



Review

Emerging green strategies for biogas upgrading through CO₂ capture: From unconventional organic solvents to clathrate and semi-clathrate hydrates

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ABSTRACT

Biogas produced from anaerobic digestion of organic materials is emerging as a renewable energy source. Unfortunately, the large quantities of CO₂ contained in the raw biogas greatly decreases its calorific value, thus efficient CO₂ separation is needed to upgrade biogas to biomethane. Several technologies, based on physical or chemical sorption of CO₂, are already available but they suffer of some drawbacks, primarily related to their negative impact on the environment and/or high energy requirements. Development of alternative green biogas upgrading technologies is therefore needed, and research is growing exponentially in this field. As a consequence, a frequent assessment of the state of the art of these rapidly evolving technologies is required.

This review summarizes the latest advances on emerging strategies for biogas upgrading based on unconventional organic solvents such as ionic liquids and deep eutectic solvents and clathrate/semi clathrate hydrates, for which low cost, ease of operation and environmental sustainability represent attractive advantages over conventional technologies. In particular, the present work is focused on the performance of these CO₂ sorbent systems in terms of CO₂/CH₄ selectivity rather than CO₂ absorption capacity. Indeed, CO₂/CH₄ selectivity is the most important parameter for evaluating the suitability of a sorbent for practical applications, as high selectivity means negligible CH₄ losses. The scientific results published in the last few years have been collected and discussed to serve as a guide for researchers in choosing the optimal technology and operating conditions in the perspective of efficient and environmentally friendly separation of CO₂ from biogas. Ionic liquids and deep eutectic solvents are excellent candidates for biogas upgrading, especially in the form of hybrid systems, which show the best performance in terms of selectivity. Similarly, biogas upgrading via clathrate hydrates can be considered efficient, environmentally friendly and cost-effective. However, some drawbacks still need to be addressed.

1. Introduction

Fossil fuels, including coal, petroleum and natural gas, are the primary source of energy and they account for more than 80 % of the energy demands around the world [1]. Alongside the advantage to be one of the most efficient energy sources, fossil fuels have several adverse effects on the environment and human health. Their combustion is primarily responsible for global warming and climate changes,

contributing to over 75 % of global greenhouse gases (GHG) and 90 % of all carbon dioxide (CO₂) emissions [2]. The devastating effects of climate changes are already visible across the planet: extreme weather events have become more frequent, causing widespread destructions and economic losses; the oceans levels are rising, and fresh and sea water is becoming more acidic; thousands of species are at risk of extinction [3].

In addition to the pollution problems, another challenge that the

Abbreviations: BMIM, 1-butyl-3-methylimidazolium; HMIM, 1-hexyl-3-methylimidazolium; EMIM, 1-ethyl-3-methylimidazolium; P₆₆₆₁₄, trihexyl(tetradecyl) phosphonium; thtdp, trihexyltetradecylphosphonium; Benz, benzimidazolium; BS_{mim}, 1-butylsulfonate-3-methylimidazolium; BS_{mpy}, 1-butylsulfonate pyridine; TMGH, tetramethylguanidinium; TETA, triethylenetetramine; TF₂N, bis(trifluoromethylsulfonyl)imide; BF₄, tetrafluoroborate; PF₆, hexafluorophosphate; dca, dicyanamide; dep, diethylphosphate; phos, bis(2,4,4-trimethylpentyl)phosphinate; Ac, acetate; Tos, *p*-toluene sulfonate; Im, imidazolate; PhO, phenolate; L, lactate; FeCl₄, tetrachloroferrate; CNPyr, 2-cyanopyrrolide; GLY, glycinate; PRO, proline; MET, methionine.

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World is called to face is that, despite energy demand is going to increase by 2 % every year, the reserves of fossil fuels are limited, and they are depleting [4]. In this scenario, Ukraine war gave rise to an unprecedented, global energy crisis, brutally reminding to the world its dependence on imported fossil fuels, especially natural gas, and the unsustainability of its current energy system. The confluence of these events is highlighting that, to mitigate global warming and allow the world to become independent of energy imports, a policy of incentives for technologies which can lead to the transition from fossil fuel to renewable energies is now imperative and there is no more time to waste.

1.1. Overview of biogas and conventional biogas upgrading technologies

Among the sustainable energy sources, biogas is a promising, green and renewable substitute for natural gas, on which to focus for the future [5]. Indeed, as reported by the IEA-World Energy Outlook 2022 [6] for the Net-Zero Emission 2050 Scenario, the overall share of low emission gases (biogases and hydrogen) will reach over 70 % of total gaseous fuels, from less than 1 % today; according to IRENA report [7], the global biogas supply, which in 2015 represented under 0.5 % of total global energy, is expected to increase tenfold by 2050.

The biogas industry has experienced substantial growth in Europe, with projections indicating further expansion to reach 40.2 million tonnes of oil equivalent (Mtoe) by 2030 [8]. Combined biogas and biomethane production reached 196 TWh or 18.4 bcm of energy in 2021. This amount is equivalent to the total natural gas consumption of Belgium and accounts for 4.5 % of the European Union's gas consumption in the same year. The number of biomethane facilities in Europe experienced a significant rise, going from 483 plants in 2018 to 729 units in 2020, and this number in the coming years is bound to increase [9].

D'Adamo et al. in 2023 described in a very detailed manner all the economic parameters and economic indicators which refer to the production of biogas and biomethane [10]. Authors reported that the cost of biogas production can range from 0.32 to 0.56 €/m³ depending on the substrate used, while the cost of biomethane production can vary significantly, ranging from 0.36 to 2.00 €/m³. These data emphasize how biogas upgrading can add significant value to the biogas produced, as biomethane can be sold at a higher price than raw biogas. At the same

time, the upgrading process also involves additional costs, including capital investment in upgrading equipment and operational costs, which is why the quest for a cost-effective and efficient separation technology remains highly active.

Biogas is a mixture of different gases whose composition depends on the raw material from which it originates. The main components of biogas are methane (CH₄) and carbon dioxide (CO₂), which account for 55–65 % and 35–45 % of the gas mixture, respectively; contaminants including water, nitrogen, oxygen, ammonia, hydrogen sulphide and siloxanes are present in trace amounts [11,12]. The percentage of the two biogas main fractions vary with the type of the source material and the operating conditions of the bioreactor. Biogas is produced via anaerobic digestion of municipal, agricultural and industrial waste, such as sewage sludge [13], crop waste [14], food processing residue [15], wet animal farm manure [16]. Through this natural process, organic carbon is converted to its most reduced (CH₄) and most oxidized forms (CO₂). The enrich-organic by-product of the bacterial fermentation, called digestate, can be used as high-value fertilizer [17], allowing to reduce the production and use of chemical fertilizers, which often have toxic and harmful effects. The anaerobic digestion process is outlined in Fig. 1, also showing its contribution to facilitate the transition to a circular economy.

Among the above-mentioned source of biogas, landfills can be considered as real and efficient biogas producers, due to the continuous supply of solid waste which undergoes to microbial digestion. Soon after its production, if not managed properly, the methane/CO₂-rich biogas will be released from landfill sites. Doka et al. have calculated that 47 % of biogas produced in landfills would be vented to the atmosphere [18]. As the carbon in biogas comes from atmospheric CO₂ fixed by plants that become biomass or are consumed by animals from which organic waste originates, biogas production and combustion, do not release new CO₂ into the atmosphere and can be considered carbon-neutral, thus contributing to maintaining the natural cycle of CO₂ [19].

Instead, the fugitive CH₄ significantly contributes to environmental degradation and climate change. Indeed, CH₄ is more effective than CO₂ at trapping heat in the atmosphere, and its global warming potential is 72 times greater than that of CO₂ over a 20-year time horizon [20]. Therefore, implementing and optimizing technologies for biogas capture and utilization represent an environmentally friendly management strategy not only to produce renewable energy and reduce the

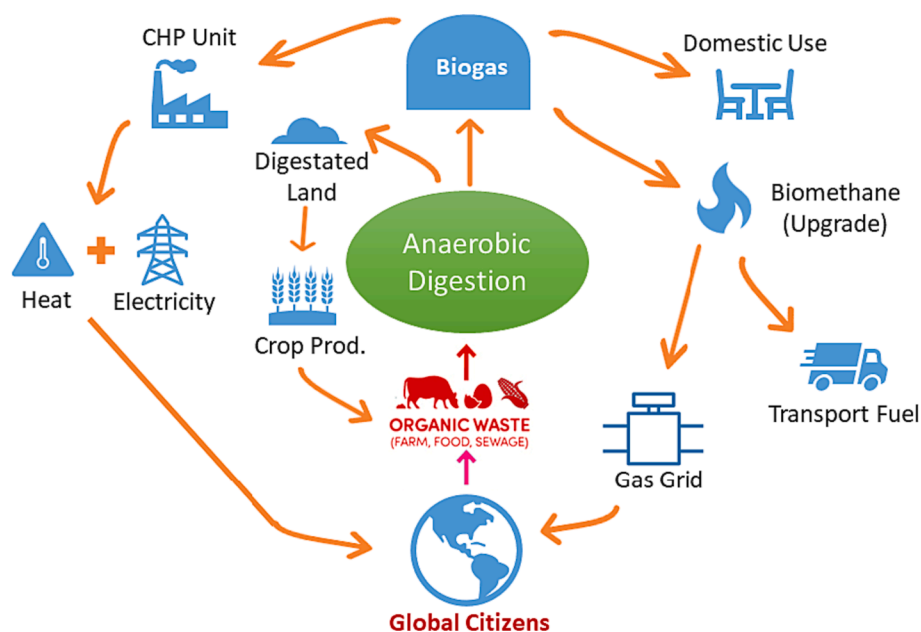


Fig. 1. Organic waste-anaerobic digestion process for a circular economy via biogas upgrading and digestate recycling.

dependence on conventional fuels, but also to sustainably manage the accumulated waste for a circular economy, and reduce emission of methane, preventing its natural release into the atmosphere during production and storage.

Biogas can be burned without further treatment and transformed in electricity (35–40 %) and heat (45–50 %), with an energy loss of about 15 % [21]. However, raw biogas produced by anaerobic digestion is low grade natural gas, due to its low methane content, which does not meet the quality specification of more than 95 % methane required to be used as vehicle fuel or to be injected into gas grids [4]. Indeed, as compared to the CH₄ content of natural gas (typically 87–97 %), raw biogas ranges from the highest value of 80 % for biogas obtained from agricultural waste, to the lowest value of 35 % for biogas obtained from landfill waste [22]. The non-combustible CO₂, which is present in biogas as the main contaminant, is the prime responsible of the low biogas quality, significantly reducing biogas calorific value [23]. On average, the calorific value of natural gas is 35.8 MJ/m³, while that of biogas is 21.5 MJ/m³ [24]. Then, to make biogas suitable as an effective substitute of natural gas, raw biogas must be upgraded by removing CO₂ and other contaminants, in order to increase methane content and enhance the calorific value of the gas. The final product of the upgrading process is biomethane, which is composed of CH₄ (95–99 %) and CO₂ (1–5 %), depending on the utilized upgrade technology [25]. Biomethane can be stored as compressed or liquid gas and directly used as fuel, injected into gas grids and/or used for further fuel synthesis, via gasification [26].

Different technologies have been developed for the upgrading of biogas, based on the different physical or chemical properties of the biogas components, among which the most employed are reported in Fig. 2:

- *Water scrubbing* and *organic physical scrubbing* are based on the different solubility of the biogas components in water [23] or organic solvents, like dimethyl ethers of polyethylene glycol [27], which have higher binding affinity for CO₂ than CH₄;
- *Chemical absorption* is based on the ability of CO₂ to reversibly react with the solvent, primarily solutions of amines which have high affinity towards CO₂ [28,29];
- *Pressure swing adsorption* is based on the selective adsorption of CO₂ over CH₄ onto porous solid materials, like zeolite, activated carbon, polymeric materials [30–32], through physical interactions;
- *Membrane separation* is based on the selective permeability of semi-permeable membranes to biogas components [33,34];
- *Cryogenic separation* is based on the different liquefaction temperatures of the biogas components [35,36].

All these methods suffer from some drawbacks, such as high energy consumption, high material costs and low CO₂ absorption capacity [8], therefore, great efforts have been made to develop environmentally friendly and economically beneficial alternative methods for biogas

upgrading, and to improve the efficiency of the CO₂ separation process.

In recent years there has been a rapid growth of published papers on current available biogas upgrading techniques (Fig. 3), and the increasing number of reviews indicates the need for a frequent evaluation of the state-of-the art of these rapidly evolving technologies. However, only a small percentage of such reviews are addressed to novel options which are emerging as potential methods for CO₂ separation from CH₄ [37–39].

This work aims to cover recent updates on biogas upgrading and to provide an overview focused on the use of unconventional organic solvents, such as ionic liquids (ILs) and deep eutectic solvents (DESs) which are exhibiting a great potential as CO₂ sorbents in the field of sustainable chemistry and engineering, as well as on clathrate hydrate-based gas separation process, the latter being potentially the greenest technology, as only water is released as a major by-product.

Indeed, these methods are receiving great attention from the scientific community due to their good safety performance, environmentally friendly characteristics, and excellent economic profiles.

To the best of our knowledge, no reviews reporting a comparative analysis of IL-, DES-, and clathrate hydrate-based biogas upgrading technologies, mainly based on selectivity data, are yet available in the literature.

2. Ionic liquids

Among the emerging biogas purification technologies via CO₂ capture, ionic liquids (ILs) have recently aroused considerable interest as they showed a great potential in the separation of CO₂ from gas mixtures, with a minimal environmental impact. However, ILs experimentation in biogas upgrading is still in the initial stage as most of the published works are focused on ILs as potential absorbent in CO₂ separation from fuel and flue gases [40–46] while very few related to their application for biogas purification, being mostly process system engineering studies, based on computer-aided process simulation, with the main aim of fine-tuning the operating system, optimizing the process and evaluating its feasibility from a technical and economic point of views [47–49].

ILs are organic molten salts, composed solely of anions and cations with a high degree of asymmetry, which are liquid at temperatures below 100 °C or even below room temperature [50]. A wide variety of cations and anions can be used to prepare ILs but most ILs are composed of nitrogen-containing cations (imidazolium, pyridinium, pyrrolidinium, ammonium) and organic or inorganic anions, such as [Tf₂N], [BF₄], and [PF₆]. Due to their unique physicochemical properties such as low volatility, low flammability, good thermal stability, which allows their use in a wide temperature operating range, and high solvation power towards many organic and inorganic compounds, ILs have been proposed as environmentally benign non-molecular ionic solvents and used as alternative reaction media to conventional organic solvents for

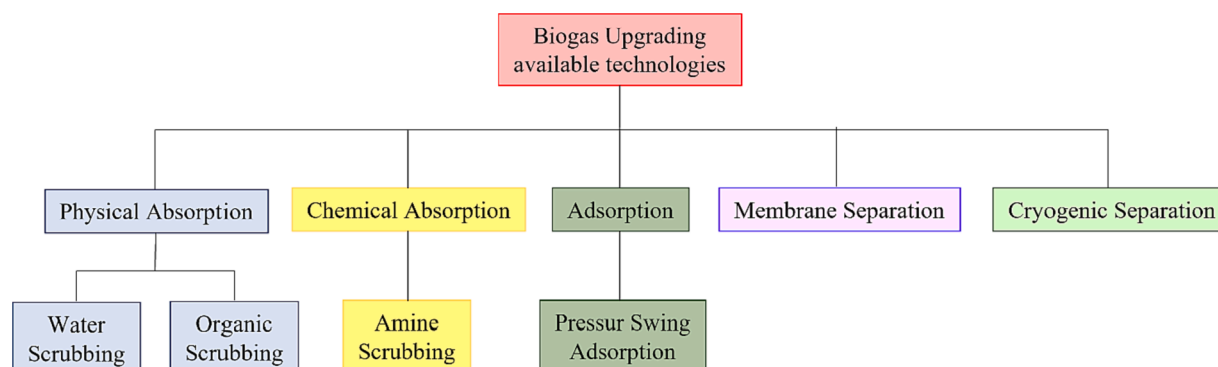


Fig. 2. Schematization of the major available technologies for biogas upgrading.

