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## Solvents for Carbon Dioxide Capture

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Additional information is available at the end of the chapter

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### Abstract

Anthropogenic CO<sub>2</sub> emissions are considered the major contributor of greenhouse gas emissions worldwide. The mitigation of this kind of CO<sub>2</sub> emissions relies on a portfolio of alternatives where CO<sub>2</sub> absorption appears as the nearest approach to be applied at industrial scale. Researchers have been focused on developing new formulations of solvents to make more competitive CO<sub>2</sub> absorption as a carbon capture and storage (CCS) technology. In this sense, this chapter summarizes both the conventional solvents and the most recent investigations on this field. Chemical absorption is more suitable for a lot of industrial process due to the flue gas conditions: ambient pressure, low CO<sub>2</sub> concentration and large volume. Therefore numerous novel solvents came up in recent years and they are further discussed in this chapter. The most recent solvents, their mechanisms and kinetics and the advantages and disadvantages are also included. Finally, physical solvents are adequate in high CO<sub>2</sub> partial pressure applications and they are reported in the last section. Although physical absorption field is constrained to high-pressure flue gas, physical solvents provided higher performance in CO<sub>2</sub> separation process and their characteristics are also summarized.

**Keywords:** solvent, CO<sub>2</sub>, CCS, absorption, capture

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### 1. Introduction

Carbon capture and storage (CCS) is one of the pathways for anthropogenic CO<sub>2</sub> emission mitigation. Among the wide portfolio of CCS technologies, physical and chemical absorption are considered the most close-to-market approaches to be applied at industrial scale, mainly focused on their implementation in energy production from fossil fuels [1]. Physical absorption is based on the CO<sub>2</sub> solubility into the solution without chemical reaction which is

based on Henry's law and hence high  $\text{CO}_2$  partial pressures and low-temperatures are highly recommended for its application. Chemical absorption is based on the reaction between  $\text{CO}_2$  and specific compounds—solvents—that lead to form a weak bond between  $\text{CO}_2$  and the solvent. Chemical absorption occurs indeed at low  $\text{CO}_2$  partial pressure. Low-temperature is also recommended for this mechanism. Numerous solvents have been developed since the first chemical absorption process was patented in the early 1930s. However, the implementation of  $\text{CO}_2$  absorption at industrial processes such as cement production, iron and steel manufacturing and fossil-fuel power plants requires novel solvent formulations that can address the main constraints limiting its deployment: the huge volume of treated gas, the low  $\text{CO}_2$  concentration in the flue gas and the presence of trace components such as  $\text{NO}_x$ ,  $\text{SO}_2$  and particulate matter which degrade the solvents [2, 3]. This chapter summarizes both conventional and newly developed solvents mainly focused on  $\text{CO}_2$  capture processes based on physical and chemical absorption. A deep revision of the solvents reported from the literature was made including primary, secondary, tertiary amines and non-amine-based solvents. Novel solvents such as sterically hindered amines and blends were discussed further. In respect to physical solvents, authors report the conventional solvents used by licensed processes such as Rectisol<sup>TM</sup>, Selexol<sup>TM</sup>, Sulfinol<sup>TM</sup> and Purisol<sup>TM</sup>. Special attention will be paid in ionic liquids and novel biphasic configurations and their use as  $\text{CO}_2$  capture solvents.

## 2. Chemical absorption solvents

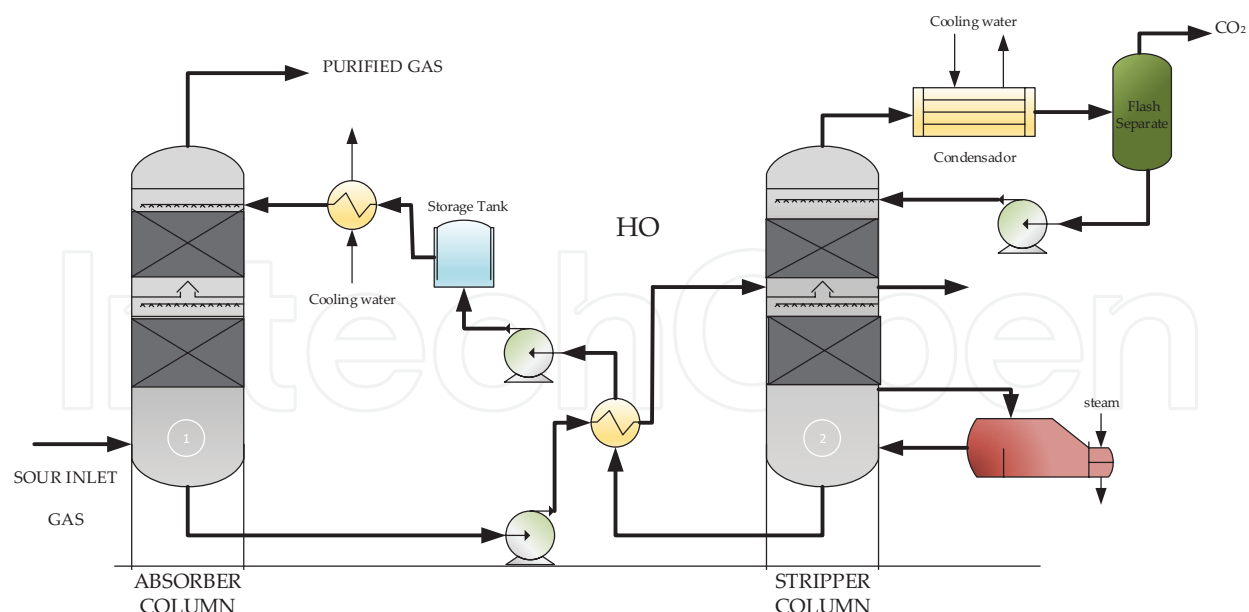
### 2.1. Conventional amine-based solvents

