

Review

New Solvents for CO₂ and H₂S Removal from Gaseous StreamsLaura A. Pellegrini, Matteo Gilardi *, Fabio Giudici and Elvira Spatolisano 

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Abstract: Acid gas removal from gaseous streams such as flue gas, natural gas and biogas is mainly performed by chemical absorption with amines, but the process is highly energy intensive and can generate emissions of harmful compounds to the atmosphere. Considering the emerging interest in carbon capture, mainly associated with increasing environmental concerns, there is much current effort to develop innovative solvents able to lower the energy and environmental impact of the acid gas removal processes. To be competitive, the new blends must show a CO₂ uptake capacity comparable to the one of the traditional MEA benchmark solution. In this work, a review of the state of the art of attractive solvents alternative to the traditional MEA amine blend for acid gas removal is presented. These novel solvents are classified into three main classes: biphasic blends—involving the formation of two liquid phases, water-lean solvents and green solvents. For each solvent, the peculiar features, the level of technological development and the main expected pros and cons are discussed. At the end, a summary on the most promising perspectives and on the major limitations is provided.



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1. Introduction

The mitigation of the climate change is one of the crucial issues to be faced in the coming decades. It has been estimated that the worldwide CO₂ emissions have grown with an average rate of 2.7% every year, reaching values 60% higher than the ones registered 30 years ago [1]. Among the main CO₂ sources, electric power generation plants and fossil fuels account for most greenhouse gases emissions. Electric power generation plants alone are responsible for about 25% of the total greenhouse gases emissions (www.epa.gov (accessed on 15 July 2021)). An efficient carbon capture from power plant flue gases and its subsequent sequestration (CCS) [2] or utilization (CCU) [3] can have a great impact in containing the global warming.

On the other hand, concerning fossil fuels, the increasing natural gas consumption has made sour and ultrasour reserves worthy of consideration for exploitation [4]. Data show that 40% of the available reserves are classified as sour, and 10% of them have a CO₂ content higher than 10 mol.% [5], which can exceed 70% in some gas fields [6,7]. In this energy scenario, biogas is also receiving attention, due to its intrinsic renewable character and, thus, its potential to serve as a replacement energy source to overcome the dependency on fossil fuels [8]. Similar to sour natural gases, biogas can contain very high amounts of carbon dioxide; the exact composition depends on the organic matter present in the waste [9] and on the type of anaerobic digestion process, which in turn depends on the origin of the residue digested. For instance, biogas obtained from the anaerobic degradation of sewage sludge, livestock manure or agroindustrial biowastes typically contains 30–47% of CO₂ on a volume basis [10]. To produce pipeline quality natural gas or biogas, such acid gases content must be reduced to 2–4 mol.% for CO₂ and 6–7 mg/m³ for H₂S [11], while in the case of LNG the CO₂ content must be lowered to 50 ppm maximum [12].

To date, the typical large-scale gas sweetening process is the chemical absorption with amines. Mono-ethanolamine (MEA) in a water 30 wt.% solution is the most common absorbing agent [13]; Methyl-diethanolamine (MDEA), 2-Amino-2-methyl-1-propanol (AMP) and piperazine (PZ) are other largely employed amines. A simplified process flow diagram of CO₂ and H₂S removal through amine washing is presented in Figure 1 [14]. The gaseous stream to be purified is contacted counter-currently with the amine-based solvent, to favor acid gases absorption. Then, the rich-solvent is regenerated in a distillation column, in which the acid gases are recovered from the top and the regenerated solvent, which is the column bottom product, is recycled back to the absorber. The main drawback of acid gas purification through amine absorption is the high energy demand associated with the regeneration column reboiler; the regeneration duty is estimated to be not less than 3.3 GJ/ton of captured CO₂ under optimal operating conditions [15]. This is mainly due both to the endothermicity of the amine regeneration reaction and to the presence of huge amounts of water, which has a high specific heat. Other major downsides of amine washing are corrosion, toxicity and volatile organic compounds emissions formed by amine degradation [16–20].

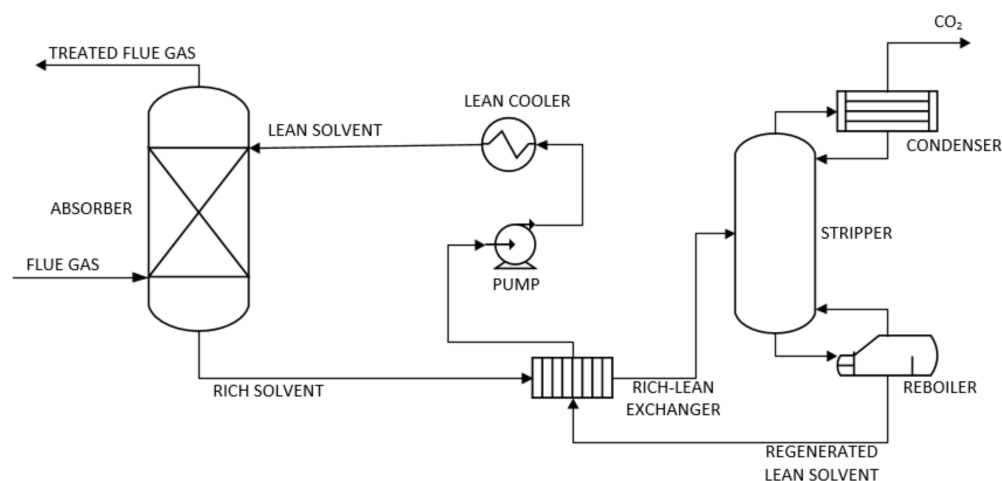


Figure 1. Typical gas sweetening by chemical absorption.

Considering all these issues, current research is devoted in finding some innovative solvents able to efficiently remove CO₂ and H₂S from different kinds of gaseous streams. These solvents should be:

- Versatile as much as possible, that is employable for treating of gases with different impurity contents;
- Nonvolatile and nontoxic;
- Characterized by a reduced regeneration heat;
- Performing if compared to the benchmark MEA process.

The aim of this paper is to present the state of the art on the latest advancements concerning innovative solvents for acid gas removal considering natural gas, biogas or flue gas applications. The panorama of novel technologies for CO₂ and H₂S removal is very wide, but emerging solvents are usually classified into three main categories: biphasic (or phase-change) solvents, water-lean solvents [21] and green solvents.

Biphasic solvents are blends which can exhibit a phase change (demixing) when loaded with CO₂. Owing to the occurrence of demixing, only a portion of the original solvent must be sent to thermal regeneration, which is potentially a great opportunity to reduce the regeneration heat. Water-lean solvents, on the other hand, contain limited amounts of water if compared with the traditional absorption agents. Finally, in view of the transition toward a green and clean energy and chemistry, green solvents derived from natural sources with limited or null toxic environmental impact are receiving attention [22].

For each category considered, two sections are developed: the first is dedicated to CO₂ removal and the second examines H₂S abatement in more detail. Some of the proposed solvents show good potential in effectively removing both acid gases, which is of special interest for natural gas sweetening.

2. Methods

Although acid gas removal through absorption has been extensively studied and analyzed in the literature, to the author's knowledge no reviews are available collecting information for different kinds of new solvents dedicated to both CO₂ and H₂S purification. CO₂ removal is typically much more studied, considering the wide variety of applications (natural gas, flue gas, syngas and biogas). Several reviews have been published in the literature with a specific focus each of the solvent categories: water-lean solvents [23–26], biphasic solvents [27–29] and green solvents [30,31]. Similar works considering H₂S are less diffuse. Shah et al. (2017) [32] screened ionic liquids for H₂S absorption, while Wazeer et al. 2021 [33] reviewed recent results on capture of hazardous gases (NH₃, SO_x, NO_x and H₂S) using different types of deep eutectic solvents.

In this work, information on acid gas absorption through innovative solvents is collected according to the three categories reported in the introduction section. For each, the available literature was reviewed and articles selected by considering the following criteria: technological maturity, process efficiency, safety and ease of implementation and scale-up, if any. For clarity, details about the numerous experimental campaigns published in the literature were organized in tables, provided in the following sections for each type of solvent analyzed.

Due to the breakthrough in this area in the last few years, recent literature was analyzed preferentially.

3. New Solvents for Acid Gas Absorption

3.1. Biphasic Solvents

Biphasic or phase-change solvents for acid gas removal are blends in which a liquid–liquid or a liquid–solid mixture formation is exploited to reduce the energy requirements for the solvent regeneration [34]. A solid–liquid equilibrium can be experienced when solvents based on amino acids [35] or amino acids functionalized ionic liquids [28] are exploited and when combining some commercial amine with an organic diluent [36]. The formation of a solid, whose nature depends on the amino acid structure (i.e., zwitterion, potassium bicarbonate), enhances the absorption reaction because the precipitating solvent from the solution forces the equilibrium toward the formation of additional absorption reaction products [35]. However, the presence of a solid phase requires a special plant design dedicated to its handling and its separation from the solution, which results in substantial modifications in the acid gas treatment plants, particularly regarding the absorption column [37,38]. As a consequence, amino-acids-based absorption can be more properly accounted for as an innovative technology rather than simply as innovative solvents for acid gas treatment. For these reasons, this section will be dedicated only to liquid–liquid demixing solvents, which can be employed without special concerns on traditional absorption-based CO₂-capture plants. The typical process scheme of the acid gas removal with a biphasic blend is depicted in Figure 2.

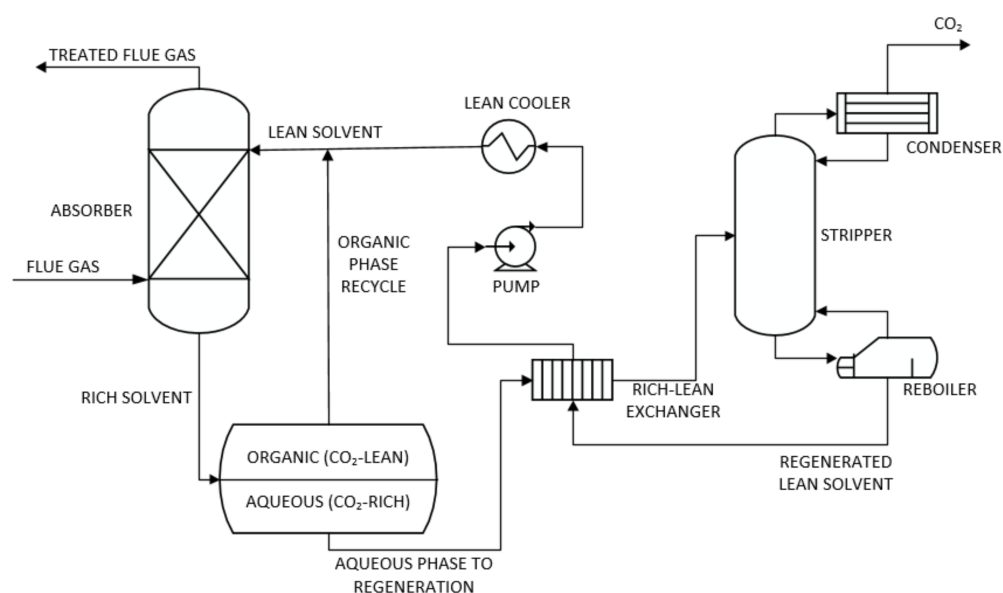


Figure 2. Typical flowsheet of a CO₂ capture process with a demixing blend.

Upon acid gas absorption or further elevating the temperature of the acid gas-loaded absorbent, it turns into two immiscible liquid phases, one acid gas-rich and the other acid gas-lean. Only the acid-rich phase needs to be sent to stripper/regenerator. The acid gas-lean phase is sent back to the absorber, combined with the regenerated gas-rich stream. In this way, the regeneration heat consumption can be drastically reduced. Among liquid–liquid equilibrium-based solvents, a wide variety of laboratory-scale and pilot-scale studies, and some patented technologies, is available [29]. Table 1 reports the advantages and disadvantages of demixing blends studied in the literature for CO₂ capture, while Table 2 summarizes the operating conditions, measured variables and the major outcomes for each experimental campaign analyzed.

In Sections 3.1.1 and 3.1.2, the detailed description of novel demixing solvents for CO₂ and H₂S removal is provided.

3.1.1. CO₂ Capture

To obtain a demixing blend for CO₂ capture, it is necessary to combine an absorption accelerator, which is a primary or secondary polyamine, with a regeneration promoter, usually a tertiary amine [39].