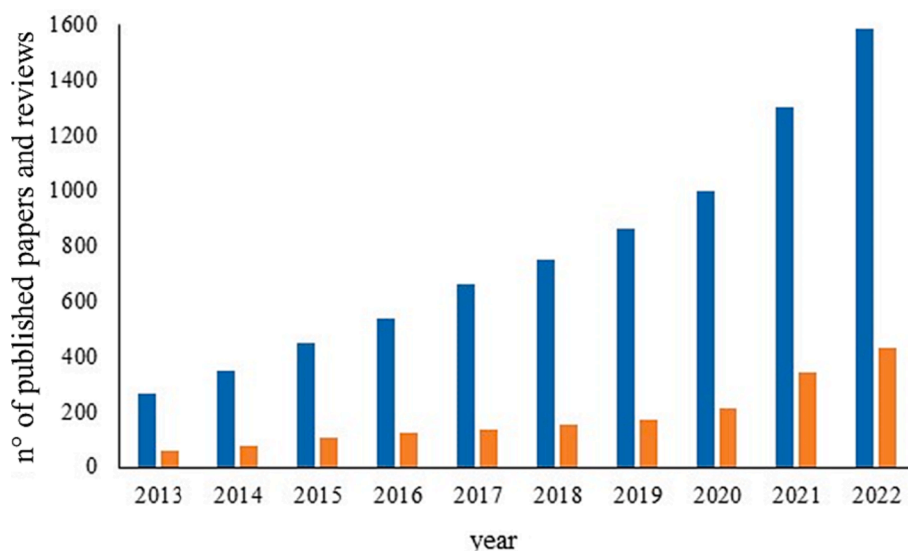


Fig. 3. Number of published papers (blue columns) and reviews (orange columns) on biogas upgrading technologies in the last ten years. Source: Web of Science.

many organic reactions [51,52] and separation processes [53,54]. Physicochemical properties of IL mostly depend on the nature and size of the constituent ions, so they can be fine-tuned simply by combining different cations and/or anions in order to “design” the best IL for a specific application [55–57]. The possibility of appropriately designing anions and cations to increase the CO₂ affinity of ILs appears very attractive to improve the efficiency of a CO₂ separation process.

In 1999, Blanchard et al. have shown that supercritical CO₂ is highly soluble in [BMIM][PF₆], up to 0.75 mol CO₂/mol IL at 298.15 K and 8.30 MPa, while this IL does not dissolve in CO₂ [58]. Since then, significant researching efforts have been driven towards the exploitation of ILs as alternatives to traditional absorbents for CO₂ capture and separation processes. Indeed, ILs appear very attractive as suitable solvents for replacing conventional aqueous amine solutions which, although being the most established chemical absorbents for CO₂ capture due to their high chemical reactivity, good kinetics and low cost [59], have some disadvantages, such as evaporation and thermal degradation, high alkalinity causing equipment corrosion, and high energy cost for regeneration, since 3.5 GJ of energy is required to remove one ton of CO₂ using an aqueous solution of 30 wt% monoethanolamine (MEA) as the sorbent [60,61]. These drawbacks, which limit their utilization on a large scale, can be potentially overcome by ILs as they have negligible vapor pressure, which prevents solvent loss and secondary pollution, and require low energy cost for regeneration, due to the lower CO₂ sorption enthalpy (~10–20 kJ mol⁻¹), as compared to amine solutions [62,63]. Energy demands for simulated CO₂ capture in [BMIM][BF₄] and [BMIM][PF₆] have been calculated to be 26.7 % and 24.8 % lower than that calculated when using MEA as the sorbent [64]. Similarly, in a COSMO-RS simulated [BMIM][TF₂N]-based decarburization of shale gas, single-stage and multistage flash processes show 42.8 % and 66.04 % reduction in energy consumption, respectively, as compared with the methyldiethanolamine (MDEA) process [65].

2.1. Ionic liquids as CO₂ sorbents

CO₂ capture by ILs can occur via physisorption or chemisorption. Physisorption occurs with traditional ILs, through electrostatic, van der Waals and/or hydrogen bonding interactions that CO₂ molecules can establish with IL anions and/or cations [66]. Computational studies, carried out to understand the factors governing the high solubility of CO₂ in ILs, have suggested that CO₂ molecules occupy the free space in the IL three-dimensional network [67,68] and a lower cation–anion interaction corresponds to a higher CO₂ solubility which increases with

the gas pressure until no further free space is available to accommodate CO₂ molecules, reaching a plateau level [69]. The solubility of CO₂ in the ILs depends on the nature of the IL ions, with the anion playing a primary role [62,68]. Recently, 400 ILs composed of 20 cations and 20 anions were screened by COSMO-RS model at different temperatures and pressures, and the results showed that the interaction between biogas and anion, almost determined by hydrogen bonding interaction, was larger than the interaction between biogas and cation, determined by weak hydrogen bonding and van der Waals interaction [70]. For ILs with the same cation, the presence of CO₂-philic groups such as fluorine groups on the anion increases the affinity of IL for CO₂, with a trend that follows the order [TF₂N] > [PF₆] > [BF₄] > [dca], and the longer the fluoroalkyl chain in the anion, the higher the CO₂ solubility [71,72]. For ILs with the same anion, the presence of long alkyl chains, especially if fluorinated, and the presence of the acidic hydrogen at C2 position on the imidazolium ring, which exhibit affinity to CO₂ and does not exhibit any affinity to CH₄, slightly improve CO₂ capture [63,73]. However, CO₂ physisorption capacity of conventional ILs requires elevated pressures which would hardly allow them to compete with traditional absorbents. Indeed, the molar fraction of absorbed CO₂ at atmospheric pressure and room temperature is only 0.035 [74].

A more efficient absorption of CO₂ could be reached under low-pressure through the functionalization of IL anion and/or cation with groups which can chemically react with CO₂, forming carbamate or carbonate [75–79]. Task-specific ILs, such as carboxyl-based ILs [80,81], amino-based ILs [82,83], amino acid-based ILs [84,85], ether-based ILs [86] were designed and developed to enhance CO₂ absorption performance. A comprehensive review on functionalized ILs for CO₂ capture has been recently published by Zhang et al [87].

Novel superbase-derived task-specific ionic liquids (STSILs), formed by a phosphonium ion as the cation and a deprotonated malononitrile moiety ([MN]) as the anion, show high CO₂ uptake capacity (0.84 mol mol⁻¹ at P = 0.1 MPa and T = 298 K) via carboxylic acid formation, favoured by the extended conjugation across the sp² carbon, the carboxylic group, and the nitrile groups [88].

Despite the undeniable advantage of tuning ILs to efficiently chemisorb CO₂, ILs still have some disadvantages which preclude their use at an industrial level, such as high purchase cost and high viscosity which significantly affects mass transfer and CO₂ absorption rates.

To overcome the limitation of the high viscosity and low mass transfer rate for separation processes, aqueous amines have been added into ILs. Xiao et al. have shown that the addition of 30 wt% MDEA to [BMIM][BF₄] reduced the viscosity of the IL from 101.2 cP to 49.5 cP at

298 K and the maximum loading of CO₂ was increased more than 2.5 times, from 0.0168 to 0.0526 g_{CO2}/g_{sorbent} [89]. A higher CO₂ loading was observed by adding MEA instead of MDEA (0.1198 g_{CO2}/g_{sorbent}) as chemical reaction happens between the primary amine and CO₂ to form carbamate. Anyway, the addition of both amines improves the CO₂ absorption efficiency as compared to the pure ionic liquids.

Recently, Orhan showed that the combination of 20 wt% MEA with different ILs in 1-hexanol increases the CO₂ absorption capacity in comparison with MEA alone [90]. According to other studies, CO₂ loading capacity depends mainly on the type of the IL anion rather than cation, with the acetate-based IL and BMIM as the cation showing the highest CO₂ uptake of 0.89 mol_{CO2}/mol_{IL}, followed by the CO₂-philic fluorinated Tf₂N anion (0.77 mol_{CO2}/mol_{IL}) and the hydrophilic Cl anion (0.52 mol_{CO2}/mol_{IL}). For the same anion, changing the cation does not lead to significant differences in CO₂ loading capacity.

Hybrid systems have recently been developed, such as membranes with supported ionic liquids [91], poly(ionic liquid)s membranes [92] and encapsulated ILs [93], which enhance the gas-liquid contact area and reduce the viscosity, increasing CO₂ absorption rate and capacity.

2.2. Ionic liquids in biogas upgrading

The solubility of CH₄ in ILs is lower than that of CO₂, suggesting that ILs could be applied as sorbents for separating CH₄ from CO₂, in biogas – and other gas mixtures – upgrading processes [94]. However, in the perspective of application in biogas upgrading and, in general, in gas separation, a good ability of the sorbent to solubilize CO₂ is not enough, as these processes involve gas mixtures, thus good selectivity for the different gas components is also a vital factor, especially in the case of physical absorption. In most of the published works, the CO₂/CH₄ selectivity is not determined experimentally from real gas mixtures but it is calculated from the solubilities of the pure gases, at a certain temperature and pressure [95–97]. Ramdin et al. have provided a comprehensive list of ideal CO₂/CH₄ selectivities calculated at 313.15 K for a large number of ionic liquids [95]. The CO₂/CH₄ selectivity values for all the ILs, listed in ascending order of molecular weight, are reported in Fig. 4, which clearly show that, apart from a few cases, ideal selectivity decreases as IL molecular weight increases, contrary to what happens for CO₂ solubility. Authors explained the observed results in terms of the increase of CH₄ solubility as the number or length of IL alkyl substituents increased.

However, ideal selectivity should not be taken as a strict measure of

real selectivity (i.e., the selectivity of CO₂ in the presence of CH₄ in the ternary mixture CO₂-CH₄-IL) as it does not consider the effects of interaction and competition between different gases when both are simultaneously dissolved in the same IL. For this reason, it is unlikely that mixed gas solubilities can be predicted from pure gas solubilities with a high degree of accuracy, especially when gas solubility is high, and the solution does not behave ideally. Hert et al. have shown that the presence of CO₂ affects the solubility of lower solubility gases in [HMIM][Tf₂N]. Indeed, in the ternary system CO₂-CH₄-[HMIM][Tf₂N], the CH₄ solubility increases remarkably at all pressures, while the solubility of CO₂ decreases, compared to the pure gas solubility [98]. The authors suggested that CO₂, which strongly interacts with the anion component of IL, increases the solubility of CH₄ through dispersion forces, while CH₄ reduces the solubility of CO₂ by occupying some of the sites around the anion.

García-Gutiérrez et al. have simulated biogas upgrading processes up to a target biomethane of 95 mol% CH₄, by [EMIM][Tf₂N], [HMIM][Tf₂N] and [P₆₆₆₁₄][Tf₂N], as physical sorbents in a pressure-swing regenerative absorption process [99]. They found that [EMIM][Tf₂N] produced more biomethane (1522 kg/h) than [HMIM][Tf₂N] and [P₆₆₆₁₄][Tf₂N] (1455 kg/h and 1264 kg/h, respectively) with the lowest production cost of 9.18 \$ per GJ of produced biomethane, despite the fact that [EMIM][Tf₂N] is the IL with the lowest CO₂ absorption capacity. These results confirm that solubility values of the pure gases in ILs are not reliable proxies of selectivity, but other thermophysical parameters, as well as the effect of the simultaneous presence of different gases in the mixture, should also be taken into consideration. Unfortunately, experimental solubility measurements are much more difficult to perform for mixed gases than for pure gases and are extremely scarce in the literature. Nonetheless, these data are necessary to evaluate real selectivity so further experimental and/or computational studies need to be performed to fully understand the behaviour of gases in mixed gas systems. Ramdin et al. have measured the solubility of gas mixtures containing CO₂ and CH₄ in [BMIM][Tf₂N], [EMIM][dep], [thtdp][dca], and [thtdp][phos] and found that they were comparable with those of conventional physical sorbents Selexol, Purisol and Rectisol [100].

Recently, the CO₂/CH₄ selectivity was determined experimentally in pure and binary mixtures of [BMIM][Ac] and [BMIM][BF₄] for three CO₂/CH₄ gas mixtures with different compositions, i.e., 75/25, 50/50 and 25/75 mol% [101], at different temperatures and pressures, and comparisons between real selectivities (S) and ideal selectivities (Sⁱ) were carried out. Interestingly, of the two tested ILs, [BMIM][Ac]

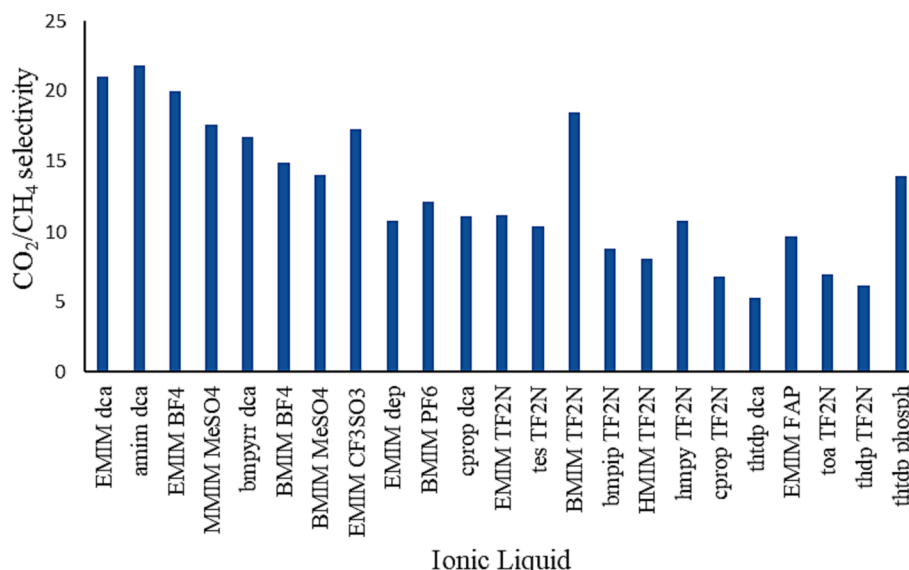


Fig. 4. Ideal CO₂/CH₄ selectivity values obtained at T = 313.15 K in ILs listed in ascending order of molecular weight. Data extracted from ref. 97.

chemically absorbs CO₂, while [BMIM][BF₄] acts as a physical sorbent [102]. [BMIM][Ac] is more efficient than [BMIM][BF₄] in absorbing both CO₂ and CH₄, at low pressure, where chemical absorption is dominant, whereas the CO₂/CH₄ selectivity in [BMIM][BF₄] increases at medium and high pressures, at which physical absorption prevails (Fig. 5).

The highest selectivity value of 23.89 has been obtained at T = 298.15 K and P = 0.108 MPa in 25 wt% [BMIM][Ac] + 75 wt% [BMIM][BF₄] mixture. The comparison between the real and ideal selectivity ($S < S^I$) shows, once again, that the real system deviates from the ideal one, due to the competition between the gases, when they are simultaneously present in a mixture.

In the last two years, research on optimization of IL-based systems for biogas upgrading has grown rapidly, with the aim to solve the major drawback of ILs, i.e., their high viscosity, which hinders CO₂ mass transfer and strongly limits ILs application at industrial scale. Hybrid solvents have been designed by combining ILs with physical absorbents, such as propylene carbonate, that efficiently moderate IL's viscosity [103], or chemically absorbents such as aqueous amines [104], taking advantage of amine and IL synergistic effect, besides the reduction of solvent viscosity. The simulations of biogas upgrading showed the potential of these blended systems in improving process performance in terms of CO₂ solubility, purity of biomethane and energy requirements.

However, innovative approaches, based on immobilization of ILs onto the surface of polymeric membranes, encapsulation into nanoparticles or sol-gel materials, impregnation into Metal Organic Frameworks, seem to lead to the best performance in biogas upgrading.

Most recent results obtained in the application of these hybrid systems in the separation of CO₂/CH₄ mixtures will be discussed in the next section.