The amine-based chemical absorption process has been used for  $\text{CO}_2$  and  $\text{H}_2\text{S}$  removal—acid gas removal—from gas-treating plants since 1950s [4] and are considered to be by far the most developed  $\text{CO}_2$  capture process.  $\text{CO}_2$  is absorbed typically using amines to form a soluble carbonate salt. The absorber operates below  $60^\circ\text{C}$  and ambient pressure (step 1 in **Figure 1**) [4].

This reaction is reversible and the  $\text{CO}_2$  can be released by heating the solution with the carbonate salt in a separate stripping column. The  $\text{CO}_2$  stripping occurs at  $120^\circ\text{C}$  and pressures ranging between 1.8 and 3 bar [6], as illustrated in the step 2 in **Figure 1**.

Nowadays, amine-based chemical absorption came up as a potential technology that can be applied to reduce carbon dioxide emissions in industrial processes such as fossil fuels power plants, cement production and iron and steel manufacturing. Post-combustion is the nearest close-to-market and industrially developed carbon capture and storage (CCS) technology.

Specifically, the alkanolamines are volatile, cheap and safe to handle compounds and are commonly classified by the degree of substitution on the central nitrogen; a single substitution denoting a primary amine; a double substitution, a secondary amine; and a triple substitution, a tertiary amine. Each of the above-mentioned alkanolamines has at least one hydroxyl group and one amino group. In general, the hydroxyl group serves to reduce vapor pressure and increases the solubility in water, while the amine group provides the necessary alkalinity in aqueous solutions to promote the reaction with acid gases. Therefore, the molecular structures of primary


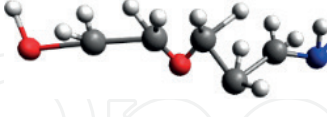
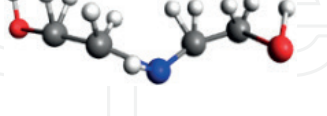
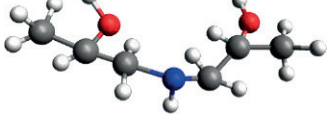
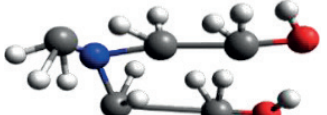


**Figure 1.** Simplified diagram of a conventional acid gas removal process using chemical absorption adapted from Ref. [5].

and secondary amines are the non-fully substituted alkanolamines and they have hydrogen atoms at the non-substituted valent sites on the central nitrogen, whereas the tertiary amines are fully substituted on the central nitrogen. This structural characteristic plays an important role in the acid gas removal capabilities of the various treating solvents [7]. **Table 1** shows the most widely used amines for the treatment of acid gases, which will be described in detail.

The performance of solvents for CO<sub>2</sub> absorption can be evaluated from several specific properties. In particular, the CO<sub>2</sub> absorption capacity, namely CO<sub>2</sub> loading, is defined as the amount of CO<sub>2</sub> that can be absorbed per mole of solvent (mole CO<sub>2</sub>/mole solvent). The maximum CO<sub>2</sub> absorption capacity can be deduced from the CO<sub>2</sub> solubility represented by vapour-liquid equilibrium (VLE) curves of each solvent, depending on the CO<sub>2</sub> partial pressure in the bulk gas and the absorption temperature [4]. The cyclic capacity, defined as the difference of the CO<sub>2</sub> loading between the rich solvent and the lean solvent, is also used for easily comparison. In terms of CO<sub>2</sub> chemical reactivity, the absorption kinetics is expressed as the rate of the CO<sub>2</sub> absorbed from the bulk gas to the bulk liquid that means mole CO<sub>2</sub> per second. Finally, the solvent resistance to be degrade in presence of O<sub>2</sub>, NO<sub>x</sub> and SO<sub>2</sub> and also under elevated temperature is compared by the solvent losses under specific operating conditions.