Ye et al. 2015 [39] proposed a methodology to carry out a first amine screening by looking at the chemical formula of the different amines; when the accelerator has 3–4 N atoms and 4–6 C atoms, an optimization of absorption and desorption performances is observed. To further guide the selection of the potential best amines to be exploited in the formation of a biphasic blend, two main parameters should be taken into account: the alkalinity, expressed by the acidic constant pK_a (throughout the manuscript pK_a stands for the protonated amine, not amine itself), and the hydrophobicity [40]. In particular, it has been demonstrated that the low primary polyamine's hydrophobicity (P) enhances the phase separation, while tertiary amine's hydrophobicity has a lower impact, even if higher values are beneficial. Concerning the alkalinity, tertiary amines having a pK_a value close to 10 are the best performing ones. In Table 3, the effect of amine's hydrophobicity on the efficiency of phase separation is shown as a result of a screening of demixing amine pairs carried out at the College of Environment, Zhejiang University of Technology, Hangzhou, China. As for acidic constant, the optimal value has been found to be 9.8. Among the screened amines, diethylethanolamine (DEEA) has an acidic constant that is very close to the optimum (approximately 9.87 [41]).

Table 1. Pros and cons of the biphasic blends studied in the literature for CO₂ capture.

Demixing Blend	References	Pros	Cons
DMX™ by IFPEN	[42] [43] [44]	<ul style="list-style-type: none"> low critical solubility absorption temperature > 40 °C estimated regeneration duty 2.3 GJ/ton CO₂ low corrosion 	<ul style="list-style-type: none"> slow absorption rate high costs for large-scale implementation
Self-concentrating absorbents (3H Company)	[29] [45]	<ul style="list-style-type: none"> low oxidative and thermal degradation low regeneration heat (1.5 MMBTU/ton CO₂) 	<ul style="list-style-type: none"> alcohol presence decreases the CO₂ loading high solvent boiling points due to presence of long-chain alcohol possible solid formation with alcohols shorter than heptanol
MEA + 1-heptanol; MEA + 1-octanol; MEA + isooctanol; DEA + 1-heptanol; DEA + 1-octanol; DEA + isooctanol	[46]	low regeneration energy	limited absorption capacity
Thermomorphic solvents by University of Dortmund	[29] [47]	<ul style="list-style-type: none"> homogeneous during absorption: lower mass transfer limitations good chemical stability low regeneration temperature (65–70 °C) 	high viscosity
DEEA-MAPA	[48] [49] [20] [50] [51] [52] [53]	<ul style="list-style-type: none"> low regeneration temperature DEEA is obtainable from green source successfully tested on a pilot scale limited corrosion 	<ul style="list-style-type: none"> DEEA is highly volatile mass transfer limitations phase separation efficient only for a highly concentrated solvent
DEEA-TETA	[54] [55] [56]	<ul style="list-style-type: none"> high absorption capacity regeneration heat up to 25% lower than MEA 30 wt.% when sulfolane is used as organic diluent good cyclic capacity 84.8% higher than MEA 30 wt.% 	<ul style="list-style-type: none"> phase separation efficient only for a highly concentrated solvent laboratory-scale characterization only very limited physicochemical characterization
DEEA-BDA	[57] [58]	efficient phase separation: >97% CO ₂ in the lower phase	very limited physicochemical characterization
DEEA-AEEA	[53]	<ul style="list-style-type: none"> nonvolatile solvent good CO₂ absorption rate 	laboratory-scale characterization only

Table 2. Demixing blends studied in the literature for CO₂ capture, with relative experimental operating conditions and provided information.

Demixing Blend	References	Gas Stream Type	Operating Conditions	Measured Variables	Outcomes
DMX TM (DMBzA + TMHDA)	[42]	Flue gas (post-combustion CO ₂ capture and storage)	P up to 10 bar; T up to 120 °C	VLE and LLE data	Solvent flowrate required for CO ₂ absorption
DMX-1	[43]	Flue gas	Thermal degradation: T = 180 °C; VLE tests: T ≤ 100 °C; P ≤ 3 bar	Phase equilibrium and heat of absorption; degradation and corrosion	DMX TM process simulation with SimSci PRO/II software
Undisclosed self-concentrating absorbent	[45]	Flue gas	Absorption: T = 35 °C; P = 1 atm; regeneration: T = 115–125 °C; P = 1 atm; oxidative degradation: T = 45 °C; thermal degradation: T ≤ 130 °C	Absorption rate and cyclic capacity; CO ₂ desorption tests and desorption rate; degradation	-
MEA + 1-heptanol; MEA + 1-octanol; MEA + isooctanol; DEA + 1-heptanol; DEA + 1-octanol; DEA + isooctanol	[29] [46]	Flue gas	Solvent concentration: 10–40 wt.%; T = 313 K	CO ₂ loading and vol.% of the two forming phases	-
MCA-DSBA DPA-DMCA	[29] [59]	Flue gas	Absorption: T = 25 °C; desorption: T = 40–90 °C	Henry constant; density; viscosity	Development and validation of a predictive thermodynamic and kinetic model for the proposed solvents
DEEA-MAPA	[20] [60]	Flue gas–CO ₂ post-combustion capture	Tests on a 90 m ³ /h flue gas flow, with a CO ₂ content variable between 1.4 and 62.2 vol.% 298 < T < 470 K	Rich loading; required solvent flow; temperature profiles; energy requirements for regeneration; volumes of the two forming liquid phases Density; viscosity (DEEA)	Development, validation and implementation of a simplified model of the DEEA-MAPA system in CO ₂ SIM Vaporization and sublimation enthalpies (Cox and Clausius– Clapeyron equations)

Table 2. Cont.

Demixing Blend	References	Gas Stream Type	Operating Conditions	Measured Variables	Outcomes
	[61]		Vapor pressures: 238 < T < 343 K. Heat capacity: 265 < T < 355 K	Vapor pressure; liquid phase heat capacity (DEEA)	Enthalpy of vaporization (Wagner and Clapeyron equations)
	[62]		300 < T < 450 K	Vapor pressure; liquid phase heat capacity (DEEA)	Antoine equation parameters
	[63]		T up to 453 K; 1 < P < 4 bar	Vapor pressure (DEEA)	
	[64]		20 < T < 80 °C	Viscosity (DEEA; MAPA; DEEA-H ₂ O; MAPA-H ₂ O)	Viscosity data correlated through NRTL-DVIS model
	[65]		303 < T < 353 K	Specific heat (MAPA and aqueous solution)	Correlation with the Sohnel and Novotny equation
	[66]		273 < T < 363 K	Vapor pressure (MAPA and aqueous solution)	
	[67]	VLE tests carried out with a N ₂ -CO ₂ gas	Concentration: 1–4 M; T = 293 K, 313 K, 333 K, 353 K	VLE data (DEEA-H ₂ O-CO ₂)	Kent Eisenberg (KE) model, electrolyte nonrandom two-liquid (e-NRTL) model and UNIQUAC model for thermodynamic equilibrium
	[68]	VLE tests carried out with a N ₂ -CO ₂ gas	T = 40, 60, 80, 100 and 120 °C; solvent concentration: 2 M and 5 M.	VLE data (DEEA-H ₂ O-CO ₂)	Development of an e-NRTL
	[69]	VLE tests carried out with a N ₂ -CO ₂ gas	60 < T < 80 °C; 3 < P < 192 kPa; solvent concentration: 3 M and 4 M	VLE data (DEEA-H ₂ O-CO ₂); heat of absorption	thermodynamic equilibrium model Development of an e-NRTL
	[70]	VLE tests with a pure CO ₂ gas	T = 40, 80, 120 °C DEEA 5M, MAPA 2M	VLE data (DEEA-H ₂ O-CO ₂ ; MAPA-CO ₂ -H ₂ O; MAPA-DEEA-CO ₂ - H ₂ O)	thermodynamic equilibrium model
	[71]			Gibbs free energy; enthalpy of formation (DEEA, MAPA and their ions)	Development of a UNIQUAC model to describe CO ₂ absorption with DEEA-MAPA
	[72]	Kinetic tests with pure CO ₂	Amine concentration: 0.8–2 kmol/m ³ ; T = 293, 303 and 318 K	Reaction rate of the global reaction (H ₂ O + CO ₂ + DEEA)	Pre-exponential factor and activation energy
	[50]	Flue gas (post-combustion CO ₂ capture)	40 < T < 80 °C; DEEA/MAPA: 5 M/2 M	Absorption and desorption tests; liquid–liquid equilibrium data	

Table 2. Cont.

Demixing Blend	References	Gas Stream Type	Operating Conditions	Measured Variables	Outcomes
DEEA-TETA	[73]	Flue gas (post-combustion CO ₂ capture)	Absorption: 30 < T < 50 °C; desorption: T = 90 °C; amine concentration: 3 M–6 M; TETA/DEEA ratio: 0.5:4.5–1.5:3.5	CO ₂ solubility and release; effect of DEEA/TETA molar ratio	Model of the CO ₂ capture process in Aspen Plus; estimation of the energy consumption
	[55]	Experimental absorption tests with a N ₂ -CO ₂ gas	TETA-DEEA solvent concentration: 20–46%; 40 < T < 60 °C	Effect of water on the reaction mechanism	
	[56]	Flue gas	DEEA-TETA- sulfolane: 4 M–1 M–2 M; T = 303 K; P = P _{atm}	Volume and CO ₂ -rich loading before and after the addition of sulfolane	
DEEA-BDA	[57]	Experimental absorption tests with a N ₂ -CO ₂ gas	BDA: 2–4 M; DEEA: 2–4 M; absorption: T = 40 °C; desorption: T = 90 °C	Amine and CO ₂ distribution in the two phases	Activation energy and pre-exponential factor
	[58]	Experimental absorption tests with pure CO ₂	BDA: 1, 2 and 3 M; DEEA: 2, 3, 4 and 5 M	Absorption capacity, CO ₂ loading and reaction rate.	
	[74]	Experimental absorption tests with a N ₂ -CO ₂ gas	25 < T < 60 °C	Absorption kinetics	
DEEA-AEEA	[53]	Experimental absorption tests with pure CO ₂	40 < T < 50 °C; DEEA: 0.1–3.8 M; AEEA: 0.1–10 M	DEEA and AEEA volatility; Henry's constant in water	Regression of parameters for a NRTL model for the DEEA-H ₂ O mixture description

A number of patents related to demixing solvents are available in the literature, the majority of which released by the Institute Français du Pétrole Energies Nouvelles (IFPEN) (Paris, France) [75–80] and 3H Company (Lexington, KY, USA) [81–86].

Svendsen et al. 2014 [87] have patented a process in which sweetening of industrial flue gases using a series of demixing blends is proposed. The proposed solvents consist of a combination of a tertiary amine and a primary or secondary amine, where the tertiary amine is DEEA and the primary and/or secondary amine(s) is (are) selected among DAB, DAP, DiAP, DMPDA, HEP, or the tertiary amine is DIPAE, or N-TBDA and primary and/or secondary amine(s) is (are) chosen among DAB, DAP, DiAP, DMPDA, HEP, MAPA and MEA. The authors claim that, by heating this solution to normal stripping temperatures of 115–125 °C, the CO₂ partial pressures obtained are much higher than those encountered under normal operation with MEA benchmark solution. This dramatically reduces the heat needed for stripping steam generation with respect to the MEA-based process, which normally makes up a substantial part of the total heat demand (about 40%).

Table 3. Effect of primary and tertiary amines hydrophobicity (P) on the efficiency of phase separation (data by Shen et al. 2018 [40]).

I Amine (Log P)	III Amine (Log P)	Lower-Phase (vol.%)	Upper-Phase (vol.%)
TETA (0.27)	DMCA (1.88)	56	44
	DMBA (1.35)	58	42
	DEEA (0.32)	67	33
	DEAPD (−0.32)	100	0
MAPA (0.65)	DMCA (1.88)	68	32
	DMBA (1.35)	72	28
	DEEA (0.32)	100	0
	DEAPD (−0.32)	100	0
BDA (1.08)	DMCA (1.88)	68	32
	DMBA (1.35)	75	25
	DEEA (0.32)	100	0
	DEAPD (−0.32)	100	0
HMDA (1.86)	DMCA (1.88)	75	25
	DMBA (1.35)	77	23
	DEEA (0.32)	100	0
	DEAPD (−0.32)	100	0

Similarly, Lu et al. 2019 [88] have patented another solvent for CO₂ capture consisting of a nucleophilic component having one or more sterically unhindered primary or secondary amine moieties, a Brønsted base component with one or more basic nitrogen moieties, a water-soluble organic solvent (5–50 wt.%) and water (5–40 wt.%). The rich forming phase contains mostly water, carbamate and conjugate acid, while the lean phase is almost made up by the organic solvent.

Kim et al. 2014 [46] collected detailed CO₂ loading and demixing efficiency data for MEA and DEA mixtures with 1-heptanol, 1-octanol and iso-octanol in a concentration range between 20 and 40 wt.%. Results show that for a benchmark 30% solvent concentration, 25% reduction in the CO₂ massive loading is experienced in the nonaqueous with respect to the aqueous blends. Nevertheless, a spontaneous and efficient phase separation occurs in the loaded solution. When MEA is used as amine constituent, the CO₂-rich phase has a volume flowrate that is approximately only the 30% of the reference aqueous MEA system, which means that only a minimal part of the original solvent must be regenerated [29].