2.3. Supported IL membranes for CO₂/CH₄ separation

Several types of hybrid IL membrane have been developed in the last years: supported IL membranes (SILMs), IL polymeric membranes (ILPMs), and IL mixed matrix membranes (ILMMMs) [105]. SILMs are porous supports in which ILs are immobilized into the pores by capillary forces. The feasibility of depositing the IL depends on various parameters such as support geometry, porosity and pore size, mechanical stability of the membrane, hydrophobicity/hydrophilicity as well as the nature of the IL [106]. In these systems, the efficiency of gas separation depends on gas solubility and diffusion.

Potentiality of SILMs in gas separation has been investigated since

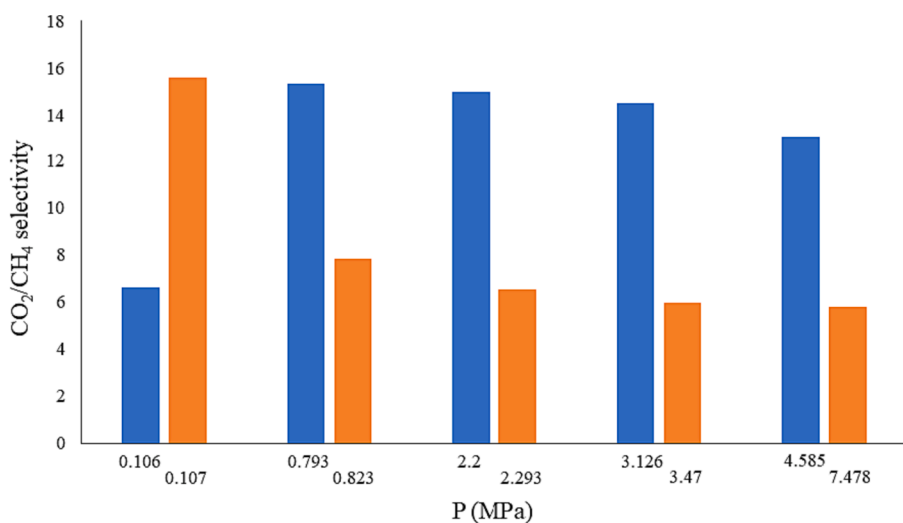


Fig. 5. Trend of CO₂/CH₄ selectivity at T = 298.15 K as a function of P in [BMIM][Ac] (orange columns) and [BMIM][BF₄] (blue columns). Biogas composition was 25 mol% CO₂/ 75 mol% CH₄. Data extracted from ref. 103.

the last decade [107–109] but recently great efforts have been made to face the challenges associated with this technology and improve SILMs efficiency by choosing the best membrane-IL combination. For example, membranes must provide strong capillary forces to allow ILs to be retained into the pores, not being pushed away under high pressures; the pore size of the SILM should be such as to accommodate CO₂ molecules but no other gaseous components of the mixture; the hybrid system must be chemically and thermally stable and reusable [110].

In SILMs, a solution-diffusion mechanism occurs in which the gas molecules are firstly dissolved in the IL, according to their different solubility, and then diffuse from the feed side to the opposite side of the membrane. The ideal selectivity of a membrane for a gas over another is due to the permeability difference of the membrane to the gases and it can be calculated as the ratio of gas permeabilities. The mixed gas selectivity can be calculated from the mole fractions of the gas mixture components in the feed and permeate.

Recently, SILMs have been prepared by immobilizing the IL [Benz][Ac] over a Polyimide P84 support for CO₂/CH₄ separation [111]. The IL was designed as task-specific due to its CO₂-philic properties and its low molar volume, and the ability of the Lewis base acetate anion to interact with the Lewis acid CO₂, improving CO₂ selectivity, as well as the dependency of selectivity on molar volume of ILs, are established [112,113]. High ideal selectivity of 37.95 and real selectivity for a CO₂/CH₄ gas mixture 50/50 wt% of 35.25 has been calculated at 298 K. Interestingly, the Authors found that selectivity depends on solubility rather than diffusion and that solubility/selectivity are inversely correlated to temperature due to the decrease of viscosity which allows more diffusion of gases, and to the increase in free volume, which enhances CH₄ permeability.

Better performances were observed with SILMs obtained from protic ILs immobilized on hydrophobic polyvinylidene difluoride. Indeed, SILMs with a hydrophobic support are more stable than those with hydrophilic ones [114]. Protic, environmentally friendly ILs, based on imidazolium and pyridinium cations with sulfonic group on lateral alkyl

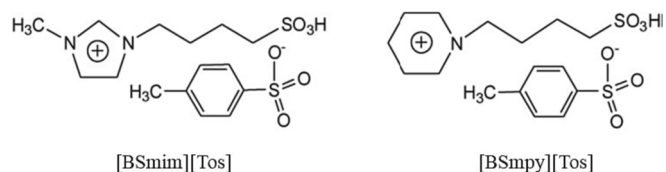


Fig. 6. Structures of tailored ILs in SILMs of ref 117.

chain, and p-toluene sulphonate anions (Fig. 6), were designed and synthesized to enhance their affinity for CO₂ through the presence of sulfo groups, which can lead to strong Lewis acid-base interaction [115].

At 298 K and 0.5 MPa, ideal CO₂/CH₄ selectivities for pure gas of 47.5 and 40.71 were calculated in [BSmim][Tos] and [BSmpy][Tos], respectively, while actual CO₂/CH₄ selectivities for mixed gas 50/50 vol % were slightly lower (about 46 and 38 for the two ILs, respectively) due to the competition between CH₄ and CO₂ for permeation and diffusion through the membrane.

Very recently, Patil et al. have tested a [BMIM][Ac] supported hydrophilic Polyether Block amide (Pebax-1657) membrane in CO₂/CH₄ separation process [116]. The maximum CO₂/CH₄ selectivity value of 9.6, obtained at transmembrane pressure = 0.25 MPa, T = 308.15 K and 20 % IL, is a modest value, although an increase in mixed gas selectivity of 78 % was observed for IL membrane compared to neat Pebax membrane, the latter showing a CO₂/CH₄ selectivity value = 5.4. Moreover, it is much lower than the CO₂/CH₄ selectivity (~96.9) obtained by Akhmetshina et al., which used the same task-specific IL embedded in hydrophobic tetrafluoroethylene vinylidene fluoride (MMFK-1) composite membrane [117]. Modest results in terms of mixed CO₂/CH₄ selectivity have been obtained also with [TMGH][Im]/Pebax and [TMGH][PhO]/Pebax blended membranes [118].

2.4. Nanoconfined IL-2D membranes

An upgrade of the SILM technology is represented by novel high-performance IL-membranes, developed by nano-confining ILs in two-dimensional (2D) nanochannels of 2D materials, which have the advantage of being ultrathin and, therefore, having minimum transport resistance, good long-term stability, and resistance against the leakage of ILs suffered by SILMs from conventional microporous supports, under high pressure. Many 2D materials have been explored as potential supports for nano-confined ILs, such as graphene oxide [119–121], mica nanosheets [122], graphitized carbon nitride [123], hexagonal boron nitride [124], molybdenum disulfide [125]. CO₂/CH₄ selectivity is low for unloaded 2D laminated membranes because gas molecules can pass through the interlayer spaces according to the Knudsen diffusion mechanism, which mainly depends on the kinetic diameter and molecular weight of the gases [126]. By adding IL, which has high CO₂ affinity, selectivity increases as it fills nanochannel and repairs membrane defects thus improving system stability and causing the gas to pass through the IL according to the solution-diffusion mechanism, for which gas molecules firstly dissolve into IL and then diffuses through the membrane. Nanoconfinement causes the stratification of IL cations and anions, and the layered anions allow a fast and selective CO₂ transport. Moreover, for negatively charged 2D materials, the electrostatic interaction with IL cations causes them to move towards the nanosheet wall, increasing the available free volume for CO₂ molecules and weakening the interaction between IL cations and anions, these latter thus becoming available to interact with CO₂ [119,121,122,124,125].

Interestingly, the best result has been obtained for ultrathin and defect-free laminated GO supported-[EMIM][BF₄] membrane which was fabricated under reduced pressure condition to transform IL into IL vapor, allowing it to penetrate into the nanochannels and repair non-selective defects of the membrane easier than systems in which IL is deposited by impregnation or spin coating process [121]. Indeed, the ultrathin active layer (down to 100 nm) allows a faster and more selective CO₂ transport than conventional SILMs produced by impregnation and spin coating of IL on porous support in which thick layers > 1 μm hinder gas transport and reduce gas permeability. Furthermore, lower quantities of IL are required compared to traditional methods, favouring the economy and eco-sustainability of the process.

2.5. Ionic liquids encaged into metal organic framework

Metal organic frameworks (MOFs) are porous materials which have

recently received widespread attention for gas adsorption. One of the most investigated MOFs for gas separations is zeolitic imidazolate framework-8 (ZIF-8), a subclass of cage-type MOFs which consists of Zn²⁺ ion linked with 2-methylimidazole, forming a 3D structure with large cages of 11.6 Å connected through small apertures of 3.4 Å. In theory, small molecules, like CO₂, can diffuse through the aperture into the cages while larger molecules, like CH₄, should be prohibited from entering the aperture. However, due to the structural flexibility caused by the swinging of the imidazolate linkers [127], also large molecules can be absorbed, leading to a poor CO₂ selectivity of the ZIF-8 membrane. Incorporation of additional molecules in the pores of the materials can enhance the moderate selectivity of ZIF-8 by fine-tuning the effective pore size and ILs, which can act both as cavity occupant and solvent, have attracted great interest in this regard [128–131]. Indeed, the addition of IL reduces the adsorption of the large CH₄ molecules, by preventing the apertures from large swing [132] and, simultaneously, enhances the adsorption of CO₂ molecules due to Coulombic interactions of CO₂ with its constituent ions, especially at low pressure, when the interactions between the adsorbate and composite overweight the negative effect of decreasing the available pore volume for absorption and become the dominant factor in gas uptake performance [133]. The incorporation of [BMIM][TF₂N] into ZIF-8 has shown a synergistic effect between the IL and the nanocages, resulting in an ideal CO₂/CH₄ selectivity of 41 which is promising in the perspective of biogas upgrading [134].

Gas mixture selectivities for 50/50 vol% CO₂/CH₄ have been calculated for IL@ZIF-8 composite materials, by using Ideal Adsorbed Solution Theory (IAST) predictions, from experimentally measured single-component gas adsorption isotherms and normalized by the corresponding value on the pristine ZIF-8 [135]. Four ILs with the same cation and different anions have been tested to determine the effect of electronic environment and anion size on the gas separation performance. As expected, the efficiency in CO₂/CH₄ separation is improved by ILs with a fluorinated anion while anion size has no significant effect.

Very recently, Nie et al. have investigated the CO₂/CH₄ separation performance of [EMIM][Ac]@UiO-66 composite material, where UiO-66 is a zirconium (IV)-carboxylate MOF [136]. IAST-based selectivity was calculated from CO₂ and CH₄ adsorption isotherms and a value of 11.2 was obtained at 298 K and 0.1 MPa.

An exceptionally high IAST-based selectivity has been predicted by Han et al. which used a new type of IL-ZIF-IL composite with an outer shell-interlayer-inner core structure, from [TETA][L] and ZIF-8 [137]. The amino-functionalized [TETA][L] of the outer layer, as well as that confined in the internal pore of the composite, strongly interacts with CO₂ but not with CH₄ molecules, allowing the adsorption and diffusion of only CO₂, thus enhancing selectivity. Predicted IAST-based selectivity at 298 K for a 50/50 CO₂/CH₄ gas mixture, ranges from 260 at 0.1 MPa to 1990 under condition of infinite dilution, which are among the highest values reported in literature for a CO₂/CH₄ gas mixture.

Recently, ionic ultramicroporous metal organic frameworks have been prepared through one-step in-situ assembly process, in which 1-aminoethyl-3-methylimidazolium phenoxylate ILs were directly incorporated onto the frameworks as competitive ligands [138] with high CO₂ affinity are constructed by one-step in-situ coordination strategy for CO₂/CH₄ separation. The obtained composites showed good adsorption selectivity in CO₂/CH₄ mixture.

However, although IL@MOF composite materials have demonstrated their potential application in CO₂ separation from biogas, experimental research in this field is still too new, and further systematic investigations are needed to provide insights on the composite structure-efficiency relationships and to rationally designing the most suitable IL@MOF system with the best performance for biogas upgrading.

MOFs modified by incorporation of ILs have been used as fillers in combination with polymeric membranes in order to obtain defect free three-component mixed matrix membranes (MMMs) and to overcome the trade-off between solubility and selectivity which limits membrane's

performance. Yasmeen et al. have implemented Polysulfone (PSF) membranes by loading RTIL 3-(trimethoxysilyl) propan-1-aminium acetate/ZIF-67 composite as the filler [139]. The obtained three-component MMMs showed an increased pure gas permeability of CO₂ by 228 % and an increased ideal selectivity of 186 % with respect to pristine PSF membrane. Indeed, the highly porous ZIF-67 provides pathways for CO₂ molecules to diffuse and the CO₂-philic RTIL enhances the solubility of CO₂ and acts as a selective barrier which allows CO₂ to pass while retaining CH₄. Thus, the combined effect of RTIL and ZIF-67 particles enhance CO₂ permeability while maintaining high mixed gas selectivity.

However, even though the combination of ILs, MOFs and polymeric membranes in MMMs looks very promising for biogas upgrading, care needs to be taken in selecting the appropriate and compatible components to avoid incomplete filler loading and interfacial voids. Moreover, the synthesis of composites is generally complicated.

Recently, MMMs have been fabricated by loading RTIL/UiO-66

composite in Pebax-1657 membranes [140]. Interestingly, the composite has been obtained via a cheap and easy procedure by combining MOF formation, IL preparation and IL impregnation in one step, thus reducing cost and time requirements. The so-obtained MMMs exhibited greater CO₂/CH₄ selectivity than pure Pebax-1657 membrane.

These studies highlight that IL-based hybrid systems are very promising as future biogas upgrading technologies as they can be easily implemented to obtain high performance in terms of selectivity, eco-sustainability and cost-effectiveness.

2.6. Encapsulated ionic liquids (ENILs)

In recent times, encapsulation of ILs in carbonaceous [141,142] or polymeric [143,144] micro and/or nanocapsules has attracted much attention from the scientific community as a viable alternative to supported IL membranes, with the aim to overcome the mass transfer and kinetic limitations of neat ILs by enhancing the active surface area and

Table 1

Gas separation performance of the most recently published nanoconfined IL-membranes, SILMs, IL@MOF and ENILs. Operating temperatures and pressures are also specified, where available.

nanoconfined IL	2D membrane	Ideal CO ₂ /CH ₄ selectivity	Mixed gas CO ₂ /CH ₄ selectivity	Conditions	Ref
[EMIM][Ac]	gC ₃ N ₄	52.41	48.41	25 °C – 1 bar	[123]
[P ₆₆₆₁₄][FeCl ₄]	GO	76	30	25 °C – 1 bar	[119]
[P ₆₆₆₁₄][FeCl ₄]	BN	38		STP	[124]
[BMIM][BF ₄]	MoS ₂	43.52	19.98	25 °C – 0.6 bar	[125]
[BMIM][BF ₄]	GO	234		50 °C – 1 bar	[121]
[BMIM][BF ₄]	mica	28.6		1 bar	[122]
[EMIM][BF ₄]	GO	53.5	51.4	100 °C – 1 bar	[120]
SILMs	membrane	Ideal CO₂/CH₄ selectivity	Mixed gas CO₂/CH₄ selectivity	Conditions	Ref
[EMIM][BF ₄]	PES	22 ^a	27	30 °C – 2.07 bar	[107]
[EMIM][TF ₂ N]	PES	12.2 ^a	17	30 °C – 2.07 bar	[107]
[HMIM][TF ₂ N]	PES	8.5 ^a	9.9	30 °C – 2.07 bar	[107]
[EMIM][dca]	PVDF	23 ^a	24	30 °C – 2.07 bar	[107]
[Benz][Ac]	Polyimide P84	37.92	35.25	25 °C – 10 bar	[111]
[BSmim][Tos]	PVDF	47.5	46	25 °C – 5 bar	[115]
[BSmpy][Tos]	PVDF	40.71		25 °C – 5 bar	[115]
[BMIM][Ac]	Pebax-1657	9.6		35 °C – 2.5 bar	[116]
[BMIM][Ac]	MFFK-1		96.9		[117]
[BMIM][BF ₄]	MFFK-1		8.7		[117]
[TMGH][Im]	Pebax-2533	8.2		23 °C – 1 bar	[118]
[BMIM][BF ₄]	Pebax-1657	17.67		STP	[153]
IL@MOF		Ideal CO₂/CH₄ selectivity	Mixed gas CO₂/CH₄ selectivity	Conditions	Ref
[BMIM][TF ₂ N]	ZIF-8	41		25 °C	[134]
[EMIM][Ac]	UiO-66	11.4		25 °C – 1 bar	[136]
[TETA][L]	ZIF-8	260		25 °C – 1 bar	[137]
[TETA][L]	ZIF-8	1990		25 °C - infinite dilution	[137]
Mixed Matrix Membrane composite^b	membrane	Ideal CO₂/CH₄ selectivity	Mixed gas CO₂/CH₄ selectivity	Conditions	Ref
IL@ZIF-67 (10 %)	Polysulfone	39.71	38.15	25 °C – 10 bar	[139]
IL@ZIF-67 (20 %)	Polysulfone	52.86	53.57	25 °C – 10 bar	[139]
IL@ZIF-67 (30 %)	Polysulfone	72.06	67.07	25 °C – 10 bar	[139]
IL@UiO-66 (10 %)	Pebax-1657	23.25	21.77	25 °C – 10 bar	[140]
IL@UiO-66 (20 %)	Pebax-1657	25.43	23.54	25 °C – 10 bar	[140]
IL@UiO-66 (30 %)	Pebax-1657	28.32	27.09	25 °C – 10 bar	[140]
ENIL	material	Ideal CO₂/CH₄ selectivity	Mixed gas CO₂/CH₄ selectivity	Conditions	Ref
[EMIM][Ac]	carbon submicrocapsules		1609	30 °C – 1 bar	[152]
[BMIM][Ac]	carbon submicrocapsules		1343	30 °C – 1 bar	[152]
[P ₆₆₆₁₄][CNPyrT]	carbon submicrocapsules		1362	30 °C – 1 bar	[152]
[BMIM][GLY]	carbon submicrocapsules		1555	30 °C – 1 bar	[152]
[BMIM][PRO]	carbon submicrocapsules		1701	30 °C – 1 bar	[152]
[BMIM][MET]	carbon submicrocapsules		1663	30 °C – 1 bar	[152]

^a The ideal selectivities and single gas permeabilities are for free liquid RTILs.