Primary alkanolamines such as monoethanolamine (MEA) and diglycolamine (DGA), provide high chemical reactivity, favored kinetics, medium-to-low absorption capacity and acceptable stability. Monoethanolamine (MEA), the first-generation and the most well-known amine-based absorbent, is highlighted by its high chemical reactivity with CO<sub>2</sub> and low cost. These properties can reduce the absorber height and ensure a feasible operation. Although MEA-based scrubbing technology is suitable for acid gas removal and, in particular, post-combustion capture from fossil-fired plants flue gas, it suffers from several issues during operation, including high energy requirements for stripping: high enthalpy of reaction, low absorption capacity, oxidative and thermal degradation and piping corrosion [8]. Hence, efforts have

Abbr.	Name	Industrial process	Structural formulae	Chemical structure	CO <sub>2</sub> loading
MEA	Mono ethanol amine	Natural and syngas purification	NH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> OH		0.5
DGA	Diglycol amine	Syngas treatment	(HO-C <sub>2</sub> H <sub>4</sub> )-O-(C <sub>2</sub> H <sub>4</sub> -NH <sub>2</sub> )		0.25–0.35
DEA	Diethanol amine	Natural gas containing high concentrations of COS and CS <sub>2</sub>	(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub> NH		0.7–1
DIPA	Diiso propanol amine	ADIP, Sulfinol: refinery gas treatment	(CH <sub>3</sub> CHOHCH <sub>2</sub> ) <sub>2</sub> NH		0.43–0.22
MDEA	Methyl diethanol amine	Solvents URCASOL, gas washing in Claus plants	CH <sub>3</sub> N(C <sub>2</sub> H <sub>4</sub> OH) <sub>2</sub>		0.1–0.3

Gray, C atom; white, H atom; red, O atom; dark blue, N atom.

**Table 1.** Most commonly amines used in acid gas treatment [4].

focused on the development of attractive solvents to achieve high absorption/desorption capacities, energy-efficient performance and oxidative and thermal stability. Furthermore, DGA presents similar properties to MEA in many aspects, except that its low vapor pressure allows its use at higher concentrations, typically between 40 and 60%wt. in aqueous solution.

Secondary alkanolamines such as diethanolamine (DEA) and diisopropanolamine (DIPA), which have a hydrogen atom directly bonded to the nitrogen, shows intermediate properties compared to primary amines and they are considered as an alternative to MEA. DEA is more resistant to degrade and shows lower corrosion strength than MEA, whereas DIPA has lower energy requirement for solvent regeneration than MEA.

Finally, tertiary amines such as triethanolamine (TEA) or methyldiethanolamine (MDEA), that are characterized by having a high equivalent weight, which causes a low absorption capacity, low reactivity and high stability.

There are three main differences in the performance of primary and secondary amines as they are compared to tertiary amines for the CO<sub>2</sub> separation process. Primary and secondary amines are very reactive; they form carbamate by direct reaction with CO<sub>2</sub> by Zwitterion mechanism. Therefore, these amines showed limited thermodynamic capacity to absorb CO<sub>2</sub> due to the stable carbamates formation along the absorption process. On the other hand, tertiary amines can only form a bicarbonate ion and protonated amine by the base-catalyzed hydration of CO<sub>2</sub> due to their lack of the necessary N–H bond [9, 10]. Hydration is slower than the direct reaction by carbamate formation and, hence, tertiary amines show low CO<sub>2</sub> absorption rates [9].

In general, the main issues that amine-based chemical absorption has to address to be applied as industrial scale for carbon dioxide emission mitigation are listed below:

- High energy consumption during the solvent regeneration.
- Corrosion requires the use of both inhibitors and resistant materials in their application.
- Scale up from actual (800 t/day) to required (8000 t/day) CO<sub>2</sub> capacity.
- Degradation in the presence of O<sub>2</sub>, SO<sub>x</sub> and other impurities such as particles, HCl, HF and Hg.