DMXTM Solvents by IFPEN

IFPEN has developed the so-called DMXTM (demixing) solvents, which are prevalently undisclosed solvents consisting of an amine blend with a lower critical solubility temperature (LCST) above 40 °C and lower than 90 °C. The only disclosed DMX blend is the one between *N,N*-dimethylbenzylamine (DMBzA) and *N,N,N',N'*-tetramethyl-1,6-hexane-diamine (TMHDA), this last solvent showing a very slow absorption rate [42]. In the DMX technology developed by IFP and licensed by PROSERNAT (Rueil Malmaison, France), absorption is performed at 40 °C in a homogeneous solvent. Then, the rich solvent is heated to 90 °C (stripper temperature). Before entering the stripper, the heated solvent goes to a decanter, where a portion of the absorbed CO₂ is directly flashed (vapor phase) and a biphasic liquid mixture forms (similar to what depicted in Table 3). Only the watery CO₂-rich phase undergoes regeneration. Laboratory-scale experimental campaigns on the undisclosed DMX-1 blend [43] showed that this solvent exhibits favorable VLE and LLE data and can guarantee a relevant energy saving at the reboiler of the regeneration column (the estimated duty is 2.3 GJ/ton of CO₂). Moreover, DMX-1 has been proven to be far less corrosive than MEA and with a limited degradability [43].

The encouraging results emerging from the laboratory-scale testing of the DMX technology led to the development of a European project for the industrial pilot scale testing of this innovative blend. Tests should have been conducted on the 3.5 MW equivalent plant of

ENEL located in Brindisi, Italy, but the testing stopped because of the required costs for the plant retrofitting [44]. At the moment, a demonstration campaign has been programmed on a pilot plant with a capacity of 0.5 metric tons CO₂ per hour from a blast furnace gas at ArcelorMittal steel mill plant in Dunkirk, France [89,90]. This project, which is scheduled to start in 2022 and involves the participation of AXENS (Paris, France), IFPEN, ArcelorMittal (Luxembourg) and TOTAL (Paris, France), is considered the last step required before the commercialization of the DMX™ technology.

Self-Concentrating Absorbents

The self-concentrating absorbents by 3H Company consist of an amine (MEA, DEA, dibutylamine, piperazine, diisopropylamine, alanine 336) dissolved into a long chain alcohol (isooctanol and decylalcohol). They can be classified as both water-lean and biphasic solvents. Upon CO₂ absorption, two phases are formed: a CO₂-rich phase consisting of CO₂-loaded amine and unreacted amine (estimated CO₂ loading close to 27%) and a CO₂-lean phase consisting of alcohol containing some traces of lean amine. This blend, whose composition is undisclosed, can reach a rich loading of 0.5 at 35 °C and 1 atm and a lean loading of 0.02 after regeneration. The regeneration heat of only 1.5 MMBTU/ton CO₂, the absence of thermal degradation at the regeneration temperature and its oxidative degradation about eight times lower than the MEA 30 wt.% benchmark solution after a time of 15 days [45] are the major positive points. Although these are proved performances, the use of the alcohol as diluent is responsible for a 23.8% reduction in the CO₂ loading. Moreover, as only long-chain alcohols (iso-octanol, decylalcohol, 1-heptanol and 1-octanol) can guarantee liquid–liquid separation with high associated boiling points (176–195 °C), operating costs can significantly increase. If shorter alcohols are used, a liquid–solid separation occurs upon CO₂ loading, regardless of the amine used [29].

Thermomorphic Solvents

Thermomorphic (TBS) solvents by the University of Dortmund consist of lipophilic amine blends that exhibit deep regeneration at temperatures well below the solvent boiling point. Because of the limited aqueous solubility, a thermomorphic miscibility gap is generated during regeneration [47]. More specifically, these systems exhibit a thermally induced liquid–liquid phase separation which enhances CO₂ desorption at a temperature of about 80 °C, allowing operation at a lower temperature (90 °C) to achieve solvent regeneration. To regulate the phase change behavior, blended amine solvents were formulated to behave as a homogeneous solution during absorption and to form a biphasic system in regeneration. MCA (Methylcyclohexylamine)-DSBA (di-sec-butyl-amine) and DPA (diphenylamine)-DMCA (dimethylcyclohexylamine) (3:1) blends have been analyzed in detail, with an estimated phase separation temperature, respectively, equal to 60 and 70 °C [29].

Afterward, a new ternary blended solvent DMCA + MCA + AMP was formulated and selected by screening tests. This solvent, called TBS-3 absorbent, has successfully met the desired phase change temperatures; it was able to guarantee a high net CO₂ loading and it exhibited a good chemical stability. Compared to MEA, the lower values for density, surface tension and contact angle of biphasic solvent on various packing materials are beneficial, while the high viscosity, pressure drop and liquid hold-up suggest that a proper modification of the amine absorption column is necessary for the solvent applicability.

DEEA—Based Blends

Diethyl-ethanolamine (DEEA) blends have been extensively analyzed in the literature, also due to this amine acidic constant value, as discussed in Section 3.1.1.

Four DEEA blends are discussed in this section: diethyl-ethanolamine (DEEA) with 3-(methylamino)propylamine (MAPA), diethyl-ethanolamine (DEEA) with triethylenetetramine (TETA), diethyl-ethanolamine (DEEA) with (1,4-butanediamine) BDA and diethyl-ethanolamine (DEEA) with amino-ethyl-ethanolamine (AEEA).

Concerning the DEEA-MAPA blend, a detailed physicochemical characterization is available in the literature, including vapor pressure, density, viscosity, specific heat and vaporization enthalpy data [60–62,64,65], Henry's constant data [63], vapor–liquid equilibrium data [67–70], free enthalpies and Gibbs free energy of formation [71] and kinetic mechanism and global reaction rate constant [72]. Several pilot plant tests have been successfully carried out with a blend of 2M MAPA + 5M DEEA at Technology Centre Mongstad (Mongstad, Norway) in the Gløshaugen (NTNU/SINTEF) pilot plant [20]. Low reboiler duties, easy regenerability, rich loadings up to 1 mol CO₂/mol MAPA (0.4936 g CO₂/g MAPA) for solvent regeneration, no foaming and limited corrosion issues were experienced despite the high solvent concentration. The best features associated with this solvent are related to the presence of DEEA. Firstly, the energy requirement of the process is minimized when working between 3 M and 4 M DEEA solution in water [91]. No relevant corrosion phenomena are expected at such low molarity. Secondly, DEEA can be regenerated from renewable ethanol [48]. In addition, DEEA forms a minimum-boiling azeotrope when mixed with water [49,52], which turns out in a slightly lower regeneration temperature (about 110 °C instead of 120 °C).

Aside from these claimed good performances, one of the concerns is related to a high heat release occurring inside the absorber, which suggests the requirement for a higher capacity cooler before entering the absorption column, and also the potential addition of some intermediate cooling beds.

The main limitations associated with the DEEA-MAPA blend by the Norwegian University of Science and Technology (NTNU) is the high volatility of the solvent, since DEEA has a 20–30 times higher vapor pressure at absorption temperature with respect to MEA [51,53]. Therefore, non-negligible amine losses are expected to occur in the treated gas stream, which may be an environmental concern [92]. In addition, a good demixing is experienced only when the solvent concentration is high; at lower concentrations, the phase separation is expected to become negligible and more than 99% of the volume is made up by the aqueous phase [40]. The available liquid–liquid equilibrium data are not sufficient for a proper characterization of the demixing of this blend [50], since they have been collected only for an overall solvent concentration equal to 7 M and in a narrow temperature range (between 40 and 80 °C). Moreover, this blend demixes upon CO₂ loading, therefore a biphasic mixture formation occurs already inside the absorber. This feature can lead to problems of liquid/liquid mass transfer limitations [44], which could negatively influence the applicability of this solvent on a large scale, where mass transfer phenomena become more relevant.

To overcome the limits of the DEEA-MAPA blends, DEEA with triethylene-tetramine (TETA) has been proposed as an alternative. In multiple screening works available in the literature [39,40], this blend has been indicated as one of the most promising, in terms of absorption and desorption performance, among biphasic solvents.

As for the DEEA-MAPA blend, in order for the DEEA-TETA solvent to be able to demix into two heterogeneous phases, a crucial role is played by the amine concentration: no phase separation occurs for concentrations below 4 M [73]. Demixing takes place in a TETA to DEEA ratio in the range between 1:9 and 3:7, and the volume ratio of the lower phase increases as the TETA to DEEA ratio increases. This means that CO₂ reacts preferentially with TETA and that the products of the absorption reaction are concentrated preferentially in the lower phase [73]. The vast majority of CO₂ absorbed by the solvent, in fact, is concentrated in the lower phase (about 99% [73]). Water content also influences the phase separation [55]: the higher the water content, the higher the volume ratio of the lower phase; on the contrary, for lower water contents, the upper phase volume is significantly higher. Compared to the MEA solution, the DEEA-TETA solvent is able to provide a higher absorption capacity [55]. Moreover, when the total amine concentration is equal to 6 M, the absorption capacity has been found to be lower than the one of the 5 M solvent. This means that, as for the DEEA-MAPA blend, the carbon capture efficiency has a trend with a maximum as a function of the solvent molarity, while traditional solvents show a linear

increase trend. In this way, high viscosity and solid formation and precipitation can be avoided. In addition, the DEEA-TETA blend has also showed a good regenerability. The energy consumption for regeneration has been found to be 25% lower than that required for the regeneration of the aqueous 30 wt.% MEA solvent, and the regeneration temperature can be lowered to 90 °C [55,73]. The solvent performance could be further enhanced adding sulfolane as a physical activator and phase splitter. It is claimed that, by adding sulfolane, the CO₂ loading in the rich phase can be increased from 3.10 to 4.92 mol/L and the solvent regeneration heat can be decreased of about 25% with respect to the base DEEA-TETA solvent owing to the reduced water content in the solvent formulation [56]. It is worth noting that this solvent has been tested at laboratory scale only and it lacks an adequate characterization in terms of physicochemical properties and vapor–liquid equilibrium data. The presence of DEEA and its high volatility is one of the major concerns for the technology scale-up [51].

Similarly to the other analyzed blends, the DEEA-BDA blend has shown both a great cyclic capacity (48% higher) and a great cyclic efficiency (11% higher) compared to the benchmark 5 M MEA solvent [57]. The optimal solvent concentration has been chosen as a result of an experimental study. By setting the DEEA concentration equal to 4 M and mixing BDA with it, the best performance of the blend was obtained for a BDA concentration of 2 M [57]. The phase separation proved to be efficient; most of the BDA was contained in the lower phase, while the DEEA was distributed in a more uniform way [57,58]. In the upper phase, the DEEA concentration increases and the BDA concentration decreases up to a total CO₂ loading of 0.37 mol/mol of amine (0.183 g/g of amine). In the lower phase, the BDA concentration first increases to 3.58 mol/kg at a loading of 0.24 mol/mol of amine (0.119 g/g of amine) and then decreases to 2.2 mol/kg when approaching equilibrium. On the contrary, DEEA concentration first decreases to 0.9 mol/kg, and then increases again to 2.4 mol/kg [57]. As for CO₂, 97.4% of the total absorbed amount was found in the lower phase.

The mechanism and kinetics of the absorption reaction with the DEEA-BDA solvent have also been studied in detail [74]. The reaction between CO₂ and DEEA occurs in parallel with the one between CO₂ and BDA, which is characterized by a second order kinetics; in this way, BDA contributes to the absorption of CO₂ and enhances the overall rate of absorption. The main limitations of this solvent are the lack of a sufficiently deep physicochemical characterization and the lack of studies of this solvent regenerability.

More recently, Liu et al. 2021 [53] have screened a new blend in which 50 wt.% DEEA is combined with 25 wt.% amino-ethyl-ethanolamine (AEEA). The idea behind the formulation of this blend is to limit the solvent volatility by combining DEEA with a nonvolatile amine. In fact, the AEEA 2.5 M solution has an extremely low partial pressure at 40 °C (0.16 Pa), two orders of magnitude lower with respect to the one of a 7 M MEA solution, owing to the presence of lipophilic groups in its structure [53]. A laboratory-scale characterization of CO₂ solubility, mass transfer phenomena and CO₂ absorption rate have been made, showing that, at CO₂ equilibrium partial pressure lower than 100 Pa, the CO₂ absorption rate of 25% AEEA/50% DEEA solution is as fast as 30 wt.% PZ and three times faster than 30 wt.% MEA. Unfortunately, the viscosity increases with respect to 30 wt.% PZ.

3.1.2. H₂S Capture

Since H₂S is similar to CO₂ as an acidic gas, for hydrogen sulfide the study of phase-change absorption behavior could also be of value in reducing energy consumption, in principle. Nevertheless, the H₂S phase-change capture has rarely been reported in the literature compared to phase-change absorption of CO₂ and SO₂.