^b IL = 3-(trimethoxysilyl) propan-1-aminium acetate.

reducing IL viscosity, thus improving CO₂ capture. Small capsules (500–700 nm) can entrap large amounts of IL, up to 75–85 wt%, higher than the 30–40 wt% achievable with supported IL membranes [145]. Several ENILs have been prepared from different materials and ILs, and their higher CO₂ absorption capacity than conventional immobilized ILs has been ascertained. Many studies on the synthesis, characterization and properties of ENILs have been conducted since the last decade and they have been recently reviewed by Solangi et al. [93]. Most research has been mainly focused on CO₂ solubility [146–148] and/or CO₂ capture in post-combustion systems [149–151] while the first (and, to our knowledge, the only) study on CO₂ separation from CO₂/CH₄ gas mixtures has been published by Lemus in 2022 [152]. Six ILs were chosen for their environmental friendliness (amino acid-based ILs) and excellent chemical CO₂ sorption capacity (acetate-based, and aprotic heterocyclic anion-based ILs) and they were encapsulated in carbon capsules, achieving a 70 wt% IL loading. The so-obtained ENILs were evaluated as sorbents in CO₂ capture from a 40/60 v/v CO₂/CH₄ gas mixture, by means of gravimetric and fixed-bed measurements. Through mathematical modeling of experimental data, the Authors found that all the tested ENILs had high CO₂ absorption capacity, following the order: acetate-based ILs > aprotic heterocyclic anion-based IL > amino acid-based ILs, at CO₂ partial pressure = 0.4 bar and 303 K, in agreement with the highest CO₂ chemical absorption capacity of acetate based-ILs.

Due to the negligible CH₄ capture, all the tested ENIL materials showed a considerably high CO₂/CH₄ selectivity, even higher than 1000, and also the reaction kinetics was favourable, due to the high gas – liquid contact area.

The CO₂/CH₄ selectivities obtained from the most recent investigations on nanoconfined IL membranes, SILMs, IL@MOF composite materials and ENILs are reported in Table 1, for sake of comparison.

The data collected in Table 1 confirm that the CO₂/CH₄ selectivity mainly depends both on the nature of the ILs, with the CO₂-philic task-specific ILs showing the best performance, and on the materials used to produce the composites, with the hydrophobic membranes that are more effective than hydrophilic ones. Furthermore, the excellent selectivity shown by ENILs is evident and the data highlight their great potential as a suitable technology for gas separation, which is why they deserve further investigations for future applications in the biogas upgrading process, as research in this field is still in its infancy. Table 1 also shows that, for many systems, data on mixed gas selectivity are still missing and this represents a serious limitation in assessing the applicability of these systems in the real biogas upgrading process.

Despite ILs are considered green solvents, they exhibit some problems [154]. First, their synthesis and purification processes are highly energy-intensive and involve the use of toxic, corrosive and volatile compounds containing C, N, S and halogens which can potentially cause human health and environmental problems. Moreover, some ILs are toxic and poorly biodegradable and could represent a serious risk to the environment if used in large quantities. For these reasons, they do not fully satisfy the twelve principles of green chemistry, which is limiting for their industrial use.

Although recently there have been attempts to make IL synthesis more environmentally friendly with the use of biomass-derived feedstocks [155], it has not yet been possible to make these processes independent of the use of toxic solvents, therefore, further efforts are needed to arrive at a truly “green” synthetic route. As regards the economic aspect, the use of low-cost raw materials, such as lignocellulosic materials, has been suggested [154].

The toxicity and non-biodegradability of some ILs are problems that researchers have tried to solve by replacing the imidazolium cation with less toxic cations, such as cholinium ion and using amino acids as anions, avoiding the fluorine ion [156]. However, all of these issues deserve further investigation.

3. Deep eutectic solvents (DESs)

DESs are a relatively new class of solvents which can be regarded, in addition and even more than ILs, as green alternatives to conventional organic solvents. They have been firstly prepared by Abbott [157] and, since then, they have gained a lot of attention from the scientific community, due to their promising properties which make them good candidates for a large-scale utilization. DESs are multicomponent, non-ideal mixtures formed by a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) interacting through an extensive network of hydrogen bonds, which is responsible of the large melting point depression relative to the individual components [157]. Indeed, DESs share with ILs some advantageous physicochemical characteristics, such as thermal stability, low vapour pressure, nonflammability, and these properties can be fine-tuned by changing the nature or ratio of their constituents to obtain the best performing DES for a specific application. However, DESs avoid economic and environmental problems associated with ILs. Unlike ILs, the synthesis of the vast majority of DESs starts from cheap materials and does not require the use of solvents, simply involving the mixing of the two or more DES components without purification steps. Moreover, most DESs are biodegradable [158] and nontoxic [159] even if this generalization is not always valid [160] and recent studies have shown contradictory results [161,162]. Recently, the so-called Natural Deep Eutectic Solvents (NADESS) have been synthesized from natural metabolites such as organic acids, amino acids and sugars, so they can be considered completely safe and environmentally friendly due to their natural components [163].

DESs have been applied to a wide-ranging area of research topics such as bioanalysis [164], electrochemistry [165], extraction [166], drug delivery [167], catalysis [168], green synthesis of nanomaterials [169]. The potential application of DESs in CO₂ capture has recently aroused particular interest from the scientific community and the CO₂ absorption capacity of a number of DESs, mainly based on choline chloride as HBA, has been extensively investigated. Indeed, choline chloride DESs have the advantage of being environmentally friendly materials.

3.1. Dess in CO₂ capture

Pure conventional DESs have shown good CO₂ solubility, comparable with the typical solubility of CO₂ in ionic liquids [170] and it increases at lower T and higher P, as physical absorption process occurs in which CO₂ solubility follows Henry's Law and is dominated by interactions between the gas and DES components [170,171], among which inter-molecular hydrogen bonds and attractive van der Waals interactions are dominant. However, CO₂ solubility in conventional DESs based on choline chloride (ChCl) as HBA and urea/glycerol/ethylene glycol as HBD (liquid mole fraction, $x_{\text{CO}_2} = 0.0240, 0.0454$ and 0.0262 , respectively) is lower than that in 30 % MEA aqueous solution ($x_{\text{CO}_2} = 0.0584$) at 298.15 K and about 10 bar [172]. Zhang et al. have exhaustively compared the performance of some ChCl-based DESs and demonstrated that for the DESs with only physical absorption, the HBD type influences the CO₂ solubility while, for the same DES, the CO₂ solubility is affected by the ChCl/HBD molar ratio and the water content [173]. Comparison between DESs and ILs shows that the CO₂ solubility follows the order: conventional ILs > ChCl-based DESs > aqueous ChCl-based DESs. However, due to the low heat capacities of ChCl-based DESs, which allows the CO₂ desorption to proceed at low temperatures, the non-ecotoxicity, good biodegradability, and their low cost, the Authors concluded that DESs can be considered as suitable alternative and eco-efficient sorbents for CO₂ separation.

Besides ChCl, DESs with different HBA components have been evaluated. Compared with ChCl-based DESs and some ILs, phosphonium-based DESs showed higher CO₂ solubility under the same conditions of T and P [172,174,175].

Some zwitterionic NADESS based on N,N,N-trimethylglycine (TMG)

and carboxylic acids have been recently investigated as environmentally friendly sorbents for CO₂ capture [176]. The highest CO₂ absorption capacity of 45.5 mg CO₂/g DES has been observed, at 313.15 K and 4 MPa, for the system phenylacetic acid/TMG. The physisorption process was confirmed by FTIR measurements and it depends on the acidity of the HBD component, the strength of HBA-HBD interactions, and the presence of water molecules. A free volume mechanism in which the CO₂ molecules are accommodated into the intermolecular spaces between the NADES components, has been suggested. High CO₂ absorption capacity (up to a CO₂ mole fraction of 0.51 at 298 K and 35 bar) and high CO₂ solubility rate have been observed in monoterpene-based hydrophobic NADES [177]. Monoterpenes are low-cost and abundant in nature, so these DESs can be regarded as promising environmentally safe CO₂ sorbents, with performances comparable with those of conventional amine solutions.

Improved CO₂ capture can be achieved by using an amine as HBD, thus switching physical sorption into chemical sorption. Polyamine-, ethanolamine-, piperazine- and imidazolium-based DESs have shown a considerably increased CO₂ absorption capacity, compared with the physical DESs [178–182]. Chemisorption is due to the CO₂-philic amine functionalities which allow CO₂ uptake to occur via carbamate formation reaction. Indeed, chemical absorption is more effective than physical sorption in which only weak forces (electrostatic interactions and/or dispersion interactions) are involved in CO₂ capture.

Recently, low-cost Transition Temperature Mixture (TTM) based on inexpensive and safe materials, as ethylene glycol and potassium hydroxide, with the addition of boric acid to ensure reversibility and small amount of water to modulate the viscosity, has been tested as CO₂ sorbent [183]. Under optimized conditions, the TTM can absorb 24 gCO₂/kg_{sorbent} in 30 min at 35 °C at 1 atm and 60 gCO₂/kg_{sorbent} in 30 min at high pressure. Moreover, the chemical reactions involved in the carbon capture have been suggested and compared with those occurring in aqueous amine solutions or aqueous alkaline hydroxides and carbonates (Fig. 7).

DESs prepared from superbases have also been evaluated as CO₂ sorbents, but most of them suffer from a significant increase in viscosity when chemical CO₂ absorption through carbonate formation occurs, which limits their potential use [184–186]. Indeed, viscosity is an important issue for industrial applications, and, unfortunately, most choline chloride-based DESs are characterized by relatively high viscosities [157] which negatively affects mass and heat transfer, thus limiting the efficiency and usefulness in the absorption process. Viscosity of DES can be significantly reduced by increasing temperature, but high temperatures negatively affect CO₂ solubility. Another method to control and reduce the viscosity of DESs is adding an appropriate amount of water to form DES aqueous solution. Indeed, Ren et al. have

demonstrated that the viscosity of a DES composed of L-arginine and glycerol (1:6) decreases with increase in water content from 0 wt% to 60 wt%, allowing a faster CO₂ capture [187]. The benefit of adding water to ChCl-MEA DES on viscosity and CO₂ solubility has been established by Wibowo et al. [188]. However, a proper compromise must be found as an excessive amount of water could destroy the structure of the DES, weakening the hydrogen bond network and negatively affecting the absorption process [189].

3.2. Dess as sorbents in biogas upgrading processes

CO₂ removal is the key step for biogas upgrading so high absorption capacity towards CO₂ is a necessary requirement for a solvent to be suitable as sorbent in the decarbonization process. However, high selectivity of CO₂ over CH₄ is also fundamental to reduce CH₄ loss and to selectively absorb CO₂ from the gas mixture. DESs, especially amine-based DESs in which CO₂ is chemically absorbed, have shown high selectivity, therefore being suitable candidates for biogas purification. For example, Haider et al. have experimentally investigated the CO₂ and CH₄ solubility in some sterically hindered quaternary ammonium salt-based DESs and found a CO₂ chemisorption 7 folds higher than CH₄ physisorption, indicating high selectivity of this type of DESs towards CO₂ [190].

Most of the studies on the purification of CO₂/CH₄ mixtures by DESs are quite recent and based on process simulations and modelling of CO₂ removal [191], mainly focusing on techno-economic assessments [192–198]. Based on these studies, DESs appear to be very promising solvents for CO₂ separation as both technical and economic aspects were found to be superior to ILs and conventional amines. However, although knowing the selectivity towards CO₂ over CH₄ is a fundamental step in choosing the best suitable absorbent to be utilized in biogas purification, experimental studies on CO₂/CH₄ selectivity in DESs are still limited.

Recently, Yan et al. have experimentally studied the CO₂ absorption capacity, CO₂ absorption rate and CO₂/CH₄ selectivity of ChCl/MEA (molar ratio 1:5) DES from a model biogas composed of 40 % vol CO₂ and 60 % vol CH₄ [199]. Interestingly, they found that CO₂ absorption capacity is improved upon addition of water, which significantly reduces DES viscosity, thus promoting mass transfer and CO₂ diffusion, and upon increasing pressure, pointing to a mechanism of physical absorption of CO₂. However, the negative effect of increasing temperature suggests that chemical absorption, due to the exothermic reaction between CO₂ and MEA, contributes to the overall absorption mechanism. The CO₂/CH₄ selectivity was positively affected by water and pressure but lowered by increasing temperature.

To improve the performance in CO₂ separation, the synergy between DES's high affinity for CO₂ and energy-efficient membrane technology

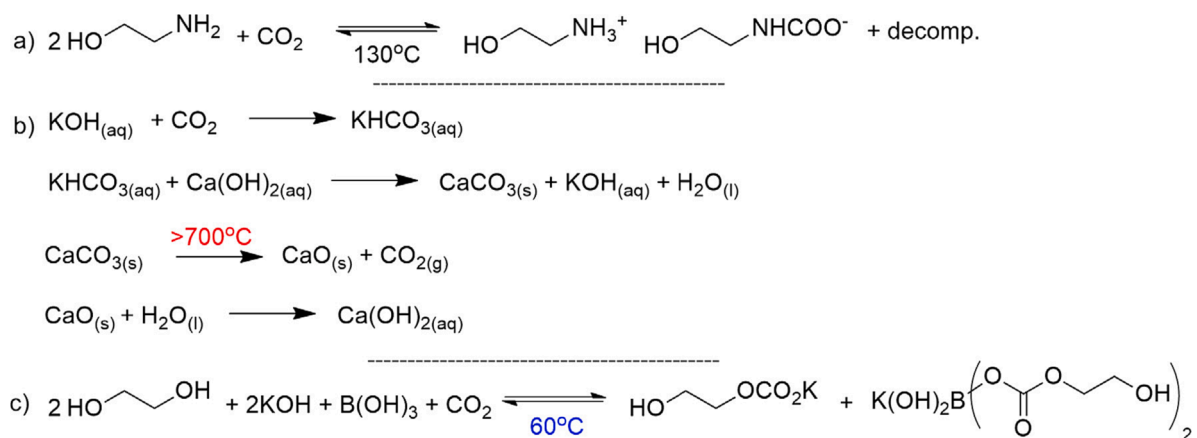


Fig. 7. Chemical reactions involved in the carbon capture strategies for a) MEA, b) KOH/CaO and c) TTM composed of ethylene glycol/potassium hydroxide /boric acid [183]. Copyright © 2021 Elsevier.

has been explored in recent years by introducing DES-supported liquid membranes. Poly deep eutectic solvents (PDESs), obtained from ChCl as HBA and polymerizable HBDs like polyacrylic acid (PAA) and polyacrylamide (PAM), have been incorporated into microporous polyvinylidene fluoride (PVDF) membranes, as schematically represented in Fig. 8 [200], in which the mechanism of solution diffusion governs the gas transport.