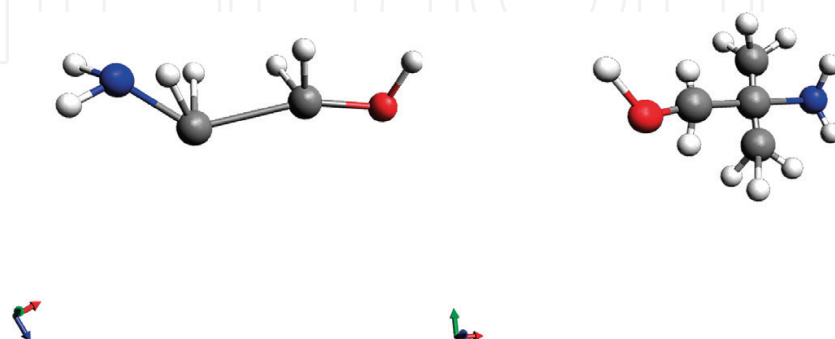
## 2.2. Sterically hindered amine solvents

Sterically hindered amines are considered a type of amines which can improve CO<sub>2</sub> absorption rates in comparison with the common primary and second amines, usually amino alcohols. A sterically hindered amine is formed by a primary or secondary amine in which the amino group is attached to a tertiary carbon atom in the first case or a secondary or tertiary carbon atom in the second (**Figure 2**).

These amines are characterized by forming carbamates of intermediate-to-low stability, introducing a bulky substituent adjacent to the amino group to lower the stability of the carbamate formed by CO<sub>2</sub>-amine reaction. This weaker bond leads to high free-amine concentration in solution, so the energy consumption to release CO<sub>2</sub> is lower than the common primary and second amines. According to Nicole Hüser et al. [11], a decrease up to 15% can be achieved using hindered amines.

The general reaction scheme of the CO<sub>2</sub>-primary or secondary amine (AmH) and the CO<sub>2</sub>-sterically hindered amine (AmCOO<sup>-</sup>) is shown in **Figure 3**. Regarding the primary or secondary reaction scheme, the symbol B represents a base that should be another amine molecule that requires to form the carbamate anion. In this case, two amine molecules are needed to absorb one CO<sub>2</sub> molecule, as it is extracted from the overall reaction.

The system CO<sub>2</sub>-sterically hindered amine requires only one amine molecule to capture one molecule of CO<sub>2</sub>. Based on this assumption, the maximum CO<sub>2</sub> loading using sterically hindered amines is higher than for unhindered, primary or secondary amines.



**Figure 2.** Molecular structure of primary amines on the left (MEA) and a sterically hindered amine on the right (AMP). Note that gray balls represent C atoms; white balls represent H atoms; red/dark gray balls represent O atoms; dark blue/black balls represent N atoms [11].



General reaction scheme of the CO <sub>2</sub> -Primary or Second amine system	General reaction scheme of the CO <sub>2</sub> -Sterically hindered amine system
<div>Amine molecule</div> $\text{CO}_2 + \boxed{\text{AmH}} \leftrightarrow \text{AmH}^+\text{COO}^-$ <div>Stable carbamate anion</div> $\text{AmH}^+\text{COO}^- + \text{B} \leftrightarrow \boxed{\text{AmCOO}^-} + \text{BH}^+$	<div>Sterically hindered amine</div> <div>Amine molecule</div> $\boxed{\text{AmCOO}^-} + \text{H}_2\text{O} \leftrightarrow \boxed{\text{HCO}_3^-} + \boxed{\text{AmH}}$ <div>Bicarbonat ion</div> $\text{CO}_2 + \text{AmH} + \text{H}_2\text{O} \leftrightarrow \boxed{\text{HCO}_3^-} + \text{AmH}_2^+$

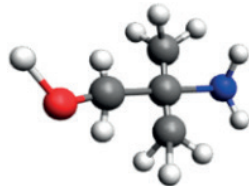
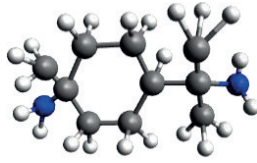
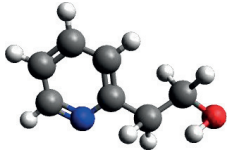
Figure 3. General reaction scheme of the CO<sub>2</sub>-amines system [11].

The use of this type of amines leads to reduce the energy requirement for the amine-based solvent regeneration up to 20% compared to conventional MEA-based scrubbing, due to the formation weak bonds [11]. Several sterically hindered amines are shown in Table 2.

2.3. Non-amine-based solvents

Non-amine-based solvents are called to those chemical solvents which do not integrate an amine group in their structure molecular. The most relevant solvent proposed as an alternative to the conventional amine-based solvents is the sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>). About 30% p/p sodium carbonate slurry is used to provide a basic environment in which CO<sub>2</sub> is absorbed as bicarbonate followed by sodium bicarbonate formation [13]. The NaHCO<sub>3</sub> precipitation enhances the bicarbonate formation and, hence, the CO<sub>2</sub> capture capacity of the solvent is improved.