Only Heldebrant reported that the solution of dimethylethanolamine (DMEA) and hexane could achieve the liquid–liquid phase-change for H₂S absorption. Recently, Xu and coworkers (2019) [93] studied the phase-change reversible absorption of hydrogen sulfide by the superbase 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) in organic solvents. This species has the highest gravimetric capacity for CO₂ capture among several amidine bases,

according to the literature. Following this path, the performances of DBN were analyzed for H₂S absorption. Analyses revealed that DBN, hexanol and H₂S concentrated in the lower phase, while hexadecane stayed in the upper phase. Low viscosity, high desulfurization efficiency and good stability of the solvent confirm the potential application of this species in natural gas sweetening.

3.2. Water-Lean Solvents

The water-lean solvents category includes solvents with a limited water content, which can be tuned to optimize the absorption performances while avoiding too high a viscosity for the solvent. The presence of a reduced amount of water, which has a very high specific heat, results in a lower regeneration heat and/or temperature without affecting the chemical selectivity and, thus, the absorption capacity [24]. Water can be replaced with low volatility species; this has great potential in reducing the solvent vaporization and the subsequent makeup rate increase, and the related environmental concerns [94]. For this class of solvents to become competitive, mainly limited loading capacity and viscosity issues have to be addressed [26].

Water-lean solvents can be distinguished into blends of traditional amines (MEA, MDEA, PZ) with an organic diluent in most cases [24] and the so-called ionic liquids (ILs). The latter are salts composed of an anion and a cation that can remain in the liquid phase in a wide range of temperatures, with a practically null tendency to evaporate. Due to their high tenability and low heat capacity, they remain in the liquid state in a wide temperature range, so that they can be used at temperatures lower than those of traditional solvents [95].

Ionic liquids can also sometimes be considered as green solvents [96]. However, their greenness depends strongly on the specific IL formulation and on its synthesis route, and their toxicity is not yet fully characterized. For this reason, they cannot be accounted for as intrinsically green compounds [97].

The following sections review the state of the art for solvents used for both CO₂ capture and CO₂ and H₂S capture, while Tables 4 and 5 report the main advantages/disadvantages and the experimental operating conditions, respectively, associated with the absorbing agents considered. Currently, all studies concerning water-lean solvent application for carbon capture are mainly limited to a laboratory scale [23]. Viscosity, high solvent costs, mass transfer limitations and slow kinetic issues are the major concerns for the scale-up of this technology. One of the rare examples of a pilot plant campaign which has been already conducted is the treatment of 5000 Nm³/h of flue gas from a NGCC power plant with a mixed MEA/IL (ionic liquid) solvent containing ricyanomethanide, developed under the European project IOLICAP (novel ionic liquid and supported ionic liquid solvents for reversible capture of CO₂) [98]. Valencia Marquez et al. 2015 [99] state that the realization of an ionic-liquid-based CO₂ capture process is expected to generate higher capital costs with respect to a MEA-based plant; however, there is potential in significantly reducing the operating costs.

3.2.1. Blends of Traditional Amines

For carbon capture with blends of traditional amines, a wide variety of possible diluents have been proposed. The main ones are methanol (Amisol[®] hybrid process [100]) and higher alcohols, acetone, MEG (mono-ethylene-glycol), NMP (N-methyl-pyrrolidone), THFA (tetrahydrofurfury alcohol), sulfolane, cyclopentanone and 1-2 propanediol [101,102].

Regarding simultaneous absorption of CO₂ and H₂S, different studies were conducted.

Shoukat and coworkers (2019) [102] considered various novel amine solutions both in aqueous and nonaqueous forms (monoethylene glycol(MEG)/triethylene glycol(TEG)) for H₂S absorption. Several of the tested amines show higher H₂S absorption capacity compared to MDEA in aqueous solutions. The results pointed out that replacing water with TEG or MEG significantly decreased the H₂S loading in all tested solvents; however, the nonaqueous solution of (DEAE-EO)-MEG showed a comparable mass loading to the aqueous MDEA one at same weight concentration (0.072 vs. 0.073 g/g).

In any case, alcohols and acetone-based blends have volatility as a major limitation. On the other hand, a very low volatility together with an effective desorption enhancement is usually associated with a lower absorption capacity and several stability problems [24]. For instance, ester and amines blends can form amides or can be hydrolyzed, leading to the formation of acid compounds; ethers are easily degradable because of their tendency to form peroxides at high temperatures, while ketones can undergo enolization followed by an aldol condensation. For this reason, apart from the self-concentrating absorbents by 3H Company and the CanmetENERGY (Varennes, QC, Canada) studies on MEA-MAE (2-methylaminoethanol) in 1-heptanol or isooctanol [103], this class of solvents has progressively lost interest in recent years.

To overcome these issues, innovative water-lean solvents with no need of an organic diluent have been studied recently [24]. Alkanol-amines such as 2-(isopropylamino)ethanol (IPMEA), 2-(methylamino)ethanol (MMEA), 2-(ethylamino)ethanol (EMEA), 2-(benzylamino)ethanol (BZMEA) and 2-(butylamino)ethanol (BUMEA) can react reversibly with CO₂ forming carbamate salts that remain in the liquid phase independently from CO₂ loading. In addition, EMEA can be combined with a tertiary amine (DEEA or MDEA) acting as co-solvent: the cosolvent does not react with CO₂ but it takes part in the absorption process by extracting protons from EMEA carbamic acid, which forms as reaction intermediate. Absorption capacities are thus higher than the ones obtained by using physical diluents such as glycol ethers.

Lee et al. 2020 [104] considered CO₂ and H₂S absorption from biogas using N-methyldiethanolamine (MDEA)-based additives. Twelve different absorbents were selected and compared according to the types of the amine group and the alcohol group. In selecting additive materials, PZ, 2-amino-2-methyl-1-propanol (AMP), diethylenetriamine (DETA), tetraethylenepentamine (TEPA), bis(3-aminopropyl)amine (APA), among others, have been proved as additives for MDEA because of their excellent kinetic rate constants for CO₂ absorption. Results showed that considering MDEA mixed with 0.5 wt.% of additives based on 4.5 wt.% of concentration, MDEA/TEPA and MDEA/DETA had high loading values because of the large number of amino groups, but in the MDEA/APA mixed absorbents, they had three amine groups and showed excellent performance in the simultaneous absorption capacity of CO₂ and H₂S (CO₂ loading equal to 0.0256 g/g amine and H₂S loading equal to 5 e−5 g/g amine). This study confirms a satisfactory CO₂ absorption and regeneration capacity of MDEA/APA as an alternative absorbent, and the superiority of absorption and regeneration of H₂S and CO₂ for reusability as an absorbent through continuous experiments. In fact, the massive rich loading is increased by 20% for CO₂ and 58% for H₂S with respect to the benchmark MDEA solvent under the same solvent composition and operating conditions, while the lean loading is comparable (0.0036 vs. 0.002 g CO₂/g amine and 1.42 e−5 vs. 1.29 e−5 g H₂S/g amine).

Xu et al. [105] also studied H₂S absorption in 30 wt.% MDEA in MEG and MEG-H₂O solutions and found that increasing the water content in solution increases the H₂S loading at a given temperature. Additionally, the increase in temperature decreases the H₂S loading for a given concentration (30 wt.% MDEA—65 wt.% MEG—5 wt.% H₂O).

3.2.2. Ionic Liquids

Typically, an ionic liquid (IL) comprises a large, low-symmetry organic cation, derived by alkyl substitution on parent cations such as imidazolium, pyridinium, ammonium or phosphonium, and an inorganic or organic anion such as tetrafluoroborate, hexafluorophosphate, acetate, methyl sulfate, ethyl sulfate or triflate. Due to their polar character, ILs show a high affinity for polar molecules such as H₂O, and H₂S, while nonpolar molecules such as CH₄ and other alkanes exhibit a much smaller solubility [32]. Additionally, ILs for post-combustion carbon capture can be exploited due to the high CO₂/N₂ selectivity.

Several patents of ionic-liquid-based absorption processes have been developed and available in the literature [106,107]. For instance, Chinn et al. 2005 [106] propose a method to treat natural gas with an IL having a carboxylated functionality in its anion. Claimed

advantages are easy regenerability and good selectivity. While high solubility and selectivity for the desired molecule form the prerequisites for an IL to be useful for separation purposes, additional criteria such as thermal and mass transport through the IL can also contribute to the overall operating cost of the absorber. Due to their high cohesive energies, ILs demonstrate high viscosities, one to three orders of magnitude higher than for the conventional solvents. Higher viscosities imply higher power consumption for gas–liquid contact, but also an unusual possibility for diffusion-based selectivity in a gas–liquid system, if planning for the application of selective H₂S absorption in acid gas mixtures.

CO₂ Capture

A wide number of studies have been reported in the literature concerning the CO₂ absorption through ionic media.

Mirarab et al. 2014 [108] investigated the CO₂ solubility in a blend made up of ethanol and 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ([EMIM][Tf₂N]). Studies have been conducted under different composition conditions to determine how the ethanol content affects the CO₂ solubility. Results show that at 313 K and 1 MPa, the mass fraction of CO₂ dissolved in the liquid phase shifts from 0.03 when ethanol makes up the 20 wt.% of the solvent, and up to 0.045 when the ethanol is the 80 wt.% (the corresponding CO₂ molar fractions for the two cases are 0.101 and 0.057, respectively). With the pure ionic liquid, the CO₂ mass fraction decreases to 0.027, and viscosity becomes too high.

Dai et al. 2015 [109] studied a system combining methanol and a [OMIM]⁺[Tf₂N][−] ionic liquid. When working at 4 bar and 228 °C or at 16 bar and 0 °C, a CO₂ molar solubility in the range 0.35–0.4 (mass solubility close to 0.283, roughly) can be reached. Owing to the presence of the ionic liquid, every concern associated with methanol volatility becomes no longer relevant.

H₂S and CO₂ Capture

H₂S solubility in ionic liquids is affected by both the cation and the anion of the IL, and it may not be possible to find the best anion and cation without trying all possible pairs. Both the cation and anion can affect the mutual solubilities between water and ILs, but the anion plays the major role in determining their phase behavior. With the aid of molecular simulations, deeper insights can be gained concerning the entropic and enthalpic contributions of H₂S solubilities in different ILs.

Jou and Mather (2007) [110] first investigated H₂S absorption in an IL, 1-N-butyl-3-methylimidazolium hexafluorophosphate, and observed that H₂S only physisorbed to the IL. This further suggests that ILs are unlikely to replace alkanolamines completely but may be useful either for the bulk removal of high-partial-pressure acid gases or for mixing with a chemical solvent to increase capacity. After that, Pomelli et al. (2007) [111] extended the investigation to a wide range of cations and anions and demonstrated that ILs show extremely high H₂S solubility.

Heintz et al. (2009) [112] considered the ionic liquid TEGO IL K5, a quaternary ammonium polyether, and measured H₂S and CO₂ solubilities and volumetric liquid-side mass-transfer coefficients (k_{La}).

Within the temperature range from 300 to 500 K, the solubility and k_{La} of H₂S are greater than those of CO₂, suggesting that not only H₂S can be more easily captured from dry fuel gas streams, but a shorter absorber can also be employed for H₂S capture than that for CO₂.

Environmentally benign solvents for absorbing and using H₂S, consisting of a series of caprolactam tetrabutyl ammonium bromide ionic liquids, were explored by Guo and coworkers (2011) [113]. The H₂S absorbed in IL remains in the molecular state without any chemical reaction, allowing the IL to be reused six times without loss of capability.

Different studies demonstrated the higher H₂S solubility with respect to CO₂, considering the ionic liquids 1-ethyl-3-methylimidazoliumtris(pentafluoroethyl)trifluorophosphate ([C2mim][eFAP]) [114], 1-butyl-3-methylimidazolium bromide ([BMIM][Br]) [115] and

1-ethyl-3-methylimidazolium tetrafluoroborate ([C2mim][BF₄]) [116]. The investigation indicates that H₂S solubility in [BMIM][Br] is comparable to or better than those in commercially available MDEA-based solvents, resulting in high H₂S/CO₂ absorption selectivity. The solubility behavior is relatively maintained after four absorption–desorption cycles.

Mixtures of diisopropanolamine (DIPA) blended with 1-butyl-3-methylimidazolium acetate ([bmim][acetate]) were analyzed by Afsharpour and Haghtalab (2017) [117]. It was found that the CO₂ and H₂S mass solubilities do not change appreciably by varying the IL concentration. Additionally, Akhmetshina and coworkers (2017) [118] studied the absorption of H₂S and CO₂ by 2-hydroxyethylammonium (MEA) or triethanolammonium cations and residues of 2-hydroxy-5-sulfobenzoic acid or pyridine-3-carboxylic acid at various temperatures and partial gases pressures. Results prove that absorbents based on the 2-hydroxyethylammonium cation performed high absorption properties toward the H₂S. The results of thermal desorption analysis demonstrate that the capture of acid gases in MEA-based absorbents occurred at two stages: through the dissolution in MEA component and in protic ionic liquid.