High ideal CO_2/CH_4 selectivity of 50.71 and slightly lower mixed selectivity for a 50:50 CO_2/CH_4 gas mixture of 49.25, due to the competition between the two gases for the sorption sites, have been calculated for 20:1 ChCl/PAA-supported liquid membrane, pointing to an excellent synergic effect of these hybrid systems compared with pure DES and membrane alone.

Further insights into the topic of DES/membrane hybrid system for biogas upgrade have been provided by Saeed et al., who tested the performance of a PVDF membrane, impregnated with three DESs obtained from a betaine as HBA and glycerol (G), ethylene glycol (EG) or urea (U) as HBD [201], for which ideal selectivities for CO_2/CH_4 separation of 46.61, 43.24 and 57.53 have been calculated, respectively. The mixed selectivities, for a 50:50 CO_2/CH_4 gas mixture, are, as expected, slightly lower than the corresponding ideal values.

The CO_2/CH_4 selectivity follows the same trend of CO_2 solubility, which increases in the order: $\text{EG} < \text{G} < \text{U}$. CO_2 solubilization is due to the interaction with the $-\text{OH}$ groups of G (more hydroxyl groups, stronger interaction with CO_2) and EG, and with $-\text{NH}_2$ groups of U. The $-\text{COO}^-$ group of the betaine can also interact with CO_2 , contributing to the affinity of the DES for CO_2 rather than for CH_4 .

The CO_2/CH_4 selectivity of supported liquid membranes of PVDF based on DESs prepared from ChCl as HBA and malic acid (MA), tartaric acid (TA) or oxalic acid (OA) as HBD and NADESs obtained from a betaine as HBA and MA or TA as HBD have been investigated by the same Authors [202,203]. High CO_2 separation performance for CO_2/CH_4 mixture has been demonstrated also for these systems, depending on the type of HBD. Indeed, although the solubility of CO_2 in these DESs can be attributed to the interaction of CO_2 with the $-\text{OH}$ groups of HBDs, the presence of large numbers of $-\text{OH}$ groups in HBD, such as in TA and MA compared to OA, allows for the development of a strong network of hydrogen bonding interaction between HBA and HBD, which reduces the interaction sites available for CO_2 resulting in decreased diffusion and solubility, and hence in decreased permeability and selectivity.

Biocatalytic supported liquid membranes are emerging as a novel approach to improve CO_2 separation performance by immobilizing DESs

together with the enzyme carbonic anhydrase (CA) which reversibly converts CO_2 into bicarbonate, thus increasing CO_2 uptake and CO_2 sorption [204]. Moreover, CA can increase the CO_2 selectivity over other gases such as N_2 and CH_4 .

The first biocatalytic system of this type has been prepared by Craiveiro et al., who immobilized ChCl-based DESs, together with CA, into hydrophilic polytetrafluoroethylene (PTFE) porous membranes [204]. CO_2 solubility and permeability were calculated in DESs obtained from ChCl as HBA and glycerol (G), ethylene glycol (EG) or urea (U) as the HBD and they were higher in the combined ChCl/urea/CA supported membranes than in the absence of CA. However, CA slightly reduced CO_2/CH_4 selectivity (Fig. 9).

The effect of CA on CO_2 absorption performance is affected by the acidity of the DES and by the presence of water, which reduce the enzymatic activity and, consequently, CO_2 uptake so that these systems can be effective only in a limited range of operating conditions [204,205].

Very recently, Zhao et al. have confined ChCl/urea DES and CA in microcapsules with a hydrophobic and permeable polydimethylsiloxane (PDMS) shell [206]. In this condition, the enzymatic activity of CA is protected from inactivation by excessive amounts of water. At 308.15 K and 1.3 atm, this system showed an absorption capacity of 248.60 mg CO_2/g DES which was 7.5 times higher than the value of 33.28 mg CO_2/g DES obtained for the DES encapsulated without the enzyme, and 10 times higher than the value of 3.34 mg CO_2/g DES obtained for the neat DES. From CO_2 and CH_4 experimental solubility values, ideal CO_2/CH_4 selectivity was calculated as 32.04 for DES/microcapsule system, and 233.96, for DES/CA/microcapsule system, which were 8.5 and 62 times higher than that of neat DES (3.75), respectively.

Ideal CO_2/CH_4 selectivities and mixed CO_2/CH_4 selectivities, when available, for the different DES-based absorbent systems are summarized in Table 2, together with those relative to the physical sorbents used in the most common commercial gas cleaning processes like Selexol (polyethylene glycol dimethyl ether), Rectisol (chilled methanol) and Purisol (N-methyl-2-pyrrolidone), for sake of comparison.

The data collected in Table 2 show that efficient biogas upgrading can be achieved by the DES-based absorption systems, with hybrid technologies appearing the most promising options. Indeed, DES performances seem comparable or even better than those obtained for IL-based absorption systems reported in Table 1, except for ENILs, for which a surprisingly high CO_2/CH_4 selectivity has been calculated. However, the advantage of DES of being cheaper, less harmfulness, more

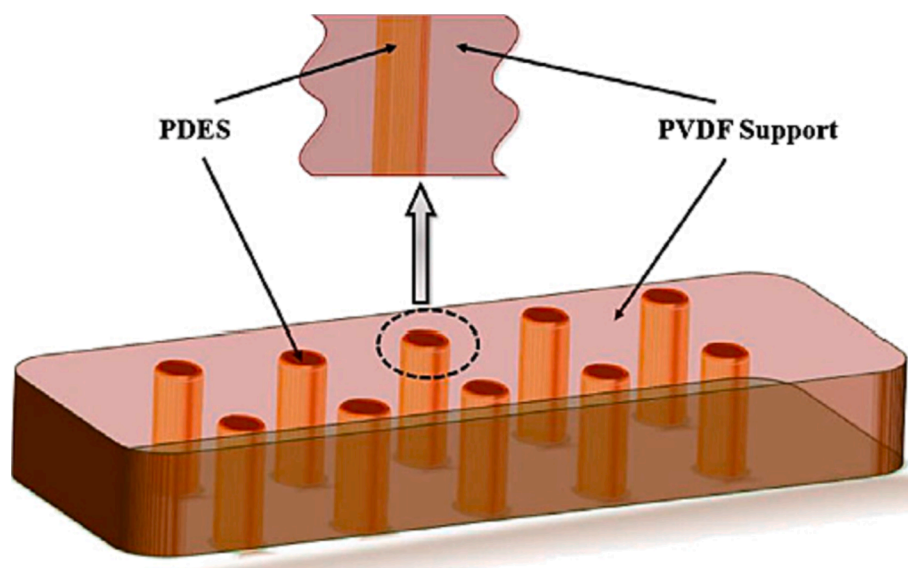


Fig. 8. Schematic representation of the DES-supported liquid membrane from ref. 203. Copyright © 2020 Ishaq, Gilani, Afzal, Bilal, Nizami, Rehan, Tahir and Khan.

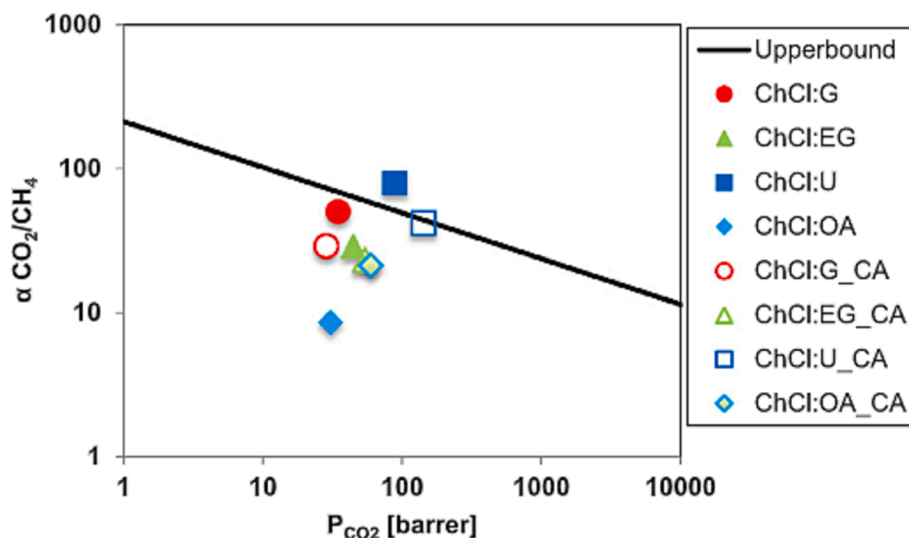


Fig. 9. CO₂/CH₄ selectivity as a function of CO₂ permeability for the tested DES supported liquid membranes (1 Barrer = 10⁻¹⁰ cm³ (STP) cm cm⁻² s⁻¹ cm Hg⁻¹) [204]. The solid line represents the Robeson upper bound correlation for CO₂/CH₄ separation. Copyright © 2021 Elsevier.

Table 2

Gas separation performance of recently published DES systems. CO₂/CH₄ selectivities in commercial Selexol, Rectisol and Purisol solvents are reported for comparison.

Sorbent System	ratio	Ideal CO ₂ /CH ₄ selectivity	Mixed CO ₂ /CH ₄ selectivity	Ref.
ChCl/MEA	1:5	12		[199]
ChCl/MEA/H ₂ O	1:5/75 % vol	25		[199]
ChCl/PAA (PVDF)	15:1	48.95	47.50	[200]
ChCl/PAA (PVDF)	20:1	50.71	49.25	[200]
ChCl/PAM (PVDF)	15:1	45.37	43.22	[200]
ChCl/PAM (PVDF)	20:1	46.55	44.03	[200]
betaine/G (PVDF)	1:3	46.61	45.14	[201]
betaine/EG (PVDF)	1:3	43.24	42.29	[201]
betaine/U (PVDF)	1:3	57.53	55.73	[201]
ChCl/TA (PVDF)	1:1	51.39	49.02	[202]
ChCl/MA (PVDF)	1:1	55.74	54.51	[202]
ChCl/OA (PVDF)	1:1	60.16	58.26	[202]
betaine/TA (PVDF)	1:1	51.1	50.92	[203]
betaine/MA (PVDF)	1:1	61.1	53.64	[203]
ChCl/U	1:2	3.75		[206]
ChCl/U (PDMS microcaps.)	1:2	32.04		[206]
ChCl/U/CA (PDMS microcaps.)		233.96		[206]
Selexol process solvent		15		[207]
Rectisol process solvent		19		[207]
Purisol process solvent		26		[207]

biodegradable and more environmentally friendly than ILs should be taken into account when comparing viability as alternatives to conventional biogas upgrading technologies, especially in the perspective of their large-scale commercial use. DES-based hybrid systems also represent a valid alternative to conventional physical solvents in terms of effectiveness, cost and environmental impact. In fact, DES systems show higher CO₂/CH₄ selectivities compared with Selexol, Rectisol and Purisol. Moreover, they do not require the extreme operating conditions and high energy consumption of Rectisol (high refrigeration costs), Selexol (efficient only at high pressures) and Purisol (high compression costs) processes. Moreover, DES systems are not subject to absorbent loss and are non-toxic.

4. Clathrate hydrates

Clathrate hydrate-based gas separation can be regarded as a promising green strategy for biogas upgrading, from both an economic and a safety point of view, as water is the main raw material. Clathrate hydrates are crystalline, polyhedral host-guest compounds which can be formed within a gas/water mixture under defined conditions of high pressure and low temperature [208]. These compounds have gained significant attention due to their potential impact in industries such as oil and gas production, where the presence of hydrates can lead to pipeline blockages, equipment damage, and even safety hazards. To mitigate the problems associated with plugging, various chemical and physical methods are employed to prevent hydrate formation. Chemical inhibitors, such as thermodynamic hydrate inhibitors (THIs) and kinetic hydrate inhibitors (KHIs), are commonly used to suppress hydrate formation by altering the thermodynamic or kinetic properties of the system [209]. Inhibitors can be injected into the pipeline or equipment to prevent hydrate nucleation and growth. Physical methods for preventing plugging include the application of heat or pressure to maintain the temperature and pressure conditions outside the hydrate stability zone, as well as the application of specific electromagnetic radiations to alter the ability of water molecules to reorganize into hydrates [210].

In gas hydrates, small molecules of gas (guests) are entrapped into the cavities of three-dimensional cages of hydrogen-bonded water molecules, arranged in an ice-like framework, acting as hosts [211]. Guest molecules are typically H₂, N₂, CO₂, CH₄ [206], but also volatile liquid organic compounds such as cyclopentane [212]. Clathrate hydrates can exist in three typical structures: a cubic structure sI, a cubic structure sII, and a hexagonal structure sH, which differ in cavity size and geometry (Fig. 10). sI unit cell consists in 2 small and 6 large cages, sII unit cell consists of 16 small and 8 large cages, and sH unit cell consists in 3 small, 4 medium and 1 large cages (Table 3), and usually requires two guest molecules of different sizes to stabilize the crystal [211,213–215].

Hydrate formation consists of two stages: nucleation and growth. Nucleation is the initial formation of hydrate crystals from a water and gas system, while growth refers to the sustained growth of hydrate nuclei. Nucleation is a random process driven by free energy, and only nuclei reaching a critical size can progress to the growth stage. According to the Labile cluster hypothesis (LCH) proposed by Sloan in 1991 [216], gas molecules dissolve in water, and labile clusters form rapidly. These clusters may form and dissolve rapidly, but once the size of the cluster reaches a critical value, hydrate growth occurs. Beside this

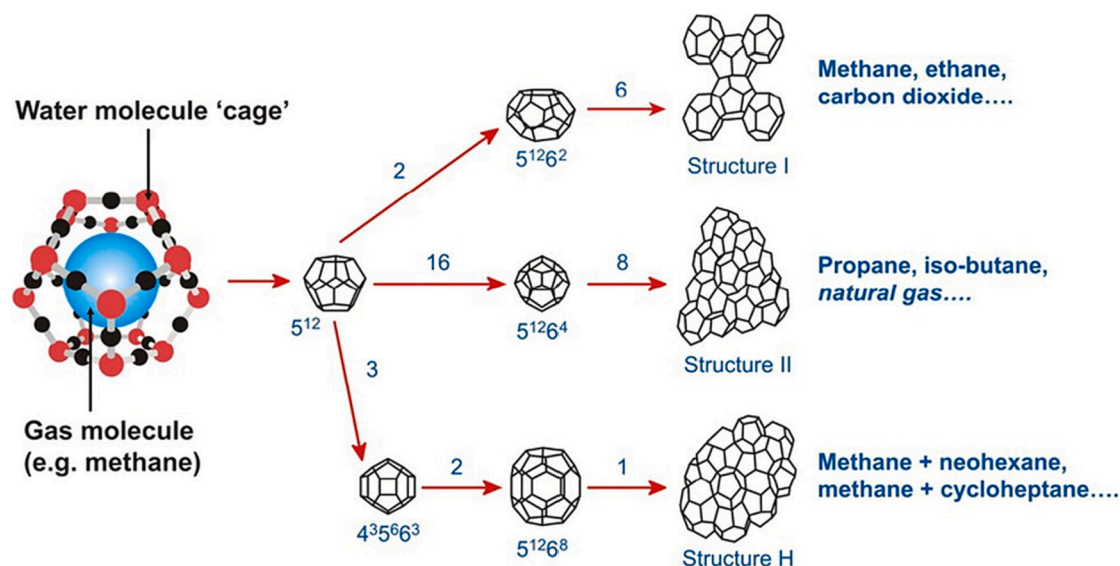


Fig. 10. Clathrate hydrate structures and some of the guest molecules that can be accommodated inside the cages. Reprinted with permission from Ref. [215]. Copyright © 2022 Elsevier.