Sodium carbonate has shown a high performance in CO<sub>2</sub> separation from flue gas in comparison with the MEA benchmark. It produces a high CO<sub>2</sub> loading capacity (0.73 mole CO<sub>2</sub>/ mole CO<sub>3</sub><sup>2-</sup>) and a reboiler duty of 3.2 MJ/kg CO<sub>2</sub> rather than 0.5 mole CO<sub>2</sub>/mole MEA and 3.5–4.2 MJ/kg CO<sub>2</sub> in case MEA is used as a solvent. Furthermore, this chemical solvent can absorb CO<sub>2</sub> in presence of pollutants such as SO<sub>2</sub> which can enable the cyclic capacity of amine-based solvents for CO<sub>2</sub> absorption [13, 14]. Despite those advantages, sodium carbonate can absorb CO<sub>2</sub> at low absorption rates, which lead to higher absorption column height. It assumes that

Abbreviation	AMP	MDA	PE
Name	2-amino-2-methyl-1-propanol	1,8-p-menthanediamine	2-piperidineethanol
Structural formulae	HO-CH <sub>2</sub> -C-(CH <sub>3</sub> )(CH <sub>3</sub> )(NH <sub>2</sub> )	(CH <sub>3</sub> NH <sub>2</sub> -C <sub>6</sub> H <sub>9</sub> -C <sub>3</sub> H <sub>6</sub> NH <sub>2</sub> )	C <sub>2</sub> H <sub>4</sub> -NH-CH-(C <sub>2</sub> H <sub>4</sub> OH)-C <sub>2</sub> H <sub>4</sub>
Chemical structure			

Gray, C atom; white, H atom; red, O atom; dark blue, N atom.

Table 2. Examples of sterically hindered amines [12].

sodium carbonate requires the use of promoters such as primary amines to enhance its CO<sub>2</sub> absorption rates [15–18]. The advantages and disadvantages to use sodium carbonate as an absorption solvent in a CO<sub>2</sub> separation process are shown in **Table 3**.

The potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) is other non-amine-based solvents that can be used as a promoter the CO<sub>2</sub> capture with amine-based solvent or other class of amine, like a sterically hindered amine [12].

#### 2.4. Solvent blends

As it was indicated in previous section, the high energy penalty related to amines regeneration and solvent degradation are the most significant issues hindering a large deployment of this technology. Solvent regeneration is a high-intensive energy process. Moreover, the stripper operating conditions and the solvent used to absorb CO<sub>2</sub> consume a high amount of energy. In this sense, amine blends could offer potential improvements in CO<sub>2</sub> chemical absorption to reduce the regular reboiler duty and the common solvent circulation rates [14, 19].

However, in view of taking advantage these main benefits, except its low reactivity, the addition of a small amount tertiary amines (MDEA, TEA) in primary or secondary amines aqueous solutions (MEA, DEA) to form a solvent blend enhances the overall behavior of the solvent in terms of lower energy requirements for solvent regeneration and higher resistance to solvent degradation [20, 21]. For this reason, different researchers are studying novel solvent formulations and blends, involving fast kinetic solvents such as MEA with other slow kinetic solvents like TEA, 2-amino-2-methyl-1-propanol (AMP), benzylamine (BZA) and MDEA [22, 23].

A huge number of solvent have been proposed for CO<sub>2</sub> chemical absorption applied to carbon capture. The first amine was combined with faster kinetic amines was N-methyldiethanolamine (MDEA). Amines such a methanolamine (MEA), diethanolamine (DEA) and piperazine (PZ) have used as promoters for MDEA blends. It is also possible to increase the reaction rate of fast solvents by combining them with an even faster solvent. For example, MEA is a fast solvent but it is almost 50 times slower than PZ. The CO<sub>2</sub> absorption rate of MEA can be significantly improved by adding small amounts of PZ as a promoter [24]. This blend improved the individual CO<sub>2</sub> absorption rate. Potassium carbonate promoted with PZ is also considered a promising solvent [25], along with the PZ and 2-amino-2-methyl-1-propanol (AMP) blends [26]. A summary of the most promising amines blends are given below (**Table 4**).

Advantages	Disadvantage
<ul style="list-style-type: none"> <li>Multi-pollutant capture system</li> </ul>	<ul style="list-style-type: none"> <li>Slow absorption rate. The solvent should be promoted with increasing rate additiveti</li> </ul>
<ul style="list-style-type: none"> <li>Use of a non-hazardous and non-volatile solvent</li> </ul>	<ul style="list-style-type: none"> <li>Solid and slurry management</li> </ul>
<ul style="list-style-type: none"> <li>Lower fouling and corrosion issues than amine compounds</li> </ul>	<ul style="list-style-type: none"> <li>High pollutant removal</li> </ul>

**Table 3.** Advantages and disadvantages of CCS based on chemical absorption using Na<sub>2</sub>CO<sub>3</sub> [14].



Solvent	Abbreviation	Reference
Piperazine and potassium carbonate	PZ+ K <sub>2</sub> CO <sub>3</sub>	[25]
2-amino-2-methyl-1-propanol and piperazine	AMP+ PZ	[26]
2-amino-2-methyl-1-propanol and 1,2-ethanediamine	AMP+ EDA	[27]
3-methylamino propylamine and dimethyl-monoethanolamine	MAPA + DMMEA	[28]

**Table 4.** A summary of most relevant solvent blends reported from the literature [14].

Some advantages of blending these amines are listed below [29]:

- Improved thermodynamic efficiency.
- Reduction in issues relating to degradation and operation of the solvent caused by corrosion.
- Flexibility in the range of amines available to tailor and optimize the composition of the solvent to achieve the highest absorption efficiency.
- High absorption rates observed in single amine solvents can often be maintained in blends of the individual components.
- Energy requirement for solvent regeneration can be reduced.