Huang et al. (2017) [119] selected a series of tertiary-amine functionalized protic ionic liquids (TA-PILs), showing low equilibrium selectivities of H₂S/CO₂. More importantly, the TA-PILs designed are featured with low cost and facile synthesis, making them more attractive than other functionalized ionic liquids reported in the literature for application in selective separation of H₂S from CO₂.

Four novel azole-based protic ionic liquids (PILs) were also prepared by Zhang et al. (2020) [120]. Among them, 1,5-diazabicyclo[4,3,0] non-5-ene 1,2,4-1H-imidazolid ([DBNH][1,2,4-triaz]) shows the highest H₂S solubility (1.4 mol/mol or 0.249 g/g at 298.2 K and 1.0 bar) and superior H₂S/CH₄ and CO₂/CH₄ selectivities compared with results reported in the literature.

Liu and collaborators (2017) [121] synthesized seven hydroxyl ammonium ionic liquids. The solution of ethanolamine/ethanolamine lactate shows the best desulfurization capacity, and the H₂S removal efficiency can reach nearly 100% for 2 h. The mass loss and foaming rates of IL solution and aqueous solution were compared, and the results showed that the operation of hydramine/ionic liquid solution was more stable. These results indicate that hydramine/ionic liquid solutions have a potential utilization value for H₂S removal.

Recently, Chiappe and Pomelli (2017) [122] reviewed the latest achievements of ionic liquids for H₂S capture. The effect of ionic liquid anions, cations and functional groups on the H₂S absorption is pointed out. According to the authors, the limited number of functionalized ILs (including also protic ILs) tested and the positive results obtained, despite the absence of a systematic investigation strategy for these experiments, suggest the existence of large margins for the further optimization of absorbents.

3.2.3. Amino Acid-Functionalized Ionic Liquids

A further step forward in the ionic-liquid-based solvent panorama is represented by amino acid-functionalized ionic liquids, in which the deprotonated amino acid is used as an anion or cation (AAILs). Such formulations have been mainly investigated as aqueous solvents in which the formation of a solid phase, that is, bicarbonate crystallization, occurs under appropriate operating conditions, i.e., high concentrations or high CO₂ loading during CO₂ absorption. These formulations allow for obtaining a good tradeoff between viscosity and absorption capacity (i.e., the 30 wt.% 1-(3-aminopropyl)-3-(2-aminoethyl)imidazolium alaninate ([Apaeim][ala]) solution [95]), but at the same time they exploit the advantages of solid-state sorbents, such as lower regeneration energy and temperature and negligible solvent losses caused by evaporation [123]. The crystallization of the amino acid salts is expected to decrease their concentration in the solution, which leads to the formation of more products that turns out in a higher CO₂ loading [27]. Furthermore, the precipitation of carbonate allows for easy separation and regeneration of the CO₂-loaded solvent. On the contrary, the main limitation is the very slow reaction kinetics [124]. The research in

amino-acid-based solvents with limited water content is unfortunately very poor, mainly due to viscosity issues becoming dominant under CO₂ loading, as observed in the experimental campaign by Zhang et al. (2006) [125], who investigated a special “task specific ionic liquid”, composed of tetrabutylphosphonium amino acid [P(C₄)₄][AA]. A possible diluent for this class of solvents is ethylene glycol [126]; it may be selected since it has a high boiling point and the flexible poly(ethylene oxide) chain is able to coordinate with alkali-metal cations, resulting in a higher capacity.

Very recently, Liu et al. (2020) [126] screened a novel amino-functionalized ionic liquid [TEPAH][2-MI] combined with N-propanol or ethylene glycol. Results show a very good absorption capacity (rich loadings up to 1.72 mol/mol—28 wt% and 257 g/L—were obtained). The viscosity turned out to be below 8 mPa·s throughout all the process, which is low in comparison to that observed for the majority of water-lean solvents.

3.2.4. CO₂—Binding Organic Liquids

A special class of switchable ionic liquids [127] is the so-called CO₂-BOLs (CO₂ binding organic liquids). CO₂-BOLs consist of an alcohol and an amidine or, more often, a guanidine base that is able to chemically bond CO₂ leading to the formation of amidinium or guanidinium alkyl-carbonate, respectively, as reaction products [25]. Alcohol and CO₂ react and form an alkyl-carbonic acid, which in turn protonates the base (which must be very strong). To limit the solvent volatility, alkanol-amidine or guanidine is the preferred species, so that both functionalities are available inside the same molecule. These innovative solvents present several important advantages [24,25]: they can be easily regenerated due to a low CO₂ binding energy, the regeneration column's temperature can be limited to 90 °C, the CO₂ uptake remains almost unchanged in time (good durability), they have low foaming tendency (on the contrary of aqueous solvents) owing to high density and low surface tension, low corrosive power and mass transfer increases at decreasing temperatures, and finally they can also efficiently remove SO₂. CO₂-BOLs for the capture of one or more impurities (CO₂, COS, CS₂, SO₂, SO₃) from gaseous streams have been patented [128,129].

Since single CO₂-BOLs form polar zwitterionic compounds, the traditional thermal regeneration can be enhanced with the PSAR technique (polarity swing-assisted regeneration), consisting in the addition of a nonpolar inert compound (called antisolvent) to the reactive system [25]. The antisolvent must have a low tendency to evaporate before performing solvent regeneration [130]; usually an alkane between heptane and decane is exploited. This antisolvent changes the polarity of the environment, which is full of polar alkyl-carbonate species, so that CO₂ release from the polar reaction products is significantly enhanced. It can be recovered after desorption by cooling the system: an L-L phase separation can be in fact be obtained below the critical temperature. The eventual presence of the antisolvent does not negatively affect absorption. Some CO₂-BOLs-based technologies exploiting these features have already been patented by Heldebrandt et al. [128,129].

However, several limitations have been detected. Application of some amines led to the formation of solid products, which is detrimental for practical applications [131]. Alkanolguanidines show an exponential viscosity increase at increasing CO₂ loadings (up to 103 cP at full loading); the only way to maintain the control of viscosity is to operate with limited CO₂ loadings. Moreover, significant mass transfer limitations and high viscosity are experienced, resulting in higher solvent circulating flows. Finally, the high viscosity and the low thermal conductivity negatively affect CAPEX.

Recently, CO₂-BOLs made up of 1,1,3,3-tetramethylguanidine (TMG) as a superbase, an alkanol (methanol, n-butanol, sec-butanol, and 1-hexanol), and an amine (EEA, MEA, AMP, DEA, AEEA, PZ, TETA and DETA) were characterized in terms of absorption rate and CO₂ loading [131]. The results show that, owing to the addition of MEA, the ternary CO₂-BOL made up of methanol-TMG and MEA does not form any bicarbonate salt, which limits the regeneration efficiency and the solvent applicability.

Table 4. Pros and cons of the water-lean solvents studied in the literature, considering both CO₂ capture and H₂S and CO₂ capture.

Water–Lean Blend	References	Pros	Cons
CO₂ capture			
[OMIM] ⁺ [Tf ₂ N] [−]	[109]	<ul style="list-style-type: none"> • low volatility; • high thermal stability; • strong soluble capacity 	<ul style="list-style-type: none"> • high viscosity; • high cost
CO ₂ -binding organic liquid	[130] [131]	<ul style="list-style-type: none"> • high CO₂ loading; • high selectivity; • high regeneration efficiency; • no foaming; • low corrosion; • good durability 	<ul style="list-style-type: none"> • mass transfer limitations; • limited CO₂ loadings; • possible solids formation; • high CAPEX
[TEPAH][2-MI]	[126]	<ul style="list-style-type: none"> • low regeneration energy; • low viscosity 	<ul style="list-style-type: none"> • possible solids formation
[EMIM][Tf ₂ N]	[108]	<ul style="list-style-type: none"> • low volatility; • low viscosity 	<ul style="list-style-type: none"> • poor characterization
CO₂ and H₂S capture			
Diisopropanolamine (DIPA) with 1-butyl-3-methylimidazoliumacetate ([bmim][acetate])	[117]	<ul style="list-style-type: none"> • at low DIPA concentration, low CO₂ solubility experienced; • the presence of the IL in each concentration may lead to intensify selectivity of solution toward H₂S 	
2-hydroxyethylammonium pyridine-3-carboxylate (MEA[Nic]); 2-hydroxyethylammonium 2-hydroxy-5-sulfobenzoate (MEA[Sulf]); triethanolammonium (TEA) pyridine-3-carboxylate (TEA[Nic]); triethanolammonium 2-hydroxy-5-sulfobenzoate (TEA[Sulf])	[118]	<ul style="list-style-type: none"> • low cost; • high absorption capacity 	<ul style="list-style-type: none"> • high density; • high viscosity
Caprolactam (CPL); tetrabutyl ammonium bromide (TBAB)	[113]	IL reused six times without loss of capability	

Table 4. Cont.

Water–Lean Blend	References	Pros	Cons
1-butyl-3-methylimidazolium bromide [BMIM][Br]	[115]	<ul style="list-style-type: none"> H₂S solubility comparable to or better than MDEA; lower energy requirement for the stripping process than amines 	lower CO ₂ solubility than amines
tertiary-amine functionalized protic ionic liquids (TA-PILs): [TMEDA][AcO]; [TMPDA][AcO]; [BDMAEE][AcO]; [BMEE][AcO]	[119]	<ul style="list-style-type: none"> high absorption capacities; low cost; facile synthesis 	high viscosity
[Bmim]BF ₄ ; [C ₃ OHmim]BF ₄ ; MEA-(C ₃ OHmim]BF ₄)	[132]	adding MEA to [C ₃ OHmim]BF ₄ increases the solubility of H ₂ S	
1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate [C ₂ mim][eFAP]	[114]		lower absorption capability compared with other ILs
1-ethyl-3-methylimidazolium tetrafluoroborate [C ₂ mim][BF ₄]	[116]		small affinity for CO ₂ and H ₂ S
ethanolamine/ethanolamine acetate (MEA-A); ethanolamine/ethanolamine formate (MEA-F); ethanolamine/ethanolamine propionate (MEA-P); ethanolamine/ethanolamine lactate (MEA-L); di-ethanolamine/diethanolamine acetate (DEA-A); tri-ethanolamine/triethanolamine acetate (TEA-A); N-methyl diethanolamine/N-methyl diethanolamine acetate (MDEA-A)	[121]	<ul style="list-style-type: none"> MEA/MEA-L could be regenerated for many times without significant mass loss; reduced corrosion 	
1-butyl-3-methylimidazoliumchloride ([C ₄ mim]Cl); 1-butyl-3-methylimidazoliumtetrafluoroborate ([C ₄ mim]BF ₄); 1-butyl-3-methylimidazoliumhexafluorophosphate ([C ₄ mim]PF ₆); 1-butyl-3-methylimidazoliumbis (trifluoromethyl)sulfonylimide ([C ₄ mim]NTf ₂)	[133]	can be recycled more than six times while keeping 100% desulfurization efficiency	

Table 4. Cont.

Water–Lean Blend	References	Pros	Cons
[H ₂ PO ₄] [−] –based ILs	[134]	<ul style="list-style-type: none"> negligible vapor pressure; high chemical/thermal stability; designable and tunable character 	
Azole-based protic ionic liquids	[120]	<ul style="list-style-type: none"> excellent absorption capacity; facile preparation process; high H₂S/CH₄ and CO₂/CH₄ selectivity 	

Table 5. Water–lean solvents studied in the literature with relative experimental operating conditions and provided information.

Water–Lean Blends	References	Gas Stream Type	Operating Conditions	Measured Variables	Outcomes
CO₂ capture					
[OMIM] ⁺ [Tf ₂ N] [−]	[109]	Syngas	228.2 < T < 273.2 K	Solubility	Fugacity coefficient; Henry's law constants
CO ₂ -binding organic liquid	[131]		T = 308.2 K; P = 25 bar	Solubility	
[TEPAH][2-MI] + N-propanol or ethylene glycol	[126]	Flue gas	303.15 < T < 393.15 K	Viscosity	
[EMIM][Tf ₂ N] + ethanol	[108]		T = 313.2 and 333.2 °C 0 < P < 7 MPa	Solubility	
CO₂ and H₂S capture					
Diisopropanolamine (DIPA) with 1-butyl-3-methylimidazoliumacetate ([bmim][acetate])	[117]	Natural gas	DIPA + ionic liquid: 50 wt.% + 5 wt.%; 50 wt.% + 10 wt.%; 30 wt.% + 5 wt.%; 30 wt.% + 10 wt.%; 50 wt.% + 50 wt.%; T = 323.15 and T = 348.15 K; 0.2 < P < 2.5 MPa	Solubility	
2-hydroxyethylammonium pyridine-3-carboxylate (MEA[Nic]); 2-hydroxyethylammonium 2-hydroxy-5-sulfobenzoate (MEA[Sulf]); triethanolammonium (TEA) pyridine-3-carboxylate (TEA[Nic]); triethanolammonium 2-hydroxy-5-sulfobenzoate (TEA[Sulf])	[118]	Biogas and natural gas	T ≤ 373.15 K	Solubility; density; viscosity	Henry's law constants

Table 5. Cont.