Table 3

Physical properties of the three common type of clathrate structure, sI, sII and sH. The number and superscripts indicate the types and numbers of polygon in the cage unit cell, respectively. For example, $5^{12}6^2$ is a tetrakaidecahedron with 12 pentagonal and 2 hexagonal faces.

Structure	sI	sII	sH
Cages (n° of cages /unit cell)	5^{12} (2)	$5^{12}6^2$ (6)	$5^{12}6^4$ (8)
Average cage radius (10^{-10} m)	3.95	4.33	4.73
n° water/unit cell	46	136	34

initial theory, other improvements were attempted to better understand the nucleation phenomena: from local structuring hypothesis (LSH) to cage adsorption hypothesis (CAH), up to the more recent two-step nucleation mechanism proposed by Molinero et al., according to which hydrate nucleation proceeds through a first step of forming amorphous clusters, followed by the transformation in crystalline hydrate [217,218]. Once grown, the whole structure of gas hydrates is stabilized by Van der Waals' interactions between the trapped molecules and the network of water molecules, which are linked together by hydrogen bonds to form the polyhedral cavities. The nucleation stage is strictly related to the phase-equilibrium of each gas, in which the pressure and temperature parameters are crucial to ensure an adequate driving force to induce the hydrate formation spontaneously and with a reduced induction time [219].

When a single gas acts as the guest, the structure formed depends on the size and shape of the gas molecules and on pressure/temperature conditions of hydrate formation. For example, pure CO_2 usually forms sI hydrates at a moderate pressure and 273 K, [211,220] whereas pure N_2 usually forms sII hydrates, at 273 K and pressures higher than 15 MPa [221].

Clathrate hydrates take up large amounts of gases in a small volume, storing up to 160–170 ($\text{CO}_2\text{-CH}_4$) or 400 (H_2) normal volumes of gas per unit volume, at standard pressure and temperature [214,222,223]. Due to their high volumetric storage capacity, clathrate hydrates have been intensively studied, in the last decades, as potential media for the storage and transportation of CH_4 [224], H_2 [225] and CO_2 [226] storage and transportation.

Another unique property of clathrate hydrates is guest selectivity

[227], i.e., they can be formed under specific conditions depending on the guest molecules. In the presence of a binary gas mixture, molecular size and guest–host interactions determine which cage arrangement in clathrate hydrate may occur (sI, sII, sH), influencing the selectivity since each gas is entrapped preferentially into a specific cage structure [227]. The rate of mass transfer, which refers to the movement of guest molecules from the gas phase to the hydrate phase, can also influence selectivity. Faster mass transfer rates can lead to preferential inclusion of certain gases in the hydrate structure [228]. Finally, thermodynamic conditions as well as the relative phase equilibrium curve typical for each gas forming hydrate are also important parameters that will lead to an increase or decrease in selectivity. In particular, the gas component with the mildest hydrate formation conditions is expected to be preferentially entrapped in the hydrate cavities leaving a gas phase enriched with the gas for which more severe conditions are requested to form hydrates so that the concentration of the different components of the gas mixture in the gas phase will be different from that in the hydrate phase [229] (Fig. 11). Altering the equilibrium conditions by using proper thermodynamic promoters may influence the relative concentrations of different guest molecules, thereby influencing their selectivity in the hydrate structure. On this basis, a target gas could be selectively removed from a multicomponent gaseous mixture by choosing appropriate operating temperature and pressure [230].

4.1. Hydrate-based gas separation

The hydrate-based gas separation (HBGS) process has been intensively studied mostly for the separation of CO_2/N_2 mixture in post-combustion CO_2 capture, and of CO_2/H_2 mixture in pre-combustion CO_2 capture [231–233]. For fuel gas, in which CO_2 and N_2 are the main components, CO_2 is preferentially taken up by the hydrates, as hydrate formation of CO_2 ($P = 1.32$ MPa at 0.6°C) [234] occurs under much milder thermodynamic conditions than N_2 ($P = 17.13$ MPa at 0.6°C) [235].

Linga et al. demonstrated that, at 0.6°C , a gas mixture containing 16.9 vol% of CO_2 and 83.1 vol% of N_2 , the minimum pressure at which hydrates form is 7.7 MPa, and that a CO_2 -rich hydrate phase containing 57.3 mol% of CO_2 can be recovered at 10 MPa [236].

The same Authors found that for a fuel gas model containing 39.2 vol% of CO_2 and 60.8 vol% of H_2 (pure H_2 hydrate formation pressure close to 300 MPa, at 0.6°C [237]), the minimum hydrate formation pressure is 5.1 MPa at 0.6°C , and that a CO_2 -rich hydrate phase containing 86.5

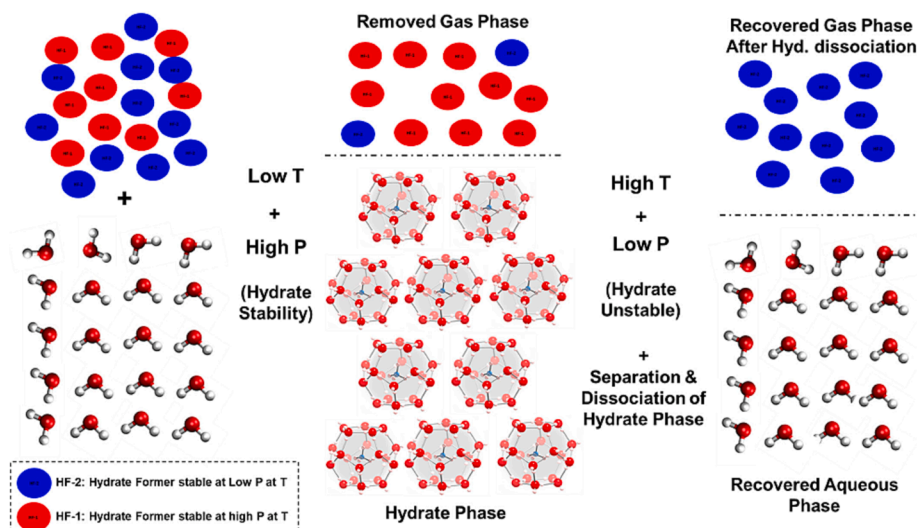


Fig. 11. Visual representation of hydrate-based gas separation (image from ref. [229] under CC BY 4.0).

mol% of CO₂ can be recovered at 7.5 MPa.

In both cases, an increase in operative pressure (higher driving force), lead to a decrease in the CO₂ recovery (from 57.3 mol% at 10 MPa to 55.1 mol% at 11 MPa for flue gas; from 86.5 mol% at 7.5 MPa to 85.1 mol% at 8.5 MPa for fuel gas) probably because, at higher pressure, more N₂ (or H₂) molecules compete with CO₂ to occupy the cavities of the hydrate cages, reducing the relative composition of CO₂ in the hydrate phase [236].

On the same basis of selective clathrate hydrate formation, HBGS can be proposed also for application in biogas upgrade but the studies on the separation of CO₂ from CH₄ are very limited. Indeed, even if CO₂ forms hydrates at lower pressure than CH₄ [238], the narrow difference in the hydrate phase equilibrium conditions makes CO₂ hydrates more stable than CH₄ hydrates in a limited range of T (0–10 °C) and P (10–60 bar) where, in theory, CH₄ is present in the gas form and CO₂ is expected to be in the hydrate state [239]. Moreover, CO₂ and CH₄ have similar molecular sizes so they share the same crystal structure sl, where CH₄ molecules preferentially occupy the large cavities with respect to the small ones in a ratio of around 1.26, while in the same sl structure, CO₂ molecules predominantly occupy large cavities [240]. Another problem to address is the slow hydrate formation kinetics, due to the development of a hydrate thin film at the gas–water interface, which limits the mass transfer between gas and liquid and the further growth of the hydrate [241,242].

For these reasons, it is currently difficult to reach a good separation efficiency for CO₂/CH₄ gas mixtures and the process is also moderately energy-intensive due to the pressurization of the feed gas and cooling the solution to achieve the required gas hydrate formation conditions.

In terms of energy requirements, HBGS offers potential advantages compared to traditional gas separation methods. Castellani et al. performed an energy evaluation to assess the competitiveness of hydrate technologies in bioenergy applications [243]. They calculated the total energy involved into a laboratory-scale experiment, taking into account the compression stages, the coefficient of performance of the chiller, energy costs for the complete separation of CO₂ for biogas mixture, etc. After a reaction time of 30 min, the energy consumption was 0.490 kWh/Kg of treated biogas, which is not so far from the energy consumption of much more consolidated technologies (0.4761 kWh h/kg biogas for a mixed fluid cascade cycle system) [244]. The same Authors believe that the energy calculation obtained for a small-scale laboratory pilot could be considerably reduced after moving to the industrial scale unit. Moreover, an improvement in efficiency related to a better control of kinetics and thermodynamics of the hydrate formation using proper promoters can significantly minimize the time and energy demand for

the HBGS.

Definitely, clathrate hydrate-based gas separation offers several advantages if compared to traditional CO₂ capture technologies such as physical adsorption, chemical adsorption, membrane separation, and cryogenic separation [245]. Hydrate-based CO₂ capture operates under moderate temperature and pressure conditions, making it relatively easy to implement and operate compared to other methods that require extreme conditions or complex equipment. Indeed, absorption/adsorption methods can be energy-intensive, especially during regeneration, while membrane separation processes are more energy-efficient, although higher pressures may be required for an efficient separation. Hydrate system, besides the other separation methods, is theoretically high selective for specific gas molecules and present a relatively high capture capacity, which means that the hydrate-based method can achieve the maximum possible capture of CO₂, leading to efficient utilization of available space. It is an environmentally friendliness option as it utilizes water as a means of capture. The water, along with non-volatile additives, can be recycled for hydrate transformation without generating any additional waste materials. Additionally, the separation process does not produce toxic pollutants.

There are still challenges to overcome in terms of practical implementation and scalability and further research and development are needed to optimize the hydrate-based CO₂ capture process, addressing any potential drawbacks or limitations [230]. In particular, the kinetics of clathrate hydrate formation and dissociation can be slow, leading to long process times and potentially limiting scalability. Mass transfer limitations can also affect the efficiency of gas capture and release within the hydrate structure. Improving the selectivity is another crucial step as there is a narrow difference in phase equilibrium conditions between CH₄ and CO₂ hydrate. Finally, scaling up clathrate hydrate-based separation processes to industrial levels is challenging due to the need for high-pressure equipment and a recycling system to address a proper water and additives management.

In general, the HBGS process can be optimized, and the separation efficiency improved, by using additives which can make the operating conditions milder and enhance the reaction rate. The most commonly promoters are summarized in Fig. 12.

Promoters can be classified into two categories:

- 1) co-formers, which can shift the equilibrium conditions of hydrate formation toward lower pressures and higher temperatures. They can be further divided into two sub-classes:
 - Additives that do not alter the structure of the water cages, like tetrahydrofuran (THF) and cyclopentane (CP) [246,247];

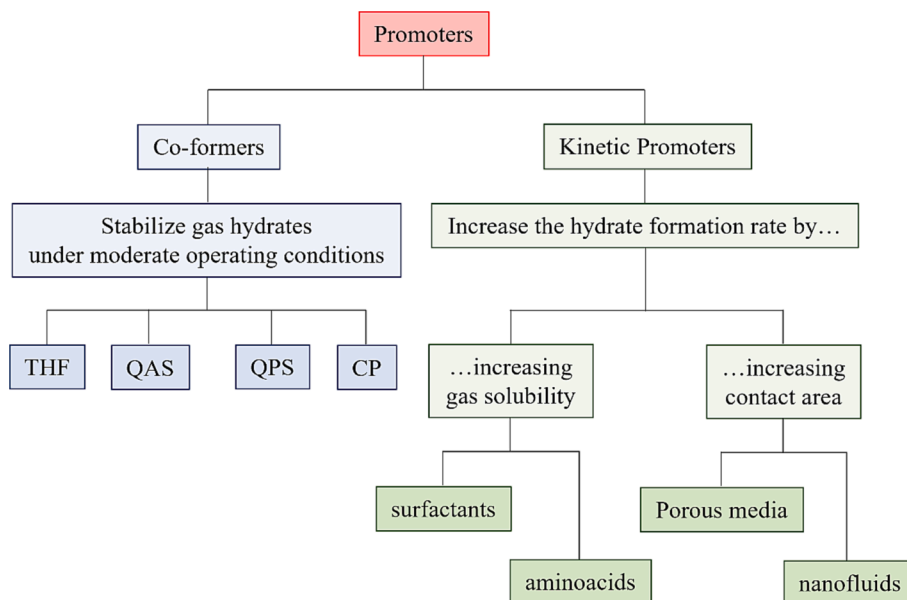


Fig. 12. Schematization of the most commonly used thermodynamic and kinetic promoters: THF: tetrahydrofuran; QAS: quaternary ammonium salts; QPS: quaternary phosphonium salts; CP: cyclopentane.

- Additives that change the structure of the water cages through chemical or ionic interactions, forming semi-clathrates in which the promoter molecules act both as guest and host as they constitute a part of the host framework, like quaternary ammonium salts (QAS) and quaternary phosphonium salts (QPS) [248].
- 2) kinetic promoters, which can increase the rate of gas uptake and reduce the induction time, such as surfactants like sodium dodecyl sulfate (SDS), porous media, graphene sheets, nanofluids [249–253].

Co-formers and kinetic promoters can be used alone or in combination to optimize the HBGS process [254]. However, most investigations have been focused on simple hydrates or CO_2/N_2 and CO_2/H_2 systems while comprehensive studies on the thermodynamic and kinetic behaviour of the CO_2/CH_4 gas mixture in the presence of hydrate-promoting additives are very scarce in the literature, being limited to laboratory scale and still exploratory. The appropriate selection of additives to improve the thermodynamic conditions for hydrate formation, reduce the energy consumption, and increase the reaction rate of the hydrate formation process, is a key step in the development of efficient biogas upgrading via HBGS.

4.2. Co-formers in biogas upgrading

THF. Tetrahydrofuran (THF) is the most common co-former which can lower the hydrate equilibrium pressure, at a given temperature, and/or increase the hydrate equilibrium temperature, at a given pressure, enlarging the hydrate stability region, without altering the lattice structure of the hydrate [246].

THF alone form hydrates with SII structure at atmospheric pressure and $T > 273 \text{ K}$ [198,255]. By XRD and Raman measurements, Lee et al. demonstrated that in multicomponent systems, i.e., $\text{THF} + \text{CO}_2$, $\text{THF} + \text{CH}_4$ and $\text{THF} + \text{CO}_2 + \text{CH}_4$, at $[\text{THF}] = 5.56 \text{ mol}\%$, THF molecules fill the large $5^{12}6^4$ cages, while the smaller molecules of CO_2 and/or CH_4 are trapped in the small 5^{12} cages of the SII hydrate, forming binary hydrates that show higher thermodynamic stability than pure CO_2 and CH_4 hydrates [256]. Sowjanya and Prasad compared the phase stability behaviours and the formation kinetics of CO_2 and CH_4 pure systems with THF-CO_2 and THF-CH_4 mixed hydrates showing that phase stability conditions are shifted higher and gas intake is much quicker in binary hydrates than in pure hydrates [257].

However, even if THF can improve the operating conditions for hydrate formation, its incorporation in the hydrate phase decreases the fraction of entrapped CO_2 . Indeed, the lowest hydration number for CO_2/THF mixed hydrate has been reported to be 8.5 (i.e., 1 CO_2 molecule per 8.5 H_2O molecules), higher than both the theoretical values of 5.75 and practical value of 7.3 reported for pure CO_2 hydrate [258,259].