## 2.5. Ionic liquid

A novel generation of solvents comes recently up as an alternative for traditional amine-based solvents, namely ionic liquids (ILs). These compounds are organic salts with elevated boiling points and thus low vapor pressure, which can selectively absorb acid gases such as CO<sub>2</sub> and SO<sub>2</sub>, involving relatively low regeneration energy requirements [3]. Recently this topic was reviewed extensively by Zhang et al. [30]

ILs are typically formed with the combination of a large organic cation, that is, imidazolium, pyridinium or phosphonium cation with either an inorganic anion such as Cl<sup>-</sup>, BF<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup>, or an organic anion, that is, RCO<sub>2</sub><sup>-</sup> and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> [31]. Special functional groups are also being under consideration for ILs formulations [30]. In general for conventional ILs, anions have more impact on the solvent performance during the absorption process, being the influence of cations considerably lower. Although ILs provide higher CO<sub>2</sub> solubility and selectivity for CCS applications, some authors stated the use of functionalized IL are required in order to make ILs competitive in comparison with amine-based chemical absorption option [30].

Conventional ILs interact with CO<sub>2</sub> as a physical solvent. They enhance the CO<sub>2</sub> solubility following a Henry's law behavior. Functionalized ILs contain an amino group to improve the CO<sub>2</sub> absorption capacity and the kinetics by means of Zwitterion mechanisms as it occurs with primary and secondary amines. Nowadays, researchers are focusing on the development of ILs as a promising CCS approach based on their exceptional properties as a solvent for CO<sub>2</sub> capture. In this respect, the key property provided by ILs derived from their extremely high capacity to be synthesized in a large number of configurations. The tuneable solvent characteristic of ILs

allows them to offer unique molecular structures specifically designed for each application, in particular for low CO<sub>2</sub> concentrated flue gas treatment [30, 32, 33]. Other properties such as their low vapor pressure must be also taking into account due to its impact on the environment. ILs are non-volatile compounds and therefore the presence of ILs in the cleaned exhaust gas after CO<sub>2</sub> separation step is negligible. In this sense, solvent losses associated to ILs are assumed to be completely avoided in a CO<sub>2</sub> capture process based on these emerging solvents. This property is also related to low energy requirements during the solvent regeneration. Several studies reported up to 15% of reduction of the specific energy consumption of MEA functionalized ILs compared to conventional MEA-based scrubbing [33, 34].

Despite their potential for carbon capture, there are some disadvantages that constrain their competitiveness of ILs compared to conventional solvents. ILs show relatively high viscosity, limiting their mass transfer capacities. Indeed, they become excessively viscous once CO<sub>2</sub> is absorbed, producing solvent pumping issues as well as mass transfer and operational difficulties during the overall CO<sub>2</sub> capture process. According to Luo and Wang [32], the increase of the viscosity after the CO<sub>2</sub> absorption is due to the formation of strong and dense hydrogen-bonded networks between the compounds formed by the Zwitterion and dication mechanisms. Authors proposed to promote ILs by the use of non-amine functionalized ILS to avoid the formation of hydrogen bonds [35, 36]. Other proposals such as introducing ether oxygen atoms into the ILs structure and adding particular molecular solvents to provide IL-based solvents were found in the literature. For instance, the use of organic amines instead of water decrease also the viscosity without reducing the CO<sub>2</sub> absorption capacity [30]. Finally, it is necessary to point out that they are also relatively expensive in comparison with common amine-based solvents [37]. Other aspect that should be further investigated in order to address the main knowledge gaps are indicated below:

- Determination of transport properties, physical properties, absorption kinetics of the best performance ILs.
- Efforts on developing new combinations of IL using membranes.
- Development of simulation tools that can predict the chemistry of the interactions in multi-components systems.
- The evaluation of the toxicity and environmental impact derived from the use of IL and its derivatives.
- Investigations on the task-specific IL and the mechanisms involved in CO<sub>2</sub>-IL interactions in order to improve the feasibility of its use as a potential CO<sub>2</sub> separation approach.

