages considering 3 m of packing height and a diameter enough to maintain a fractional capacity of 75%. The structured packing Flexipac 700Y was used in the internals of both columns.

The compression step was modelled as a multistage isentropic compressor with 2 stages and equal pressure compression ratio with an

intercooling stage to $50\text{ }^{\circ}\text{C}$. The mechanical and isentropic efficiency of the compressor used were 0.8 for each stage. Finally, the stripping air (28% O₂ and 72% N₂) is introduced by a blower, which is designed as an isentropic compressor with a ΔP of 0.1 bar.

In order to compare the performance of this proposal with available technologies, the installed equipment cost of this process configuration is calculated using the economic analysis tool included in Aspen Plus process simulator (Aspen APEA), representing the investment required to purchase and installing the process equipment. The mapping and sizing of both columns were done considering them as single diameter packed towers; heater and cooler were defined as shell and tube heat exchangers; the pump was mapped as reciprocating positive displacement plunger pumps, which is the model suited to pump viscous fluids; and finally, the compressor is mapped as a reciprocating compressor.

4. Results

Two working pressure scenarios were considered and evaluated, 1 and 6 bar. For each case, working temperatures on the absorber and the stripper were modified and the IL flow is calculated to maintain a purity of 97% of methane at the absorber outlet. Fig. 2 presents the solvent requirements and specific energy consumptions of the process at 1 bar of working pressure, in the range of $40\text{--}90\text{ }^{\circ}\text{C}$ absorber temperature and $70\text{--}120\text{ }^{\circ}\text{C}$ stripping temperature.

As expected, the IL consumption (Fig. 2A) is reduced when decreasing the absorber temperature, due to the increase on CO₂ absorption capacity. A similar effect is observed when the regeneration temperature is increased, improving the quality of the IL recirculated and, in fact, increasing the process cyclic capacity (defined as the difference of the IL load at the inlet and outlet of the absorber). This combined effect minimizes the solvent requirements to achieve the separation at the limit conditions (T_{abs} : $40\text{ }^{\circ}\text{C}$ T_{str} : $120\text{ }^{\circ}\text{C}$). On the opposite side, reducing the difference between absorber and stripper temperatures rapidly increases the amount of IL required, caused by the combined effect of a minor absorption capacity due to the increasing on the absorption temperature and an incomplete regeneration in the stripper column. In fact, as can be seen in Fig. 2A, there is an operating range when the difference in the operating temperatures is lower than $35\text{ }^{\circ}\text{C}$ that it is impossible to achieve the required purity with the proposed configuration. In the case of the specific energy consumption, when the absorber temperature increases, the specific energy consumption increases. Although ΔT in the heat exchangers is reduced when working at higher absorption temperatures, the increase of the IL flow required to achieve the desired purity imposes a high energy demand. In the case of stripping temperature, increasing T_{str} value decreases the energy required, related to the lower IL needed from a more complete regeneration. However, after reaching $90\text{--}100\text{ }^{\circ}\text{C}$ the reduction in the IL flow does not compensate the increment in the working temperatures, reaching a minimum energy duty in this interval. By combining both effects Fig. 2B shows an minimum value around T_{abs} : $50\text{ }^{\circ}\text{C}$ and T_{str} : $95\text{ }^{\circ}\text{C}$. The detailed contributions to the energy demands are in Table 2.

At the minimum energy case, 90% of the energy is required for IL stream heating and cooling, being the other contributions -such as compression and pumping- almost constant at the different temperatures studied. There is also another synergic effect that leads to this minimum, due to the exothermic reaction between CO₂ and the IL. The solvent increases the temperature (almost $20\text{ }^{\circ}\text{C}$) reducing the heating needed. A major IL flow dissipate this heat, reducing the heating in the absorption column. A similar effect occurs in the stripping column regarding the cooling effect of the air stream. Finally, in the composition of the resulting biomethane it appears some traces of O₂ and N₂ from the stripping stream but below specifications (1000 ppm for grid injection from Spanish quality standards [47]). These values can be lessened, if necessary, by increasing the regeneration temperature involving an increase in the specific energy consumption.

Table 1

Properties of biogas inlet stream.