Water–Lean Blends	References	Gas Stream Type	Operating Conditions	Measured Variables	Outcomes
Caprolactam (CPL) and tetrabutyl ammonium bromide (TBAB)	[113]	Natural gas	$303.2 < T < 363.2 \text{ K}$; $P = P_{\text{atm}}$	Solubility	
1-butyl-3-methylimidazolium bromide [BMIM][Br]	[115]	Natural gas	$T = T_{\text{amb}}$; $P = P_{\text{atm}}$	Solubility	Selective absorption of H_2S over CO_2 ; molecular simulation and density functional calculations
TEGO IL K5 (quaternary ammonium polyether)	[112]	Dry fuel gas and syngas	$T \leq 500 \text{ K}$; $P \leq 30.0 \text{ bar}$	Solubility	Henry's law constants; volumetric liquid-side mass-transfer coefficients
Tertiary-amine functionalized protic ionic liquids (TA-PILs): [TMEDA][AcO]; [TMPDA][AcO]; [BDMAEE][AcO]; [BMEE][AcO]	[119]	Natural gas	$298.2 < T < 333.2 \text{ K}$; $P = P_{\text{atm}}$	Solubility; density; viscosity	Absorption kinetics
[Bmim]BF ₄ ; [C ₃ OHmim]BF ₄ ; MEA-([C ₃ OHmim]BF ₄)	[132]		$T = 25 \text{ }^\circ\text{C}$	Solubility	
1-ethyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate [C ₂ mim][eFAP]	[114]	Natural gas	$303 < T < 353 \text{ K}$; $P \leq 2.0 \text{ MPa}$	Solubility	Henry's law constants; $\text{CO}_2 + \text{H}_2\text{S}$ selectivity
1-ethyl-3-methylimidazolium tetrafluoroborate [C ₂ mim][BF ₄]	[116]	Natural gas	$298.15 < T < 353.15 \text{ K}$; $P \leq 2.0 \text{ MPa}$	Solubility	Henry's law constants; partial molar volumes at infinite dilution
MDEA blendend with: PZ; 2-amino-2-methyl-1-propanol (AMP); diethylenetriamine (DETA); tetraethylene-pentamine (TEPA); bis(3-aminopropyl)amine (APA); 1-dimethylamino-2-propanol (DEP); 2-Amino-1-butanol (AB); 5-Amino-1-pentanol (AP); N-Propylethylenediamine (PED); 1,4-diaminobutane (DAB); dibutylamine (DBA)	[104]	Biogas	Absorption: $T = 30 \text{ }^\circ\text{C}$; regeneration: $T = 80 \text{ }^\circ\text{C}$	Absorption and regeneration tests	

Table 5. Cont.

Water–Lean Blends	References	Gas Stream Type	Operating Conditions	Measured Variables	Outcomes
ethanolamine/ethanolamine acetate (MEA-A); ethanolamine/ethanolamine formate (MEA-F); ethanolamine/ethanolamine propionate (MEA-P); ethanolamine/ethanolamine lactate (MEA-L); di-ethanolamine/diethanolamine acetate (DEA-A); tri-ethanolamine/triethanolamine acetate (TEA-A); N-methyl diethanolamine/N-methyl diethanolamine acetate (MDEA-A)	[121]		T = 25 °C; P = P _{atm}	H ₂ S removal efficiency	
1-butyl-3-methylimidazoliumchloride ([C ₄ mim]Cl); 1-butyl-3-methylimidazoliumtetrafluoroborate ([C ₄ mim]BF ₄); 1-butyl-3-methylimidazoliumhexafluorophosphate ([C ₄ mim]PF ₆); 1-butyl-3-methylimidazoliumbis(trifluoromethyl)sulfonylimide ([C ₄ mim]NTf ₂)	[133]		80 < T < 180 °C; P = P _{atm}	Solubility	Absorption mechanism
Azole-based protic ionic liquids	[120]	Natural gas	298.2 < T < 333.2 K; 0 < P < 1 bar	Solubility; density; viscosity	Henry's constants; equilibrium constant

3.3. Green Solvents

The last group of solvents for acid gas removal is the so-called green solvents, which are receiving more interest in recent years as a result of the increasing environmental policies and regulations.

To the green solvents group belong all those species with at least some of the following characteristics:

- Good biodegradability;
- Low toxicity;
- Low volatility and low associated emissions to the atmosphere;
- Renewable origin;
- Low environmental impact.

The green solvent selection is performed with reference to the green-chemistry principles stated by Anastas and Warner (1998) [135].

The most widely investigated green formulations showing a potentiality in carbon capture applications are some ionic liquids and the deep eutectic solvents (DESs) [31,136]. The general properties of ionic liquids (combustible nature, high viscosity and toxicity, complex synthesis routes involving a number of precursors [137]) are the reasons why they are often not included in the list of green solvents. Only amino-acids-based ionic liquids can strongly reduce nonbiodegradability and toxicity, enhancing at the same time CO₂ absorption. A brief introduction to these AAIL-based formulations is reported in Section 3.2, since ILs can be employed also as water-lean solvents. Apart from the viscosity concerns associated with nonaqueous AAILs, the water-based AAILs have also not been

widely investigated since the unsatisfactory kinetics is a major limitation to large-scale applications [124].

In contrast, deep eutectic solvents are mixtures whose melting points are considerably reduced when their constituents are mixed, as illustrated in Figure 3. Thus, even though DES is being formed from solid components with very high melting points, the mixture can be liquid at room temperature. They typically consist of a hydrogen bond donor (HBD) combined with a hydrogen bond acceptor (HBA), which is a coupling of Brønsted or Lewis acid–base.

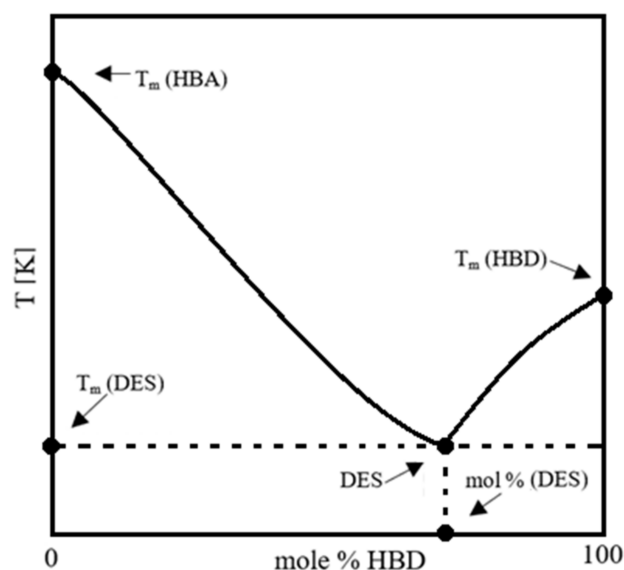


Figure 3. Schematic solid–liquid phase diagram for a binary mixture between an HBA and an HBD. T_m stands for the melting point.

They share a lot of features with ionic liquids, but in general they have a lower toxicity, limited price, higher biodegradability, stability and biocompatibility and they have lower flammability [22,31]. A great variety of DES exists (from 10^6 to 10^8 possible combinations). Even if potential DES toxicity effects are still under debate and a detailed DES characterization under different environmental impact categories is not yet available [138], it is undoubted that these solvents present several environmentally benign features in comparison to the traditional solvents commonly employed in chemistry.

DESs are generally classified into four main categories depending on different combinations and types of components, as summarized in Table 6.

Table 6. Classification of deep eutectic solvents (adapted from Karivayev (2020) [139]).

Type	General Formula	Terms
I	$\text{Cat}^+\text{X}^-z\text{MCl}_x$	$\text{M} = \text{Zn, Sn, Fe, Al, Ga, In}$
II	$\text{Cat}^+\text{X}^-z\text{MCl}_x \cdot y\text{H}_2\text{O}$	$\text{M} = \text{Cr, Co, Cu, Ni, Fe}$
III	$\text{Cat}^+\text{X}^- \text{RZ}$	$\text{Z} = \text{CONH}_2, \text{COOH, OH}$
IV	$\text{Cat}^+\text{X}^-z\text{MCl}_x$	$\text{M} = \text{Al, Zn}$ $\text{Z} = \text{CONH}_2, \text{OH}$

Type I DESs are mixtures of quaternary ammonium salts and metal chlorides; Type II are mixtures of quaternary ammonium salts and metal chloride hydrates; Type III are mixtures of quaternary ammonium salts and hydrogen bond donors; and lastly, Type IV are mixtures of metal chloride hydrates and hydrogen bond donors. Similar to ILs, the components of DESs can be tailored depending on the desired application. The most

widely employed are the TYPE III-DESs, which are made up of a quaternary ammonium salt in combination with an amide, amine, carboxylic acid or polyol [30].

Moura and coworkers [140] reported the solubility of many gases considering several DES.

The main pros and cons related to their application are summarized in Table 7, considering the available examples studied in the literature. In Table 8, the operating conditions, measured variables and the major outcomes for each experimental campaign are summarized. The DES general positive characteristics are a very low volatility and vapor pressure (no solvent losses are expected), high thermal stability, biodegradability (many have low toxicity), low price and easy preparation (the simplest technique just involves heating and stirring under an inert atmosphere, no purification steps are required). On the contrary, the main expected limitations are viscosity, lack of adequate physicochemical characterization and inadequacy of the available thermodynamic models to well represent the strong hydrogen-bond generated interactions between the molecules that occur in these kind of systems, huge variability of DESs properties and behavior as a function of pressure, temperature and composition of the HBA:HBD mixture [22,30]. The high viscosity typical of DESs is generally managed by mixing them with water; PEG100 can sometimes also be added as a diluent.

As for the ionic liquids, DESs are currently still investigated at a laboratory scale. It is therefore too early to understand their real potential for large-scale applications. As recommended by Wazeer et al. (2021) [33], pilot plant campaigns should be performed in order to move toward an industrial scale utilization of the selected DESs in the capture of CO₂ under different operating conditions.

3.3.1. CO₂ Capture

Deep Eutectic Solvents

Concerning CO₂ capture, it has been observed that CO₂ absorption depends on the strength of inter- and intramolecular interactions or the free volume [141]. A wide class of DESs formulations has been tested in terms of CO₂ capacity and water content effect [141,142].

Mirza et al. (2017) [143] have studied the performance of some DESs as a new solvent for CO₂ capture. Four different formulations were prepared by mixing guanidine carbonate, malic acid, ethylene glycol, arginine and water in certain molar ratios. Water content not higher than 15–30 wt.% is reported to be sufficient to moderate the solvent viscosity while maintaining the uptake capacity. Therefore, such mixtures could share their green character with the advantages of a water-lean solvent (see Section 3.2).

Choline chloride + urea and choline chloride + ethylene glycol are among the most promising DES for CO₂ capture because they show high CO₂ uptake with limited viscosity [144]. The great majority of DESs formulations can absorb CO₂ just through a physisorption mechanism. However, some special DESs able to react with CO₂ also exist. An example is the [EMIM][2-CNpyr]: EG (1:0.5–1.10) solvent studied by Lee and coworkers [145]. The authors carried out a detailed reaction mechanism investigation, pointing out that carbonate formation is the dominant reaction while carbamate formation is minimal. Such formulations show optimal selectivity, since CO₂ is mainly chemisorbed while CH₄ and other gases are only partially physisorbed [146].

A particular group of deep eutectic solvents for CO₂ capture is made by hydrophobic DESs which are able to demix upon a temperature change. For this reason, they are potentially both green and biphasic solvents. In recent years a list of possible hydrophobic DESs have been characterized, but mainly for applications related to the removal of pollutants, pesticides and pigments from water and diluted aqueous solutions [147–151]. Zubeir et al. (2018) [152] were the first to measure CO₂ solubility in a number of hydrophobic DES.

More recently, Haider et al. (2020) [153] investigated the performances of a DES composed of tetrabutyl ammonium bromide (TBAB), which is the hydrogen bond acceptor, and combination of two fatty acids among capric, lauric and oleic acid, performing as

hydrogen bond donor. A quite limited CO₂ uptake was observed: at 298 K, the CO₂ solubility reaches values up to 0.3 and 0.2 mol CO₂/mol DES (0.048 and 0.0355 g CO₂/g DES) at 15 bars with both oleic-capric and lauric-capric fatty acid blends. A similar study was realized by Gu et al. (2020) [154], in which a new kind of hydrophobic DES formed by polyamine hydrochloride and thymol (1:3) was synthesized. The CO₂ capacity reaches a value up to 1.355 mol CO₂/mol DES (0.353 g CO₂/g DES) at 40 °C and 101.3 kPa; this blend is reported to be able to capture carbon dioxide both physically and chemically.