As it was mentioned previously, numerous ILs formulae have been developed for last 20 years. Pure ILs configurations, typically referred as room-temperature ionic liquid (RTILs), retain CO<sub>2</sub> by physisorption mechanism showing an unfeasible CO<sub>2</sub> absorption performance in comparison with conventional amine-based solvents. The next generation of ILs was defined from the combination of conventional ILs with a functionalized amine group, preferable. Based on this configuration, amine-functionalized IL, also called task-specific IL, reacts with CO<sub>2</sub> by chemisorption showing further improvements on the CO<sub>2</sub> capture process derived from physisorption-based ILs. The development of this type of ILs enhanced the performance of IL in both biogas/natural gas treatment and CCS. **Table 5** summarizes the best performance IL reported from the literature.

IL	Abbreviation	Field	Ref.	$\mu^*$ (cP)	CO <sub>2</sub> ** load.
1-butylpyridinium tetrafluoroborate	[Bpy] [BF <sub>4</sub> ]	Post-combustion	[34]	150	<0.05***
Tryhexyl(tetradecyl)-phosphonium imidazole	[P <sub>6614</sub> ]	Post-combustion	[35]	223–1077	0.3–0.91
1-butyl-3-methyl-imidazolium hexafluorophosphate	[bmim][PF <sub>6</sub> ]	Post-combustion	[38]	—	0.75
(Trifluoromethyl sulfonyl)imide-based IL	[Tf <sub>2</sub> N]	Biogas/natural gas upgrading	[39]	—	0.66–0.84
1-butyl-3-methyl-imidazolium acetate	[bmim][Ac]	Biogas/natural gas upgrading	[39]	—	—
Allyl-pyridinium bis(trifluoromethylsulfonyl)imide	[Apy] [Tf <sub>2</sub> N]	Pre-combustion	[40]	17.7–28	—

\*Viscosity measurements below 300 K.  
 \*\*Pressure over 1 MPa.  
 \*\*\*Ambient pressure.

**Table 5.** Summary of the best performance IL applied as solvents for CO<sub>2</sub> separation.

The basic of the minimum energy requirement for CO<sub>2</sub> release from ILs consist of the weak interaction between both species. In general, some studies indicated that CO<sub>2</sub>-IL interaction strongly depend on van der Waals forces in case small and symmetric molecular structures are provided, whereas electrostatic interactions dominates as large and asymmetric molecular structures are used. Besides the acid-base interaction also plays a key role as a mechanism for CO<sub>2</sub>-IL interaction. It should be noted that some authors state the relevant impact that the structure of IL has on the CO<sub>2</sub> solubility. The amount of free space provided by means, that is, the length chain, the presence of species such as F<sup>−</sup> increase the CO<sub>2</sub> capacity of IL. The higher free volume available, the higher CO<sub>2</sub> solubility of the IL [30].

Most recent applications of IL involve the use of membranes for CO<sub>2</sub> separation. Research on this field demonstrate the combination of IL with membrane significantly reduces the viscosity during the CO<sub>2</sub> absorption process and also ensures further improvements of the gas separation performance in terms of CO<sub>2</sub> permeability and selectivity [30]. The supported IL membranes (SILM), the poly(ionic liquid)-ionic liquid composite membranes, the combination of facilitated transport membranes with IL and the incorporation of task-specific IL into mixed matrix membranes have shown a high potential as a CO<sub>2</sub> separation approach. Based on the literature, two main mechanisms are identified for IL-based membranes, namely solution-diffusion and facilitated transport mechanism [30]. The new pathway discovered regarding IL and its use as a CO<sub>2</sub> separation approach requires further investigation.

## 2.6. New generation solvents for carbon dioxide capture

New generation solvents proposed are focused on energetic consumption reduction in order to make CO<sub>2</sub> chemical absorption a cost-competitive technology to be deployment at CCS industrial scale. It is well-known that most of the energy consumption takes place in the regeneration step

of the CO<sub>2</sub> capture process. Two main research lines about new generation solvents will be discussed in this section, namely water-free solvents and biphasic solvents.

### 2.6.1. Water-free solvents

Despite the benefits of using water as a diluent in order to reduce the corrosion and viscosity issues along the CO<sub>2</sub> chemical absorption plant, its presence in solvent formulation increases the energy requirements in the regeneration stage. In this sense, several novel water-free solvents are being formulated such as non-aqueous organic amine blends, aminosilicones or amines with superbase [41].