Temperature	35 °C
Pressure	1 bar
Flow	300 Nm ³ /h
Composition	
	x_{CO_2}
	x_{CH_4}
	0.4
	0.6

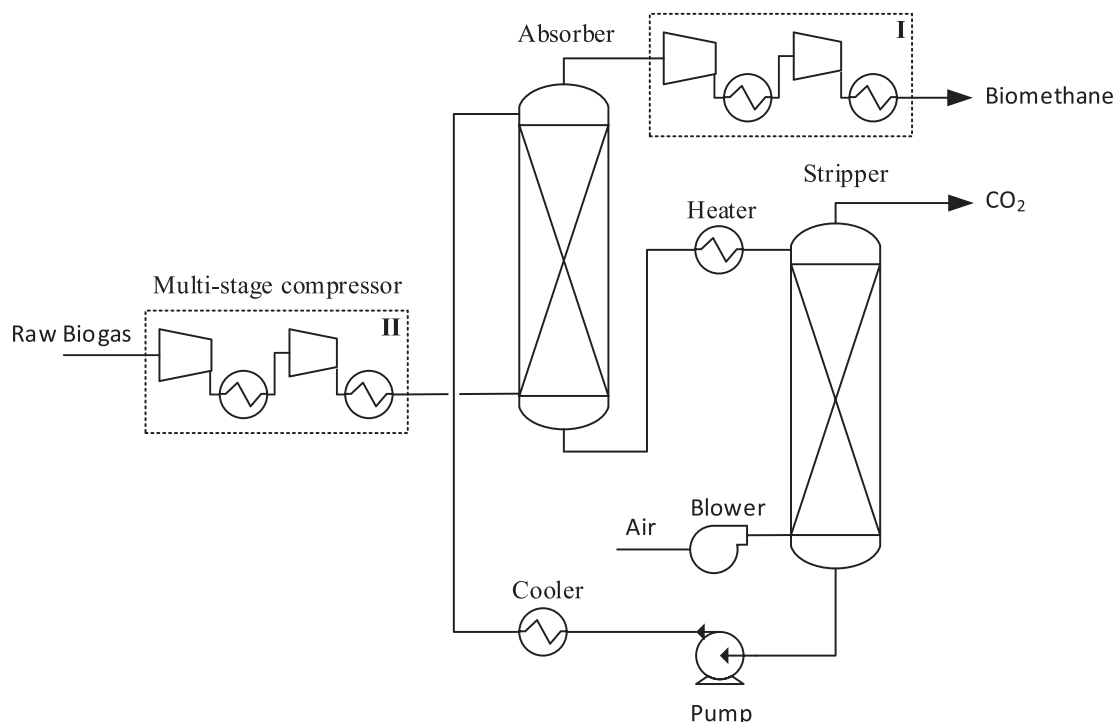


Fig. 1. Process diagram of the upgrading system based on ILs at 1 bar (compressor at I) and 6 bar (compressor at II) of operating absorption pressure.