Longeras et al. (2020) [155] studied a special DES which is able to demix into an organic and an aqueous phase upon a change in the temperature. However, this phase separation temperature is too low in order to be able to work under homogeneous conditions inside the absorber. Moreover, unfortunately the 62% of CO₂ dissolves in the organic phase, which means that the phase separation is not very efficient, and in general the CO₂ solubility is very low (molar solubility close to the one of CO₂ in water). In order to enhance the absorption capacity and the phase separation efficiency, while keeping all the advantages of a biphasic DES (low volatility and environmental impact, easy tenability of the phase separation temperature by properly modifying the DES HBA/HBD ratio, lower regeneration heat), DES-amine blends have been investigated. Sarmad et al. (2020) [156] functionalized DES made up of choline chloride-ethanolamine with different types of amines: diethanolamine (DEA), methyldiethanolamine (MDEA), piperazine (PZ) and 1-(2-aminoethyl)piperazine (AEP). The solubility of CO₂ was determined at a temperature of 298.15 K in a pressure range up to 2 MPa. Loadings close to 0.16 g CO₂/g DES were obtained at a pressure of 20 bar (0.4 in molar terms) in absence of blended amines. When MDEA was added (1 mol MDEA/8 mol DES), the loading was lowered to 0.15 g CO₂/g DES; in contrast, by adding PZ, an increase of the loading up to 0.22 g CO₂/g DES was detected.

Physical Absorbents

Recently, research attention has also been focused on some naturally derived compounds that show good CO₂ solubility and which can, therefore, represent a valid alternative to the commonly used solvents for physical absorption of CO₂ (such as methanol, dimethyl-ether of polyethylene glycol (DEPG) and propylene carbonate (PC)) [157].

In this kind of absorption no chemical reaction occurs, which results in a lower regeneration heat, but also in a more limited loading and absorption capacity.

Several absorbing agents have shown good potential to physically absorb CO₂. Among them, dihydrolevoglucosenone, also called CyreneTM [158], is a derivative of levoglucosenone, which is in turn obtained directly from cellulose (Figure 4). Circa Group PTY produces levoglucosenone through a continuous process using sawdust as renewable raw material. Final hydrogenation can be performed using Pd catalyst with yields higher than 90% [159]. This solvent is attractive due to its similar dipolarity with respect to NMP, DMF, DCM and sulfolane, which are toxic and oil-derived solvents [160].

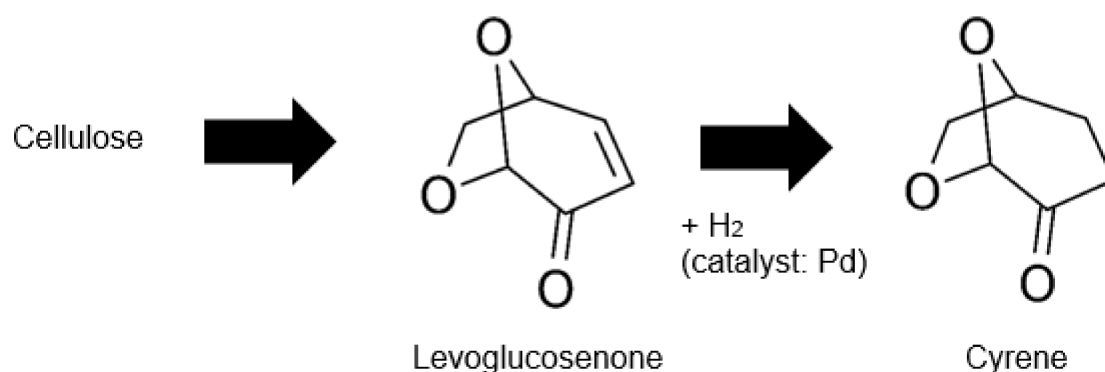


Figure 4. Synthesis of Cyrene, a derivative of cellulose.

It is claimed that even better performance can be obtained by adding Cyrene™ to renewably produced ethylene glycol, forming the so called Cygnet 0.0 solvent (ketal derivative of Cyrene™). At the moment, the main uses of this solvent are beyond carbon capture and related to fluorination (widespread in the pharmaceutical industry) and Heck reactions. An application as an alternative solvent in polymer synthesis (i.e., for the nanocomposite polymer production) has been patented, considering its great performance in terms of dispersion and solvation [161]. This solvent has a physicochemical behavior that is very close to that of NMP [160], which has been considered as a physical solvent for gas sweetening in the Purisol™ solvent by Lurgi [157]. Therefore, a satisfactory CO₂ solubility is expected, even if there is still lack of literature data.

Carbonate-based solvents have shown promising results for potential carbon capture applications, particularly for the case of dimethyl-carbonate (DMC). DMC is considered as a potential green solvent because its leaving group decomposition leads to the formation of only CO₂ and methanol as byproducts. It can be produced by a reaction between CO₂ and an epoxide or between urea and methanol, in which no Cl-containing molecules are involved [162]. DMC is claimed to be a good physical solvent for CO₂ capture, because at ambient temperature the CO₂ solubility in DMC is comparable to methanol, which is a benchmark CO₂-capture physical solvent (0.33 wt.% versus 0.39 wt.% at a pressure of 3 MPa), it is nontoxic and chemically stable and it has low volatility and good selectivity [163]. A process for CO₂ removal by dimethyl-carbonate was patented in 2016; DMC absorbs CO₂ and is then regenerated through a two-stage expansion and stripping with N₂. The claimed advantages are a CO₂ capture efficiency up to 95%, milder temperature conditions than Rectisol® process (CAPEX reduced of 30%), limited viscosity (0.9–6 mPa·s) and low price.

Another potential physical solvent for CO₂ removal is 1,2,3 trimethoxypropane (1,2,3 TMP) that is characterized by properties comparable to diglyme, a key component of the SELEXOL™ solvent [164]. 1,2,3 TMP is a low-toxicity solvent obtainable with 78% yield and 96% selectivity, without any need for a solvent or heat power, directly from glycerol, which in turn can be derived from vegetable matter or animal fats. Currently, this solvent is primarily investigated for applications in reduction of nitro, ester and acid functions [165], transesterification reactions between glycerol and vegetable oils organometallic, C-C coupling and etherification reactions, solvation of metal cations (such as Li⁺ and Na⁺) and solubilization of polymers such as polystyrene and polycaprolactone (at high extent), and of cellulose acetate and PVC, at moderate extent [165]. Flowers et al. (2017) [164] has shown that TMP has low toxicity, negative skin synthetization and mutagenicity, and low toxicity for the aquatic environment, and has the same molecular weight and similar CO₂ solubility, density and viscosity in comparison with diglyme. When compared to DMPEG (Selexol™ solvent), TMP has 10–15% higher CO₂ solubility (mol/L) at 25–30 °C and more than five times lower viscosity at 25 °C [164]. Moreover, the selectivity of CO₂ toward methane absorption reaches values up to 15 [166]. The main limitation is related to its synthesis that still requires the use of nongreen compounds, such as DMS (dimethyl-sulfate), KOH and TABHS as catalyst [167]. In principle, DMC could be used as a methylation agent, but yields are almost null (<2%). Some alternative routes have been proposed, but without an effective application; for example, a reaction between glycerol and tert-butyl-alcohol could be possible, but unfortunately a sulfonated catalyst is still necessary [168]; a reaction between glycerol and methanol or ethanol in presence of an anion exchange polymeric resin is another possible solution [169]. Other limitations are low biodegradability and high volatility [164,166].

3.3.2. H₂S and CO₂ Capture

There are only few references available in the literature reporting H₂S capture by DESs. Compared with other solvents (e.g., ionic liquids), DESs exhibited almost the same capacity for H₂S [170]. It should be noted that ILs could also be deemed as the raw materials of DESs. When an IL is one of the components in DESs, the advantages of DESs over ILs

disappear [171]. Wazeer et al. (2021) [33] reviewed recent results on capture of acid gases using different types of DESs and confirmed the lack of research on H₂S capture through DES.

Among the newly designed DESs, a combination of caprolactam and tetrabutylammonium show the highest desulfurization efficiencies. Following this path, Karibayev and Shah (2020) [139] explored the formation of caprolactam-based DESs using molecular dynamics (MD) simulations and ab initio computations. Additionally, they also compared caprolactam-based solvent performances with two other different DESs composed of monoethanolamines/methyltriphenylphosphonium bromide and urea/choline chloride. It was observed that the caprolactam-based DESs are highly efficient, particularly at low temperatures, low pressures and low fuel/DES mole ratios.

Wu et al. (2019) [170] studied the solubility of hydrogen sulfide in tetrabutylammonium bromide (TBAB)/carboxylic acid and choline chloride (ChCl)/carboxylic acid. It was observed that the mass solubility of H₂S in the DESs increased with decreasing concentration of carboxylic acid.

Wang et al. (2020) [172] synthesized four deep eutectic solvents (DESs) and 5–30% polyethylenimine (PEI) was added to make functional DESs (FDESs) for dynamic absorption experiments of hydrogen sulfide. The interaction between H₂S and the FDESs was discussed at a molecular level via the quantum chemical calculations. It was noticed that FDESs prefer chemisorption on H₂S. In this work, the 25% PEI/FDES@EG showed the highest desulfurization performance: it could remove H₂S efficiently over a low H₂S concentration.

Wu et al. (2021) [173] examined 1-ethyl-3-methylimidazolium chloride ([Emim]Cl) + imidazole as the physical solvents for H₂S and CO₂ absorption. The results were compared with other liquid solvents, and [Emim]Cl + imidazole DES showed extremely high efficiency for H₂S absorption and large selectivity toward CO₂. Results were also explained by the molecular dynamics (MD) simulations and density functional theory (DFT) calculations.

Table 7. Pros and cons of the green solvents studied in the literature, considering both CO₂ capture and H₂S and CO₂ capture.

Green Solvent Blends	References	Pros	Cons
CO₂ capture			
DecA:N8881–Cl (2:1) DecA:N8881–Br (2:1) DecA:N4444–Cl (2:1) DecA:N8888–Br (2:1) DecA:N8888–Cl (1.5:1) DecA:N8888–Cl (2:1)	[156]	The functionalized with piperazine DES showed the highest CO ₂ absorption capacity and the fastest absorption kinetics	<ul style="list-style-type: none"> • high viscosity; • low thermal stability
choline chloride-ethanolamine (1:7) + diethanolamine (amine type 2); methyldiethanolamine (amine type 3); piperazine (amine type 2); 1-(2-aminoethyl)piperazine (amine type 1 and 2).	[164]	less toxic than conventional or “linear” triethers such as diglyme	

Table 7. Cont.

Green Solvent Blends	References	Pros	Cons
1,2,3-Trimethoxypropane (1,2,3-TMP)	[154]	<p>The increase of thymolin DESs could decrease the viscosity and density of DESs:</p> <ul style="list-style-type: none"> • capacity of CO₂ in DES could reach up to 1.355 mol CO₂/mol DES in [TEPA]Cl-thymolDES (n[TEPA]Cl/nthymol = 1:3) at 40 °C and 101.3 kPa; • efficient CO₂ capture even at low partial pressures; • still hydrophobic after saturated with CO₂ 	
[TETA]Cl-thymol [TEPA]Cl-thymol	[146]	<ul style="list-style-type: none"> • low viscosity; • higher CO₂ uptake 	
2-Methylaminoethanol (MAE); TetrabutylAmmoniumBromide (TBAB); BenzyltriethylammoniumChloride (BTEACl); Ethylaminoethanol (EAE); TetrabutylAmmoniumBromide (TBAB); BenzyltriethylammoniumChloride (BTEACl)	[144]		
BTEA-AC; BTMA-AC; ChCl-EA; Gua-EA; MTPP-AC; MTPP-LV-AC; TBAB-AC; TBAB-EA; TBAC-AC; TEAC-AC; TEAC-OCT; TEMA-AC; TMAC-AC; TPAC-AC; TPAC-EA	[142]	By functionalization, the CO ₂ solubility increased from 1.4 to 3.2 mol/kg DES for TPAC/ EA (1:4), giving rise to better performance compared with that of the common ILs	
guanidine carbonate; malic acid; ethylene glycol; arginine; water	[143]	low vapor pressure	high viscosity
choline chloride-ethanolamine (1:7, mol:mol) DES using different types of amines: diethanolamine (amine type 2); methyldiethanolamine (amine type 3); piperazine (amine type 2); 1-(2-aminoethyl)piperazine(amine type 1 and 2).	[156]	<ul style="list-style-type: none"> • low melting point; • tunable physicochemical properties; • high thermal and/or chemical stability; • high ionic conductivity; • low flammability; • negligible vapor pressure; • low cost; • simple preparation process without further purification 	

Table 7. Cont.