Lee et al. have demonstrated that, at $[\text{THF}] = 5.56 \text{ mol}\%$, the concentration of CO_2 recovered in the hydrate phase is lower than in the vapor phase, suggesting a selective incorporation of CH_4 , rather than CO_2 , in the SII hydrate [256]. Indeed, at stoichiometric concentration, THF molecules completely fill the large cages of SII hydrates so that CH_4 and CO_2 compete to occupy the small cages in which CH_4 molecules are preferentially entrapped.

Moreover, THF worsens the selectivity for CO_2 removal from the CO_2/CH_4 mixture, even at non-stoichiometric concentrations. Zhong et al. performed experiments of hydrate formation with the CO_2/CH_4 gas mixture at $T = 277.15 \text{ K}$, $P = 2.8 \text{ MPa}$ and in the presence of 1.0 mol% THF, resulting in a CO_2 recovery = 49.9 mol% and a separation factor $S = 3.5$, which is lower than the corresponding values of 52.3 mol% and 8.8, respectively, obtained in water with no additives [260].

Recently, Kida et al. studied CO_2 separation from a CO_2/CH_4 mixture, using stoichiometric THF hydrate as solid phase, in a gas–solid contact mode, by means of solid-state NMR and Raman spectroscopy [261]. Two fixed pressure of 3 MPa and 0.9 MPa and temperatures in the range 253–273 K have been chosen to test the effects of operating conditions on CO_2 uptake. In a gas–solid contact model, the gas molecules are adsorbed onto the particle surface, and then they diffuse through the solid particles, filling the empty cages [262]. In a gas–liquid contact model, gas molecules are adsorbed during water structuring processes at the gas–liquid interface [208].

Due to the different gas uptake models, it is reasonable to expect different trends of gas inclusion. In fact, in the gas–solid contact system, the mole fraction of CO_2 in the THF hydrate was higher than the initial mole fraction in the vapour phase, showing that CO_2 molecules was preferentially incorporated into the hydrate phase, in contrast with the selective incorporation of CH_4 molecules found for the gas–liquid contact system [256]. This result has been interpreted in terms of different stabilization effects of CH_4 and CO_2 on the hydrate framework, in the gas–solid and in the gas–liquid systems [261]. Moreover, in the gas–solid contact system, under both fixed pressures of 0.9 MPa and 3

MPa, CO₂ recovery increased when contact temperature decreased from 273 to 253 K, and, for each temperature, CO₂ recovery increased when pressure increased, separation factors varying in the range 2–8 for P = 3 MPa and 1–6 for P = 0.9 MPa. These results suggest that at higher pressures and lower temperatures, a higher separation performance is achieved, i.e., higher amounts of CO₂ are trapped into the hydrate phase, in contrast with results obtained in the gas–liquid contact system, in which a higher driving force for gas uptake resulted in a decrease of CO₂ recovery and separation factor [260].

The effect of temperature and pressure on the biogas upgrading by clathrate hydrates, in the presence or absence of THF as the promoter, has been recently investigated by Kudryavtseva et al. [263]. The best separation factor of 11.12 was observed in THF-SDS aqueous solution at T = 272.15 K and P = 2.00 MPa. This result suggests that a low process temperature, high driving force and the addition of THF as the promoter improve the performance of the clathrate hydrate-based CO₂ separation method.

Besides the low selectivity for CO₂, drawbacks to the application of thermodynamic promoters such as THF and CP are their carcinogenicity, high toxicity, and high volatility [264] so that great efforts have been made to find alternative and more environmentally friendly promoters to improve the CO₂ separation efficiency.

4.3. TBAB and semi-clathrate hydrates

Tetra-*n*-butyl ammonium bromide (TBAB) is a cheap, water soluble and environmentally friendly alternative to THF. It forms semi-clathrate hydrates even under atmospheric pressure (at 273–284 K [265]), where the structure of water cages rearranges in order to encage the large tetra-*n*-butylammonium moiety [266]. In the semi-clathrate hydrate, the negatively charged anions replaces some water molecules to form hydrogen-bonding cavities, while the hydrophobic TBA cation occupies a four-polyhedral fused-cage, for example, three tetrakaidecahedral cages plus one pentakaidecahedral cage, incorporating each carbon chain into one of the four cages [267,268], while all the dodecahedral cages, formed around the large cages, are empty.

TBAB semi-clathrates can entrap small gas molecules, such H₂ [269], CO₂ [270], CH₄ [271] in the available small pentagonal-dodecahedral cages, under significantly milder thermodynamic operating conditions.

TBAB semi-clathrate hydrates have also shown high selectivity for CO₂, without lowering CO₂ recovery when compared to the absence of additive, while phase equilibrium conditions are significantly improved. For this reason, TBAB is considered as one of the most promising promoters to optimize the CO₂ separation process from gas mixtures. Several studies have been carried out, in the past decade, on the use of TBAB to remove CO₂ from CO₂/CH₄ mixtures and on the effect of TBAB concentration on the equilibrium conditions, CO₂ recovery, separation factor and CH₄ enrichment of the residual gas phase [272–274]. The hydrate crystal formation pressure needed to form TBAB semi-clathrates in the presence of CO₂ is reduced compared to that requested for CO₂ hydrate formation in pure water, thus reducing energy consumption. It should be noted that, under low pressure conditions, gas removal due to semi-clathrate formation may cause the pressure to drop below the equilibrium value of hydrate formation, which, in turn, leads to a reduction in gas uptake.

Li et al. demonstrated that separation efficiency can be improved by performing multiple sequential hydration reactions [275]. A first stage of CO₂ separation from a CH₄(67 mol%)/CO₂(33 mol%) mixture was conducted at P = 3 MPa, T = 278 K and in the presence of 5 wt% TBAB. The best results in terms of CH₄ concentration in the residual gas phase (92.76 mol%) and separation factor (21.2) were obtained at a gas–liquid volume ratio (R_v) of 3.61. A second stage of hydrate separation process from a CH₄(89.5 mol%)/CO₂(10.5 mol%) mixture was performed at the same temperature and pressure conditions, with 0.05 wt% TBAB and at R_v = 7.9. The CH₄ concentration in residual gas phase was enriched up to 97.00 mol % and the separation factor increased to 24.9. However,

increasing the number of stages leads to an increase in energy consumption due to multiple compression and cooling operations.

Fan et al. have proposed a pressure recovery method, in which a TBAB solution was continuously injected into the reactor to compensate for the pressure drop due to the gas uptake, thus allowing the continuous hydrate formation and gas separation [276]. They found that, under constant pressure, both the final gas uptake and CH₄ fraction in the gas phase are higher than those obtained in unrecovered pressure experiments. In pressure recovery conditions, the addition of 0.293 mol% of TBAB, at 1.14 MPa and 281.3 K led to a CH₄ fraction in the residual gas phase of 93.52 mol% and a maximum CO₂ separation factor of 42.17.

The pressure recovery method has been also applied to perform a mild separation of lean-CH₄/CO₂ binary mixture under low pressure, by continuously injecting TBAB solution into the reaction vessel to avoid pressure drop, concomitantly providing more hydrate cages to capture further gas molecules and enhance gas uptake [277]. At a constant pressure of 1 MPa, T = 280 K, and 5 wt% TBAB, compared to non-constant pressure experiments, the CH₄ fraction in residual gas phase increased from 17.2 to 66.2 mol%, CO₂ recovery rate increased from 45.3 to 97 % and the separation factor increased from 18.07 to 31.55. Upon increasing TBAB concentration up to 10 mol%, a decrease of CH₄ concentration in the residual gas was observed, due to capture of CH₄ in the extra 5¹² cages.

Wang et al. have studied the TBAB hydrate formation kinetics with CH₄/CO₂ mixture, and CO₂ separation efficiency at different TBAB concentrations and subcooling degrees as the driving force for hydrate formation, in order to determine the optimum conditions for CO₂ capture, using TBAB semi-clathrate hydrate [278]. Experimental results have been discussed in terms of induction time, normalized gas consumption, CO₂ contents in the gas phase and hydrate phase, CO₂ recovery rate, and CO₂ separation factor, and compared with those obtained in common gas hydrates, such as THF and THF/SDS systems. They found that, for a gas mixture of 40 mol% CO₂ and 60 mol% CH₄, at P = 2.8 MPa, a CO₂ selectivity factor of 36.5 was obtained at 2.57 mol% TBAB, which was higher than the values obtained in 1 mol% THF (3.3), 1.0 mol% THF/500 ppm SDS (6.2) and 2.57 mol% tetra-*n*-butyl phosphonium bromide (31.1). Moreover, the temperature used for the HBGS process in the presence of 2.57 mol% TBAB (284.8 K), was higher than that with THF (277.15 K). The gas consumption obtained with TBAB was less than 50 % of that obtained with THF therefore the Authors concluded that, even if TBAB is promising in terms of CO₂ selectivity, an increase of the gas uptake is needed for TBAB to be used on an industrial scale.

The analysis of the energy consumption of hydrate-based CO₂ separation from biogas is a necessary step to evaluate if the process is commercially viable. Very recently, Huang et al. have simulated a two-stage hydrate-based CO₂ separation from biogas in the presence of 5 wt % TBAB and calculated the energy consumption of the process, taking into account the energetic expenditure for compression, refrigeration, mechanical stirring and pumping fluid steps [279]. The main energy consumption was that referred to the compression, which accounted for over 45 % of the energy utilized in the entire process at P = 4 MPa. It can be reduced by 39.7 % upon reducing the formation pressure to 1 MPa. A lower pressure implied a higher refrigeration energy consumption (13.5 % higher than that calculated at P = 4 MPa), nevertheless the energy consumption of the entire process and the energy cost per kg of CO₂ were reduced from 4372 kW to 3581 kW and from 0.618 kWh/kg_{CO2} to 0.506 kWh/kg_{CO2}, respectively.

Optimizing the hydrate-based separation process by using the cold energy (cooling power) of hydrate dissociation to precool the compressed feed gas, and by adding a pressure energy recovery device, the calculated energy cost was 0.451 kWh/kg_{CO2}. The comparison with common method of biogas upgrading (Fig. 13) showed that the energy cost for optimized hydrate-based CO₂ separation in the presence of TBAB is lower than those calculated for chemical absorption [280] and cryogenic separation [281], but similar to that obtained for water

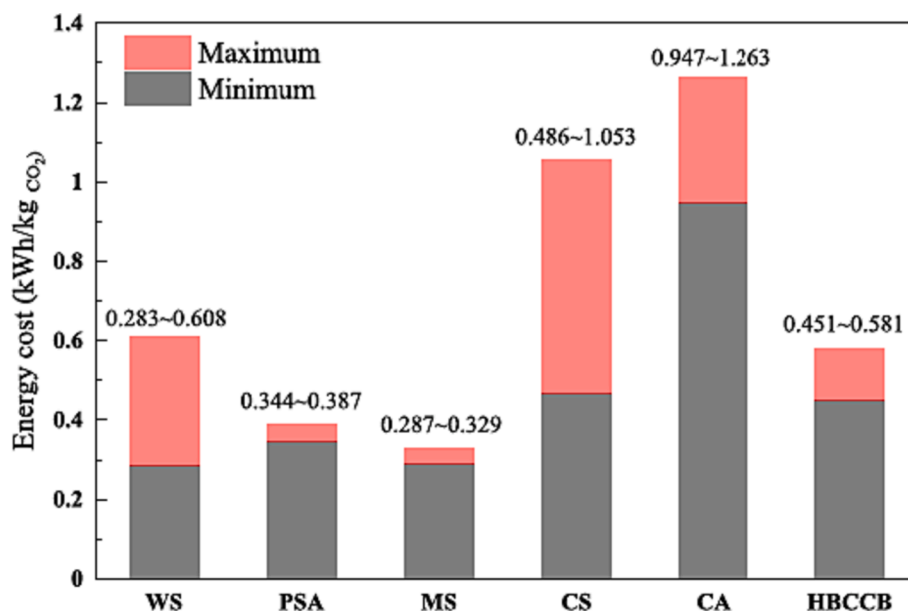


Fig. 13. Energy cost comparisons of different CO₂ capture technologies from biogas. Reprinted with permission from ref [279]. Copyright © 2022 Elsevier.

scrubbing [282]. Even if the energy cost was higher than those calculated for pressure swing adsorption and membrane separation [283], the latter did not take into account the cost of the expensive materials needed for the respective methods.

4.4. Kinetic promoters in biogas upgrading

The growth of gas hydrates is a complicated interfacial phenomena, in which multiple components (water, gas and hydrate) are distributed in multiple phases, and the growth kinetics is strongly influenced by the extent of subcooling, gas concentration, and mass transfer of water or/and gas through hydrate film [241,284].

Stirring can be helpful but the mechanical energy consumption is not negligible, accounting for 21 % of the energetic requirements for the entire process energy consumption at 1 MPa, in the presence of TBAB [279]. Several additives have shown to accelerate the formation of gas hydrate and reduce or avoid mechanical stirring, by decreasing the induction time and promoting CO₂ capture without shifting the equilibrium curve [285]. Surfactants such as sodium dodecyl sulfate (SDS) [251,286] and sulfonated lignin [287] are the most widely used kinetic promoters, alone or in combination with co-formers [288–290]. They act by increasing the gas solubility in water and reducing the interfacial tension at the gas liquid interface, thus enhancing the mass transfer of the gas to the forming hydrate [291]. However, most kinetic studies are focused on simple hydrates or CO₂/N₂ and CO₂/H₂ systems, while data available in the literature on CO₂/CH₄ mixtures are scarce and limited to laboratory scale studies [254,257,292].

By studying the effect of several anionic and zwitterionic surfactants and some lignin derivatives on the kinetics of hydrate formation in 60 mol% CH₄/40 mol% CO₂ mixture at P = 2.5 MPa, Di Profio et al. [250] demonstrated that, even if hydrate formation rate was enhanced by promoters, the process occurred with very low selectivity and the separation factor resulted lower than in non-promoted water. They suggested that the kinetic promotion exerted by surfactants favours the entrapment of the less soluble CH₄ at the expense of CO₂, and that finding additives able to promote the enclathration of one of the two gases while inhibiting hydrate formation by the other is a key challenge to obtain a more efficient CH₄/CO₂ separation.

The simultaneous use of kinetic promoters and co-formers has also been assessed. It turned out that this combination can improve both the thermodynamic conditions and the rate of the hydrate formation in

CO₂/CH₄ mixture, but it reduces the selectivity in CO₂ separation [293].

Recently, 1,1-dichloro-1-fluoroethane (HCFC-141b) has been evaluated as a possible promoting additive for capturing CO₂ from biogas by a HBGS process [294]. Indeed, HCFC-141b can form s-II hydrate, at room temperature and pressure, in which it occupies the large 5¹²6⁴ cages [295], allowing gas molecules to fill the small 5¹² empty cages. It has been proved that HCFC-141b exerts a promotion effect on hydrate formation from CO₂/CH₄ mixtures, mitigating hydrate formation conditions so that CO₂ separation could be performed under milder thermodynamic conditions [296]. Wang et al. have demonstrated that HCFC-141b acts both as thermodynamic and kinetic promoter, reducing the hydrate formation pressure and selectively promoting the rate of CO₂ hydrate formation while inhibiting the rate of CH₄ incorporation. [294]. The best performance for hydrate-based CO₂ separation from a 67 mol% CH₄/33 mol% CO₂ mixture was obtained at a feed gas pressure = 2.0 MPa, T = 284.1 K, [HCFC-141b] = 5.6 mol% and at an initial gas/liquid volume ratio of 5.10. In these conditions, the CH₄ concentration in the residual gas phase and the separation factor were 97.81 mol% and 61.38, respectively. Moreover, the CH₄ recovery ratio and the CO₂ removal ratio were 65.22 and 97.03 %, confirming that CO₂ capture is dominant with respect to CH₄. This result may seem unexpected, as it has been demonstrated that the hydrate equilibrium conditions for CH₄ + HCFC-141b + water system are milder than those needed for CO₂ + HCFC-141b + water system [291]. Authors suggested that HCFC-141b, which is not miscible with water, prevents the contact between water and the H₂O-insoluble but HCFC-141b-miscible CH₄, while it promotes a more rapid diffusion of the H₂O-soluble CO₂ in solution, by increasing the interfacial areas between H₂O and the gas. At pressures above or below 2.0 MPa, CO₂ separation is less efficient as a high driving force allows more CH₄ to enter the hydrate cages and a low driving force makes it more difficult to enter hydrates for CO₂ than for CH₄.