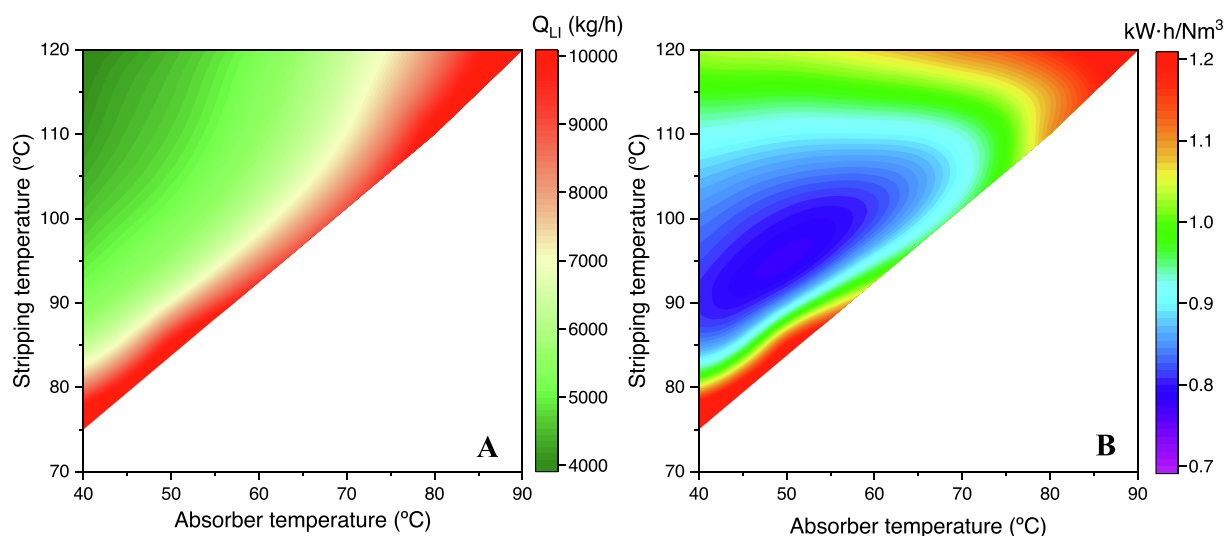


Fig. 2. IL mass flow required (A) and specific energy consumptions (B) at absorber pressure of 1 bar to obtain a methane purity of 97%.

Once the process has been evaluated at 1 bar of total pressure, the flow diagram is modified by moving the compression step before the absorption, to increase the operating pressure up to 6 bar. The results of this configuration are shown in Fig. 3A and Fig. 3B.

The IL requirements are almost half of those needed at 1 bar, following a similar trend with the operation temperatures. This reduction is explained by the combined effect of a greater absorption capacity at higher pressures together with a better regeneration caused by the decompression at the stripper column. The reduced IL flow also produces a more intense heating effect related to the exothermicity of the reaction. In Fig. 3A there is marked a black dotted zone where the IL leaving the absorber is at higher temperature than the regeneration temperature due to the exothermic $\text{CO}_2 + \text{IL}$ reaction. This zone implies cooling the IL before entering the stripper, which has no sense from the process point of view, so these points are out of the analysis. The energy

consumption of this process configuration at 6 bar follows a totally different pattern than at 1 bar, being the energy minimum a zone that crosses the entire operation range near the operating limit marked by the dotted zone. For each regeneration temperature, the minima correspond to a process configuration where no cooling is issued after the regeneration step, so it is used an absorption temperature equal to the outlet of $T_{\text{Abs}} = T_{\text{Str}}^{\text{Out}}$. This particular configuration is marked in Fig. 3B as a red line. A detail of this region as a function of the stripping temperature is in Fig. 4.

The specific energy consumption of the different points is in a very narrow range (0.18–0.23 kWh/Nm³), so the selection criterium will be the IL consumption. An minimum in the IL consumption can be clearly observed at $T_{\text{Str}} = 100$ °C. In this case, the heater duty is the only component of the energy balance varying, considering pumping power

Table 2

Process conditions and energy consumption for the process configurations selected.

Pressure		1 bar	6 bar
Q_{IL} (kg/h)		5909	3666
T (°C)	In Abs	50.0	68.8
	Out Abs	69.4	97.2
	In Str	95.0	100.0
	Out Str	74.4	68.0
Biomethane	CH ₄	97.0%	97.0%
	CO ₂	2.8%	2.9%
	N ₂	840 ppm	533 ppm
	O ₂	726 ppm	487 ppm
Column Diameter (m)			
Absorber		0.46	0.34
Stripper		0.51	0.48
Specific energy consumption (kWh/Nm ³)			
Heating	Heater	0.349	0.025
	Cooler	0.317	–
Cooling	Compressor	0.051	0.074
	Compressor	0.063	0.101
Electric	Blower	0.005	0.005
	Pump	0.00017	0.00632
Total		0.785	0.210

depreciable (Table 2). When increasing the stripping temperature, the fraction of the IL regenerated increases reducing the actual flow required to meet purity specifications, after reaching 100 °C further increases in the regeneration temperature makes the resulting regenerated IL entering the absorption column at very high temperature (95 °C in the case of T_{str} : 120 °C) reducing the absorption capacity and increasing the IL requirements. Given these reasons, the point at minimum flow is selected for comparison purposes with the case at 1 bar. A more detailed description of this point is in Table 2. As can be seen, only an adjustment of the temperature of a few degrees is needed before the stripping operation. This along with the exothermic nature of the process is enough to maintain a ΔT of 30 °C in the process and to achieve a good regeneration of the solvent. Compared to the 1 bar process, the energetic requirements are drastically reduced (from 0.785 to 0.211 kWh/Nm³), considering that there is no cooling, and the heating is only required to maintain the temperature, being an autothermic process, considering almost no external thermal energy is required to maintain the temperature difference between the absorption and the stripping columns. In this case, the main contribution is the power consumption in