Green Solvent Blends	References	Pros	Cons
CO₂ and H₂S capture			
1-ethyl-3-methylimidazolium chloride ([Emim]Cl) + imidazole (2:1); 1-ethyl-3-methylimidazolium chloride ([Emim]Cl) + imidazole (1:1); 1-ethyl-3-methylimidazolium chloride ([Emim]Cl) + imidazole (1:2);	[173]	<ul style="list-style-type: none"> highest H₂S solubility compared with other physical solvents; easy regeneration; unchanged solubility upon 10 absorption cycles; 	<ul style="list-style-type: none"> low selectivity than chemical solvents; corrosive properties
HBD: EG, urea, glycerol, and propylene glycol (PG) + HBA: chlorinated choline Functionalized agent: polyethylenimine (PEI)	[172]	<ul style="list-style-type: none"> FDESs have a relatively high desulfurization performance; the H₂S removal efficiency could remain above 80% 	without water, a decrease in H ₂ S removal efficiency after 3 cycles
CPL/TBABr (1:1); CPL/TBACl (1:1); ChCl/urea (1:2); MTPPBr/MEA (1:6)	[139]	highest desulfurization efficiency	
tetrabutylammoniumbromide (TBAB)/carboxylic acid (1:1); Choline chloride (ChCl)/carboxylic acid (1:4)	[170]	<ul style="list-style-type: none"> the solubility of H₂S in TBAB-based DESs was comparatively higher than ChCl-based DESs; no loss in performance after regeneration and recycling 	
N-ethylmorpholine acetate; N-ethylmorpholine propionate; N-ethylmorpholine butyrate; N-ethylmorpholine methoxyacetate; 4-(2-hydroxyethyl) morpholine acetate; 4-(2-hydroxyethyl)morpholine methoxyacetate; triethylamine acetate; triethylamine propionate; triethylamine propionate; triethylamine methoxyacetate	[174]	<ul style="list-style-type: none"> high thermal stability; lower viscosity than MDEA-based IL; excellent H₂S absorption capacity 	

Table 8. Green solvents studied in the literature with relative experimental operating conditions and provided information.

Green Solvent Blends	References	Gas Stream Type	Operating Conditions	Measured Variables	Outcomes
CO₂ capture					
DecA:N8881–Cl (2:1) DecA:N8881–Br (2:1) DecA:N4444–Cl (2:1) DecA:N8888–Br (2:1) DecA:N8888–Cl (1.5:1) DecA:N8888–Cl (2:1)	[152]		298 < T < 323 K; P up to 2 MPa	CO ₂ solubility	Henry's law constant; enthalpy and entropy of solvation
1,2,3-Trimethoxypropane (1,2,3-TMP)	[164]	Flue gas	20 < T < 80 °C	CO ₂ solubility; density; viscosity; vapor pressure	
[TETA]Cl-thymol [TEPA]Cl-thymol	[154]	Biogas and natural gas		Volatility; water solubility; density; viscosity	Henry's law constant; equilibrium constant
2-Methylaminoethanol (MAE); TetrabutylAmmoniumBromide (TBAB); BenzyltriethylammoniumChloride (BTEACl); Ethylaminoethanol (EAE); TetrabutylAmmonium Bromide (TBAB); BenzyltriethylammoniumChloride (BTEACl)	[146]	Shale gas	303.15 < T < 323.15 K; P ≤ 15 bar	Viscosity; gas solubility	
lidocaine + oleic acid	[155]		30 < T < 50 °C	Quantification of chemicals in both phases; dyes extraction efficiency	
BTEA-AC; BTMA-AC; ChCl-EA; Gua-EA; MTPP-AC; MTPP-LV-AC; TBAB-AC; TBAB-EA; TBAC-AC; TEAC-AC; TEAC-OCT; TEMA-AC; TMAC-AC; TPAC-AC; TPAC-EA	[142]		293.15 < T < 333.15 K; P up to 2 MPa	Viscosity; CO ₂ solubility	
guanidine carbonate; malic acid; ethylene glycol; arginine; water	[143]	Flue gas	303.2 < T < 330.2 K	Viscosity	Henry's law constant
choline chloride-ethanolamine (1:7, mol:mol) + diethanolamine (amine type 2), methyldiethanolamine (amine type 3), piperazine (amine type 2), 1-(2- aminoethyl)piperazine (amine type 1 and 2).	[156]		T = 298 K; P up to 2 MPa	CO ₂ solubility	Henry's law constant

Table 8. Cont.

Green Solvent Blends	References	Gas Stream Type	Operating Conditions	Measured Variables	Outcomes
CO₂ and H₂S capture					
1-ethyl-3-methylimidazolium chloride ([Emim]Cl) + imidazole (2:1); 1-ethyl-3-methylimidazolium chloride ([Emim]Cl) + imidazole (1:1); 1-ethyl-3-methylimidazolium chloride ([Emim]Cl) + imidazole (1:2)	[173]	Natural gas	H ₂ S: 0 < P < 2 bar; CO ₂ 0 < P < 5 bar; 298.2 < T < 352.2 K	Gas solubilities	Enthalpy changes of gas absorption; molecular dynamics (MD) simulations and density functional theory (DFT) calculations
HBD: EG; urea; glycerol; propylene glycol (PG) HBA: chlorinated choline Functionalized agent: polyethylenimine (PEI)	[172]	Natural gas	30 < T < 70 °C; dry and wet solvents	H ₂ S removal efficiency	-
CPL/TBABr (1:1); CPL/TBACl (1:1); ChCl/urea (1:2); MTPPBr/MEA (1:6)	[139]	Natural gas	H ₂ S concentration: 5000 < x < 10,000 ppm; 25 < T < 60 °C; 1 < P < 10 bar	-	Molecular simulations and ab initio calculations
tetrabutylammoniumbromide (TBAB)/carboxylic acid (1:1) Choline chloride (ChCl)/carboxylic acid (1:4)	[170]		298 < T < 318 K; 0.10 < P < 0.60 MPa	H ₂ S solubility; viscosity	
N-ethylmorpholine acetate N-ethylmorpholine propionate N-ethylmorpholine butyrate N-ethylmorpholine methoxylacetate 4-(2-hydroxyethyl)morpholine acetate 4-(2-hydroxyethyl)morpholine methoxyacetate triethylamine acetate triethylamine propionate triethylamine propionate triethylamine methoxylacetate	[174]	Natural gas	298.2 < T < 333.2 K; P = P _{atm}	Density; viscosity; H ₂ S solubility	Henry law's constant

Zhao et al. (2018) [174] synthesized ten carboxylate protic ionic liquids (PILs), containing N-ethylmorpholine acetate, N-ethylmorpholine propionate, N-ethylmorpholine butyrate, N-ethylmorpholinemethoxylacetate, 4-(2-hydroxyethyl) morpholine acetate, and 4-(2-hydroxyethyl) morpholine methoxyacetate, triethylamine acetate, triethylamine propionate, triethylamine propionate, and triethylamine methoxylacetate. The densities and viscosities of these carboxylate PILs were measured in the temperature range of 298.2 to 333.2 K at atmospheric pressure. Comparisons of PILs with the common ILs and organic solvents were also done to demonstrate the advantages of PILs.

However, still a lot of work must be performed to think to industrial applications for hydrogen sulfide capture.

4. Technological Assessment Overview

Considering the state of the art of innovative solvents for acid gas removal from gaseous streams, a number of very promising approaches can be followed in order to

reduce the energy and environmental impact of this process. Nevertheless, much effort is still needed to exploit the presented innovative blends on a commercial scale. Currently, a large majority of studies related to this topic are limited to academia research. Only a few biphasic amine-based mixtures have already been tested on a pilot scale with successful results in terms of reduced energy requirements, reduced corrosion and degradation extent [20]. This is an extremely important aspect since one of the major concerns of MEA is its environmental impact given by releases of harmful degradation products such as NH_3 , acetaldehyde, nitramines and nitrosamines. Unfortunately, detailed lifecycle assessment analyses for capture processes exploiting these innovative amines are not yet available. Biphasic blends-based technologies are privileged by the fact that the reaction mechanism and the interactions among the different components in the system are already well known. In addition, very minor modifications are required to implement them in existing gas treatment plants. However, high volatility [53] and low-efficient phase separation [40] have proven to be major concerns. In particular, the high volatility results in the need for additional flue gas treatments (i.e., water washing) in order to avoid the release of amines to the atmosphere, which is responsible for an increase of the operating costs. Moreover, data on CO_2 and H_2S removal selectivity are still lacking, along with a systematic investigation of liquid–liquid equilibrium under different solvent compositions and operating conditions, which is extremely relevant for the development and application of a large-scale technology. The available experimental data are not sufficient to allow a proper characterization of the behavior of these blends under the operating conditions typical of the regeneration (high temperatures).

Notable water-lean solvents have been tested at the bench scale for flue gas and natural gas applications. Lower reboiler duties and higher-than-expected mass transfer have been observed, at the expense of an intrinsic viscosity increase (for some but not all solvents), which will have to be addressed. Among water-lean solvents, ionic liquids are gaining more interest for both CO_2 and H_2S removal, mainly due to their null volatility. Their ability to effectively remove both acid gases suggests that they could be employed in natural gas treatment. However, there are relevant issues that still need to be addressed, especially the high investment costs, the limited biodegradability [175] and the effective control of viscosity (which is two or three order of magnitude higher with respect to the main traditional solvents at ambient temperature (Jacquemin et al., 2006 [176])). To reduce solvent viscosity, water can be added in their formulation, thus limiting the water-lean potentiality of these solvents. Regarding the operating costs [177], a preliminary evaluation for a hypothetical biogas upgrading process using common ILs (including $[\text{C2MIm}][\text{Tf}_2\text{N}]$) shows that the CAPEX are 3.4 times higher the ones associated with benchmark MEA (15.18 vs. 4.45 MUSD. On the other hand, the expected OPEX are only slightly increased (3.10 vs. 2.59 MUSD. A major reason for the high investment cost is given by the high price of ionic liquids, since their synthesis is rather complex; most ILs are produced at a laboratory scale and their prices are in the range 1–10 USD/g, which is 100–1000 times higher compared to those of conventional solvents [178].

Deep eutectic solvents (DESs) are more environmentally friendly and generally less expensive due to the low cost of their constituents, such as urea and choline chloride, but they require a blend with an amine or other solvents to reach satisfactory CO_2 uptakes; with DESs alone, the CO_2 solubility is limited [155]. Studies on DES and/or IL-amine blends have just arisen in the last few years, to combine the absorption and kinetic advantages of traditional amines with the volatility, environmental issues and tunable water content of ILs and DESs. Luo et al. (2021) have compared the performances of a DES (tetrabutylammonium bromide decanoic acid) and benchmark MEA in a carbon capture unit operating on a coal-fired power plant flue gas [179]; this study points out that, due to the limited CO_2 uptake, the required solvent flowrate is 2.85 higher. As for the energy requirements, a 20% reduction in the required thermal energy is expected, but, on the other hand, there is a relevant increase in electricity consumption due to the much higher flowrates circulating in pumps and compressors. A quantification of the environmental impact reduction associ-

ated with replacement of MEA with DESs has been assessed through a comparative LCA between a MEA-based and a DES-based (tetrabutylammonium bromide decanoic acid) post-combustion capture process. When comparing the two scenarios, DES results in a reduction of 99% in HT (human toxicity), 90% in EP (eutrophication), 80% in FAE (freshwater aquatic ecotoxicity), 30% in GWP (global warming) and 10% in AP (acidification). When comparing DESs (reline and glyceline) to a conventional physical solvent such as DEPG (SelexolTM), DESs can guarantee a significantly lower duty requirement for regeneration but, at the same time, a less favorable behavior from an exergy point of view; the exergy destruction increases by 50–70% [180]. It is important to underline that, at the moment, there are no green solvents showing satisfactory performances without being blended with other nongreen compounds. Dihydrolevoglucosenone, 1,2,3-trimethoxypropane and dimethyl-carbonate have been proposed as naturally derived compounds with good potential in carbon capture [158,164]. However, a green origin is insufficient for considering a solvent as green. Moreover, these solvents behave as physical solvents, which means that their absorption capacity is not enhanced by any chemical reaction. Therefore, they could find application in the treatment of sour gases (having high acid gas contents), for which chemical absorption becomes no more energetically convenient [181].

5. Conclusions and Future Developments

Increasing large-scale air pollution by acid gases, such as carbon dioxide and hydrogen sulfide, has pushed research toward the field of carbon capture and sequestration. CCS and CCU are undoubtedly among the most diffused matter of debate in the scientific panorama.

To overcome the limits of the traditional chemical solvents for acid gas removal, the formulation of novel absorbing agents has emerged as a popular topic of investigation. Although the novel solvents scenario is quite wide, many efforts are needed in order to:

- Carefully explore solvent chemical/physical properties, with a special focus on thermodynamic equilibrium and kinetic data able to cover the whole range of operating conditions of interest (absorption and regeneration). After performing the experimental campaigns, then collection, cataloguing and publishing of all conceivable properties is needed.
- Model the sophisticated mixtures—through appropriate law and computational techniques, it could be necessary to find new relationships or empirical fits suitable for describing the behavior of these new solvents, particularly regarding ionic liquids and deep eutectic properties.
- Investigate the liquid-phase dynamics and understand the CO₂ and H₂S absorption mechanism.

After thorough property knowledge and the predictive models are in place, research can and should solve the related engineering problems, which include scaling-up of these new technologies at the industrial level.

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