4.5. Porous materials

A novel approach to improve the gas hydrate formation kinetics is the addition of materials with high specific surface area, such as active carbon, coal, and silica, which can increase the gas–liquid contact area, thus increasing the heat and mass transfer at the gas–liquid interface during the hydrate formation process and offer multiple nucleation points [245,297]. In the presence of a porous material, such as active carbon, zeolites, coal and silica nanoparticles which preferentially

adsorb CO₂, the separation of a gas mixture could be improved by the synergistic effect of gas adsorption and hydrate formation in a hybrid separation method.

During the past decade, Zhang et al. [298] have performed CO₂ hybrid separation from a CO₂/CH₄ mixture (22.9 mol% CO₂ + 77.08 mol% CH₄) by using active carbon as the adsorbent. They showed that not only CO₂ molecules adsorption in the pores of active carbon occurs preferentially over CH₄ molecules, but also that more CO₂ hydrates are formed in the pores than CH₄ hydrates, thus achieving good separation efficiency. By testing different water contents, they found that, at 269.2 K, gas–solid ratio = 200 and at water content = 10.97 wt%, the molar fraction of CH₄ in the residual gas phase and the separation factor (81.89 % and 6.89, respectively) were lower than those obtained in dry active carbon (83.71 % and 7.35, respectively), as H₂O molecules occupy part of the adsorption sites without forming hydrate. However, on increasing water content to 19.23 wt%, the CH₄ molar fraction and the separation factor increased to 84.70 % and 9.99, respectively, as H₂O molecules begin to form hydrate in which CO₂ molecules are preferentially enclathrated. The best separation performance was obtained at gas–liquid ratio = 626 and initial pressure = 2.86 MPa; under these conditions, highest values of molar fraction of CH₄ in the residual gas phase (86.58 %) and of separation factor (14.26) are obtained, while the molar fraction of CH₄ in the solid phase attains a minimum value (31.16 %).

Based on the knowledge that CO₂ molecules are preferentially adsorbed on zeolite 13X compared to CH₄ molecules [299], Zhong et al. carried out hybrid CO₂ separation from a 40:60 CO₂/CH₄ gas mixture on a water-saturated fixed bed of zeolite 13X [300]. At T = 277.1 K and P = 5.2 MPa, hydrates can be formed only in the presence of 500 ppm SDS. Moreover, the best obtained separation factor of 3.55 is still too low to consider zeolite X13 a convenient candidate to improve hydrate-based CO₂ capture from CO₂/CH₄ gas mixtures.

Li et al. [301] studied the synergistic effect between hydrate formation and adsorption on a fixed bed reactor (FBR) filled with mesoporous coal particles, on CO₂ separation from a 40 mol% CO₂/60 mol% CH₄ mixture at 277.2 K, initial pressure of 3.7 MPa or 5.2 MPa, and at two bed heights of 4 cm and 6 cm. Gas uptake and rate of gas consumption were higher in the water-saturated coal FBR than in the absence of water, due to the gas hydrate formation into the pores and interstitial spaces of coal particles, and to the enlarged gas–liquid interface. Moreover, multiple nucleation for gas hydrates has been demonstrated. An increase in separation factor from 4.0 to 37.6 was observed at 277.2 K, as the initial pressure decreased from 5.2 MPa to 3.7 MPa and the bed height increased from 4.0 cm to 6.0 cm.

A particularly good separation factor of up to 257.34 and a CO₂ ratio into the hydrate phase of 99.60 % were obtained by using a silica gel bed to remove CO₂ from a CH₄/CO₂ gas mixture (60.65:36.35) with hydrate formation at P = 2.6 MPa and T = 271.1 K [302]. The formation of discontinuous ice crystals on the silica gel surface, when the temperature rose from 258.1 to 271.1 K, was demonstrated and the unstable hexagonal ice was prone to form hydrate. A normalized gas consumption of 0.018 mol/mol and a CH₄ proportion in the gas phase of only 67.18 % were still unsatisfactory and 6 stages of hydrate-based separation were estimated to be necessary for the CH₄ ratio to reach 97 %.

Very recently, silica nanoparticles, with or without potassium hydroxide, and silica nanoparticles surface-modified with (3-aminopropyl) triethoxysilane (APTES) were evaluated as suitable additives to improve hydrate-based CO₂ separation from a gas mixture composed of 74 mol% of CH₄ and 26 mol% of CO₂ [303]. Experiments were conducted at T = 277.15 K, at different pressures, particle concentrations and gas–liquid ratios. As CO₂ is acidic in water, alkaline KOH was added to increase the adsorption of CO₂ in the liquid phase, and subsequently in the hydrate phase. The obtained results showed that in 0.1 wt% silica nanofluid, P = 4.0 MPa, and gas–liquid ratio = 0.71, a significative increase in CO₂ recovery factor (+11.7 %) and in separation factor (+20.5 %) occurred, suggesting that silica nanoparticles have higher selectivity for CO₂ than

pure water, as they increase the mass transfer from gas to liquid. The addition of 0.3 wt% of KOH improved all the parameters of the separation process, with respect to pure water and the silica nanofluid. In particular, separation factors increased from 8.44 in pure water and 10.17 in silica nanofluid, to 10.90, and CO₂ recovery factor increased from 57.2 % in pure water and 63.9 % in silica nanofluid, up to 70.9 %, in the presence of KOH and in the same conditions of pressure, nanoparticle concentration and gas–liquid ratio. The concentration of CH₄ in the residual gaseous phase ($x_{CH_4}^{gas}$) was also increased by KOH, but it still remained low (86.86 mol% against 84.47 mol% in pure water and 85.57 mol% in 0.1 wt% silica nanoparticle). The highest, but still low, $x_{CH_4}^{gas}$ value (89.21 mol%) was obtained by decreasing the gas–liquid ratio to 0.14, at the expense of the separation factor which decreases to 8.65. The effect of surface modification of silica nanoparticles with APTES was also investigated and the obtained results were compared with those obtained in the presence of KOH. Indeed, amines are well-known for their reversible reactions with CO₂ [304] so the functionalization with APTES could enhance the CO₂ adsorption and selectivity, through the chemisorption of –NH₂ bond from the amine [305]. Even if APTES-modified silica nanoparticles increased gas consumption, compared with pure water, no difference was observed if compared with the system composed by silica nanoparticles and KOH. Surprisingly, the separation factor was 8.35, a value even lower than that of pure water, and the concentration of CO₂ in the hydrate phase was the lowest (56.74 mol % vs 60.83 mol% in pure water and 62.29 mol% in silica nanoparticles + KOH), indicating that the selectivity for CO₂ was reduced, compared to the other tested systems.

In Fig. 14, a comparison between the best results, in terms of concentration of CH₄ in the residual gas phase, $x_{CH_4}^{gas}$ (mol%) and separation factor, SF, obtained for hydrate-based CO₂ separation from CO₂/CH₄ mixtures in the presence of different additives and at the best experimental conditions, is reported.

As shown in Fig. 14, a multistage hydrate formation process is a fundamental prerequisite to achieve the best CH₄ enrichment in gas phase, with a huge separation factor of 257.34 when hybrid adsorption-hydrate formation with silica gel is performed. For one-stage hydrate-based separation, the technical expedient of working in pressure recovery significantly increases the process selectivity, while among all the added promoters, the most effective in improving the efficiency of hydrate separation, both in terms of separation factors and concentration of CH₄ in the residual gas phase, was HCFC-141-b which acts as a kinetic and thermodynamic promoter. It is noteworthy that HCFC-141-b shows a residence time in the atmosphere which is shorter, and an ozone depleting potential which is lower, than those of chlorofluorocarbons [306]. Moreover, it has low acute and sub chronic toxicity due to its rapid uptake and elimination [306,307], but other studies have associated overexposure to HCFC-141b with parenchymal lung injury [308].

5. Conclusions and future prospects

In this work, the most recent studies on three unconventional biogas upgrading technologies, based on ILs, DESs and clathrate hydrates, which are emerging as promising alternatives to the traditional technologies, currently available at the commercial scale, have been reviewed. Advantages, limitations, and challenges of these CO₂/CH₄ separation methods have been highlighted and their feasibility in improving the efficiency, economics and environmental benefits of biogas production has been discussed.

- The peculiar physicochemical properties, such as non-volatility, make ILs good candidates for future development in the field of biogas upgrading. The tunability of the properties of ILs by simply choosing the best combination of constituent ions or functionalizing cation and/or anion with appropriate substituents, such as carbonyl, amine, and fluorine, allows to improve IL affinity toward CO₂. ILs

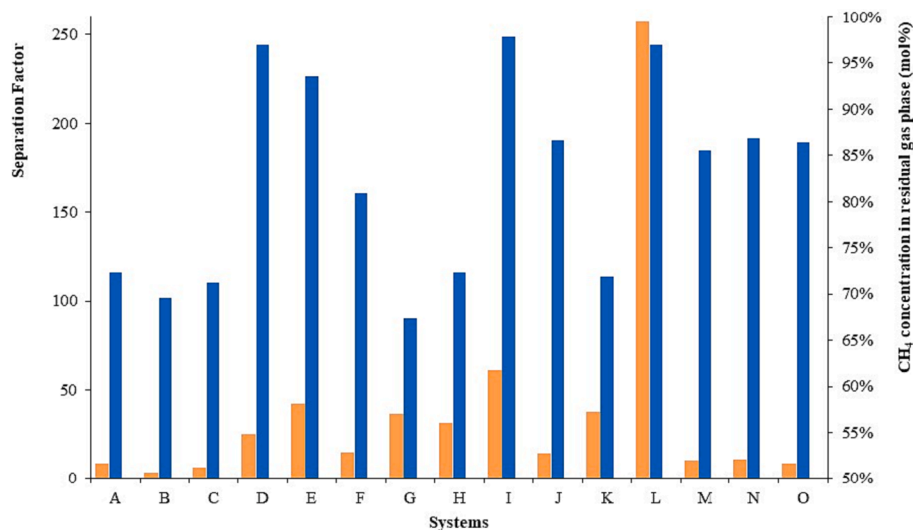


Fig. 14. Separation factors (orange columns) and concentration of CH₄ in the residual gas phase (blue columns) obtained for the different considered systems. A: pure water, T = 277.15 K, P = 2.5 MPa [260]; B: THF 1 mol% T = 277.15 K, P = 2.5 MPa [260]; C: THF 1.0 mol% + SDS 500 ppm T = 277.15 K, P = 2.5 MPa [260]; D: TBAB 5 wt%, T = 278 K, P = 3.0 MPa - after 2 stages [275]; E: TBAB 0.293 mol%, T = 281.3 K, P = 1.14 MPa - pressure recovery [276]; F: TBAB 0.29 mol%, T = 281.3 K, P = 3 MPa [294]; G: TBAB 2.57 mol%, T = 284.8 K, P = 2.8 MPa [278]; H: TBPB 2.57 mol%, T = 284.2 K, P = 2.8 MPa [294]; I: HCFC-141-b 5.6 mol%, T = 284.1 K, P = 2.0 MPa [294]; J: active carbon, T = 269.2 K, P = 2.86 MPa [298]; K: coal particles, T = 277.2 K, P = 3.7 MPa [301]; L: silica gel, T = 271.1 K, P = 2.6 MPa after 6 stages [302]; M: silica nanoparticles 0.1 wt%, T = 277.15 K, P = 4.0 MPa [303]; N: silica nanoparticles + KOH 0.3 wt%, T = 269.2 K, P = 2.86 MPa [303]; O: APTES-modified silica nanoparticles, T = 269.2 K, P = 2.86 MPa [303].

have shown competitive CO₂ solubilities and remarkable CO₂/CH₄ selectivities, especially in the form of hybrid systems based on IL immobilization onto the surface of polymeric membranes, impregnation into Metal Organic Frameworks, encapsulation into nanoparticles or sol-gel materials, which provide a synergistic effect and avoid the high viscosity of ILs and mass transfer limitation.

The use of IL-based systems for biogas upgrading is a promising field of research, however, despite IL high process efficiency, their synthesis is complex and expensive, some of them are toxic and have negative impacts on aquatic environments.

To consider ILs potentially useful for future commercial-scale operations, research efforts must be focused on improving the cost-effectiveness of IL solvents, by rationally designing task-specific ILs to further enhance CO₂ solubility, selectivity and absorption kinetics. Proper functionalizations of ILs, to promote chemical absorption of CO₂, should be investigated or ILs with low molecular weight, low viscosity and reduced pumping costs for recycling should be selected. Further studies must be carried out on the environmental impact and toxicity of ILs by testing different cation-anion combinations. Finally, data under realistic operating conditions need to be collected and pilot-plant experiments must be carried out to enable IL large-scale application, in the future.

- Compared to ILs, DESs are cheaper, easier to prepare, more biodegradable and less eco-toxic. The performances of traditional DESs in CO₂/CH₄ separation are comparable or even better than those obtained with ILs as sorbents. A highly efficient biogas upgrading can be achieved by DES-based hybrid systems in which DESs are confined into polymeric porous membrane or microcapsules. These characteristics make DESs an ideal replacement for typical organic solvents. However, the research on gas capture and separation with DESs and DES-based membranes is relatively new and experimental data for actual CO₂/CH₄ selectivities in these systems are very scarce at the present so further studies are needed to demonstrate the great potential of DES as an alternative to commercially available absorbents. Adequate knowledge of the physicochemical properties of a large number of DESs and how these properties may influence their biogas

upgrading performance is desirable to better guide the selection of the best HBA-HBD combination in task-specific DESs with high CO₂ absorption capacity and selectivity. Extensive work should be carried out to investigate the absorption performance of DES-based systems in the presence of gas mixture, as the potential competition between CO₂ and CH₄ for the sorption sites must be taken into consideration, to prove the feasibility of DESs in real biogas purification. Moreover, the possibility of a large-scale implementation of this emerging biogas upgrading technology should be explored, highlighting the possible technoeconomic benefits of using DESs as sorbents. Indeed, industrial-scale studies are still lacking and further work is needed to mature this technology for commercialization. Future research should also be directed to the investigation of ecotoxicological aspects in order to consider DESs as truly eco-friendly solvent systems which meet the criteria for green and sustainable technology.

- Biogas purification via gas hydrate-based separation can be regarded as a promising and economically advantageous method with respect to the other separation technologies. Indeed, it is a simple and green process as low-cost, non-polluting, and recyclable water is the main raw material for hydrate formation. Moreover, the large gas storage capacity of hydrates and the potential combination of the hydrate-based biogas upgrading with the conversion of captured CO₂ in synthetic methane, methanol or other chemicals, can significantly contribute to the mitigation of the GHG effects on climate. However, hydrate-based biogas upgrading technology is at its early stage and some drawbacks, such as low selectivity of CO₂ in hydrate phase and CH₄ in the residual gas phase, are still unresolved. The use of additives, despite the mitigation of the operating conditions of pressure and temperature, does not always allow to reach a CH₄ concentration in the equilibrium gas that satisfies the standards for its commercial use. Moreover, some additives are toxic and highly volatile, and their use could affect human health and pollute the environment during the separation process. The direction of future research should be focused on finding new type of low toxic, low volatile, and highly effective promoters for CO₂ hydrates, and implementing technical aspects to make the operating conditions convenient, in the perspective of an industrial application of this emerging biogas upgrading technology.

Synopsis

This review summarizes the recent advances on the potential of ILs, DESs and clathrate hydrates for CO₂ separation from biogas.

CRedit authorship contribution statement

Pietro Di Profio: Conceptualization, Investigation, Supervision. **Michele Ciulla:** Visualization, Investigation. **Stefano Di Giacomo:** Investigation, Resources. **Nadia Barbacane:** Investigation, Resources. **Rafal Damian Wolicki:** Investigation, Resources. **Antonella Fontana:** Samanta Moffa: Investigation, Resources. **Serena Pilato:** Investigation, Resources. **Gabriella Siani:** Conceptualization, Investigation, Supervision, Writing – original draft.

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. Dr. Serena Pilato thanks MUR National Innovation Ecosystem-Recovery and Resilience Plan (PNRR) Italy - Vitality (CUP D73C22000840006) for supporting her work.

Data availability

No data was used for the research described in the article.

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