the compressor, that is increased in almost 40% since the pressurized raw biogas presents a larger volumetric flow than the purified biomethane stream. A comparative with traditional technologies for biogas upgrading can be seen in Table 3, in terms of specific energy consumption, considering both thermal and electric contributions.

The energy consumption in the case of 1 bar is very similar to the case of chemical absorption with amines, in which the principal expense is the thermal requirements of the solvent regeneration. In the case of the process at 6 bar, the energy consumption is lower than the reported values for other technologies (Table 3), as the only requirement is the raw biogas pressurization and we are operating at lower pressures than the other technologies like water scrubbing or PSA. With respect to the thermal energy consumption of this case, most of them comes from the intercooling step in the compressor train, which is not considered in the other technologies description as it is usually a very small contribution.

In order to compare the potential cost of this proposal, Fig. 5 represents the installed process equipment cost of the two configurations evaluated as calculated by Aspen plus economic analyzer. As can be seen, the principal equipment cost in the process comes from the compressor, representing almost the half of the total, which is in the same order of magnitude when comparing the cost distribution of other upgrading technologies that require a compression step [62]. The higher-pressure option is the most economic approach, since the reduction in the IL flow needed implies more compact packed towers and heater, and also the elimination of the cooling step; even when operating at 6 bar in the absorber incurs in a more expensive compression cost. Current proposal improves the previous CO₂ capture process for biogas system by chemical absorption using ILs with close gas stream feed (590 Nm³/h, 38% mol CO₂) [34,35], since remarkably decreasing specific energy consumption (from 0.44 to 0.18 kWh/Nm³) but maintaining the process equipment cost (from 0.91 to 0.99 M€).

Finally, Table 3 compares current results with commercially available technologies for biogas upgrading in terms of specific investment costs, calculated as the equipment installed cost divided by the biogas stream. This is only a brief estimation of the proposed IL-based technology, but seems to be in the same order of magnitude that the cheapest biogas upgrading technology available, such as water scrubbing. It is needed to note that these costs do not include IL pricing, which nowadays is a difficult parameter to estimate as only laboratory scale prices are available. As rough estimation, previous studies, a scaled production price of 50 \$/kg for the IL shows an increase of around 10% in the inversion cost for a biogas plant of similar size [35].

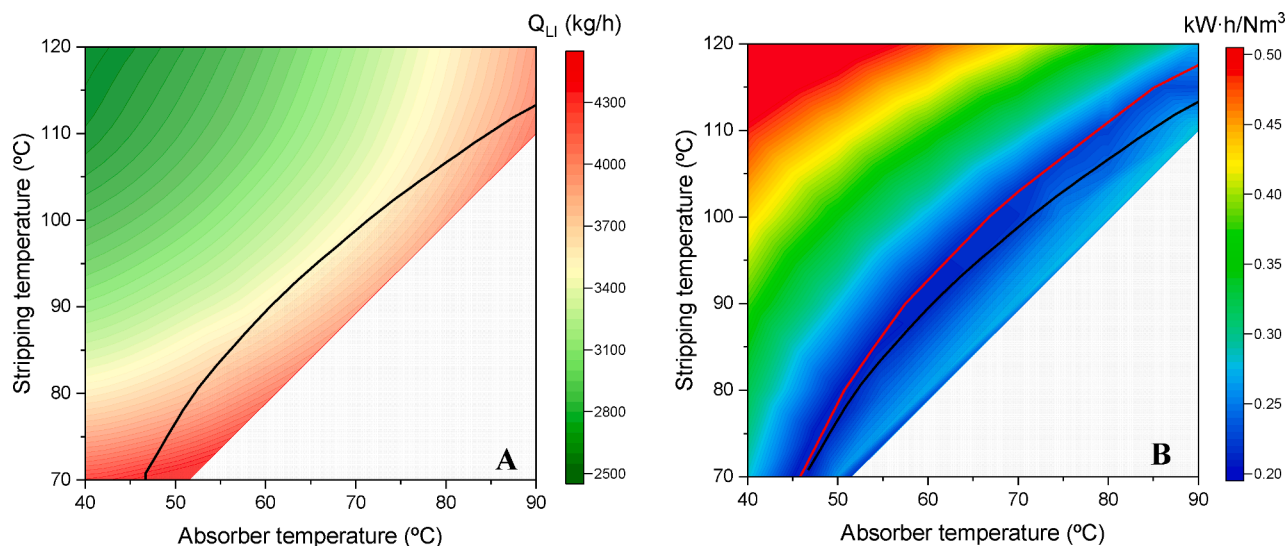


Fig. 3. IL mass flow required (A) and specific energy consumptions (B) at absorber pressure of 6 bar and a methane purity of 97%. Dotted zone corresponds to operating limits ($T_{Abs}^{Out} > T_{Str}$). Red line in B are the cases where no cooling after regeneration is provided.

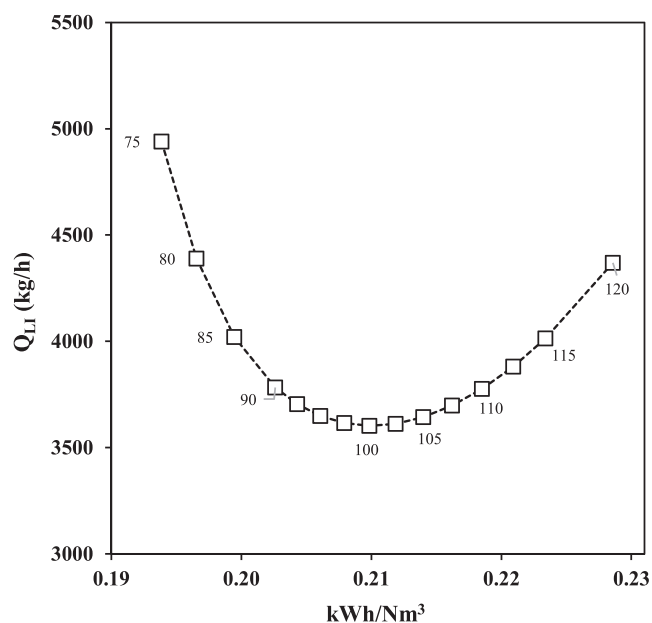


Fig. 4. IL mass flow required and specific energy consumptions at absorber pressure of 6 bar considering no cooling after stripping. Numbers in graph correspond to stripper inlet temperatures in °C.

Table 3

Characteristic parameters of the available upgrading technologies and the IL based technologies considered in this study.

Technology	Electric energy ² kWh/Nm ³	Thermal energy ² kWh/Nm ³	Equipment Investment cost ¹ €/ (Nm ³ /h)
Water scrubbing	0.25–0.30	–	3300
Amine scrubbing	0.10–0.15	0.40–0.75	4200
PSA	0.20–0.30	–	3800
Membrane	0.30	–	3400
IL at 1 bar	0.10	0.72	3545
IL at 6 bar	0.11	0.07	3271

¹ Results from reference [2] and extrapolated to a plant of 300 Nm³/h of raw biogas.

² Averaged results from references [16,48–61].

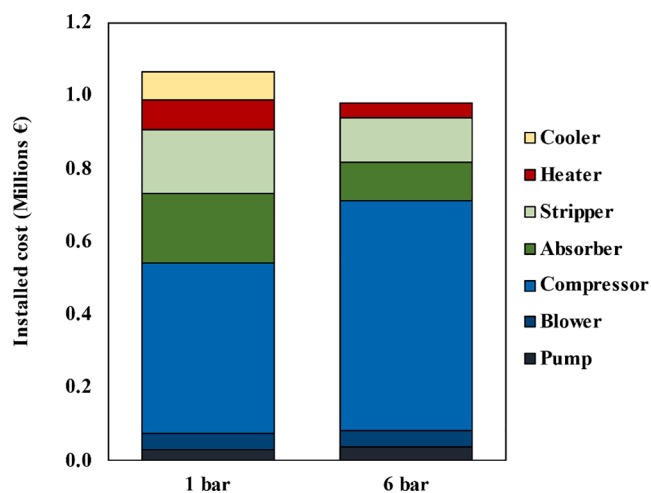


Fig. 5. Installed equipment cost of the proposed biogas upgrading process at 6 bar and 1 bar.

In order to test the effect of the biogas impurities in the proposed IL-based upgrading process, a realistic multicomponent biogas stream is treated in the configuration at 6 bar. The used inlet biogas stream (Table 4) is saturated in water (2%) and contains H₂S and siloxanes in a typical concentration equivalent to a biogas originated in waste water treatment processes [63].

The characteristics of the produced biomethane and process consumptions are collected in Table 4. The biomethane purity is maintained at the expense of slightly increase on the IL consumption (3%). Remarkably, the rest of the biogas impurities are efficiently retained (>90%) by AHA-IL, to obtain purities below legal limitations (1 mg_{Si}/Nm³ and 15 ppm of H₂S) according to Spanish regulation for gas grid injection [64,65]. The IL also captures almost all the water present in the biogas stream, increasing the circulating IL water content to a 2.5%wt. The high affinity of the IL for the impurities implies some degree of accumulation in the circulating IL, especially for H₂S where it accumulates up to 800 ppm at this inlet concentrations, so it would be recommendable to make a pretreatment to reduce the inlet concentration in the case of high sulfur biogas streams, as it is the usual case in almost all available upgrading technologies. The energy consumption in the process remains nearly constant, since the only terms increasing are minority contributions to the total energy consumption, as the heating duty (1% increment) and the pumping (5% increment).

5. Conclusions

The complete CO₂ capture process for biogas upgrading based on chemical absorption with [P₂₂₂₈][CNPyr] ionic liquid was modeled and improved to minimize solvent and energy consumptions by means of COSMO-based/Aspen methodology. Temperatures of absorption (40–90 °C) and stripping (70–120 °C) columns were screened to reach a biomethane product with 97 % purity from upgrading an industrial flow (300 Nm³/h) of raw biogas with 40 % (mol) of CH₄ and 60% of CO₂ in two scenarios to deliver biomethane at 6 bar: pressurizing biogas before feeding to absorber and comprising biomethane once left the absorber. It was found that using an absorber operating pressure of 6 bar allows to efficiently use the exothermic nature of the reaction to cover the thermal energy requirements of the process, reaching a nearly autothermic CO₂ capture process, with specific energy consumption (0.211 kWh/Nm³) lower than all reported data of conventional technologies, and, correspondingly, competitive process cost (but without considering IL price).

Finally, the improved process was successfully applied in the upgrading of an industrial biogas stream, demonstrating efficient

Table 4

Process specifications and energy consumption for the biogas multicomponent stream.

Composition	Biogas	Biomethane
CH ₄	60%	97.0%
CO ₂	38%	2.9%
N ₂	–	533 ppm
O ₂	–	487 ppm
H ₂ O	2%	892 ppm
H ₂ S	100 ppm	7 ppm
Hexamethylcyclotrisiloxane (D3)	10 ppb	0.4 ppb
Octamethylcyclotetrasiloxane (D4)	100 ppb	6 ppb
Decamethylcyclopentasiloxane (D5)	1.65 ppm	100 ppb
Total Si (mg/Nm ³)	10.9	0.66
Q _{IL} (kg/h)	3726.6	
Specific energy consumption (kWh/Nm³)		
Heating	Heater	0.025
Cooling	Cooler	–
	Compressor	0.074
Electric	Compressor	0.101
	Blower	0.005
	Pump	0.0066
	Total	0.210

multicomponent capture with high recovery of CO₂, H₂S, H₂O and siloxanes. The biogas upgrading process based on AHA-ILs was found able to produce biomethane with standard of quality and with specific energy consumption and investment cost competitive with conventional technologies. Future work will be conducted to validate the proposed technology by pilot-plant experiments and revising IL selection in terms of more relevant criteria as price, recyclability, and environmental impacts. In addition, detailed cost estimations and life cycle assessment have to be performed in the future to evaluate the sustainability of the proposed IL-based biogas upgrading process.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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