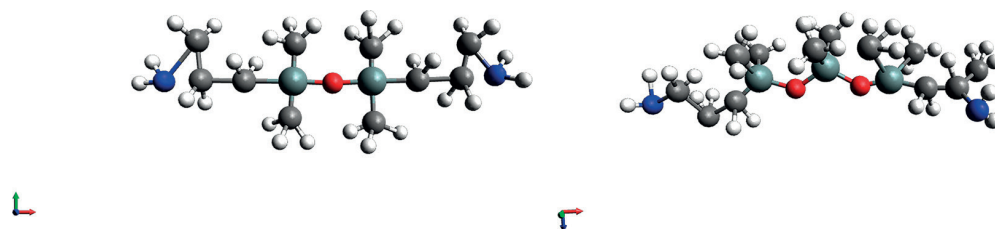
#### 2.6.1.1. Aminosilicones

Aminosilicones are one of the most relevant solvents currently under investigation. Besides the absence of water in its formulation, the hybrid nature of this type of solvents (physisorbing and chemisorbing) provides a potential improvement in CO<sub>2</sub> capture due to the possibilities that its chemical nature offers.

Perry et al. developed GAP-0 and GAP-1 aminosilicones formulated as a CO<sub>2</sub>-philic siloxane backbone and a CO<sub>2</sub> reactive amino group (**Figure 4**) [42, 43]. The absorption capacity of these compounds is higher than the theoretical of the selected amino group due to the physisorption phenomenon that occurs in this type of blends. However, the possibility of solid formation and the increase of viscosity during the absorption process make necessary to use cosolvents in order to avoid the above-mentioned issues.

#### 2.6.1.2. Non-aqueous organic blends

This type of solvents has been studied by some research groups including, for example, Kim et al. In this work, sterically hindered amines 2-[(1,1-dimethylethyl)amino]ethanol (TBAE) and 1-[(1,1-dimethylethyl)amino]-2-propanol (TBAP) were tested using organic compounds as solvents such as methanol and ethylene glycol [44–47]. The efficiency of this type of solvents is also revealed by Mani et al. In this work, AMP mixed with different alkanolamines (DEA, MDEA, MMEA and DIPA) and using organic solvents were analyzed [48, 49]. The tests concluded that, among other considerations, the absorption efficiency at equilibrium ranged 73–96% (**Table 6**).



**Figure 4.** GAP-0 (on the left) and GAP-1 aminosilicones (on the right). Note that gray balls represent C atoms; white balls represent H atoms; red/dark gray balls represent O atoms; dark blue/black balls represent N atoms; black small balls represent Si atoms.

Entry	Amine	Solvent	Amine conc. (wt%)	Loading capacity (wt%)	Average absorpt. efficiency and desorpt. temp (°C)	
					65	80
1	AMP/DEA	DEGMME	18.3	31.7	73.1	91.6
2	AMP/MDEA	EG/methanol	20.7	28.7	—	93.5
3	AMP/MMEA	EG/methanol	16.9	43.4	76.7	95.9
4	AMP/MMEA	EG/ethanol	16.8	40.7	—	92.6
5	AMP/DIPA	EG/ethanol	22.6	27.3	—	93.1

Adapted from Ref. [49].

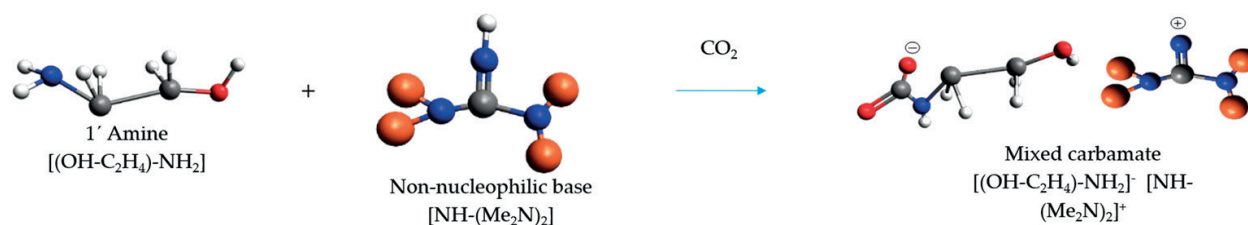
**Table 6.** CO<sub>2</sub> loading capacity at 20°C and absorption efficiency by different amines at increasing desorption temperatures. The overall amine concentration is 2.0 mol dm<sup>-3</sup>.

### 2.6.1.3. Amines with superbase promoters

Amines with superbase promoters might allow an increase in the CO<sub>2</sub> capture efficiency. This type of solvents combines a primary amine and a strong non-nucleophilic base which enhances the proton transfer from the primary amino group, facilitating the carbamate formation (**Figure 5**). CO<sub>2</sub> capture efficiency and the kinetic behavior of a primary amine using a superbase promoter could be increased over 30%. In addition, several solvents are able to work even at high temperatures (over 50°C), which make them useful in high temperature process. Nevertheless, these blends present similar issues than aminosilicones. The possibility of solid formation and the increase of viscosity during the absorption process make necessary to use organic cosolvents such as dimethylsulfoxide (DMSO), especially with nucleophilic polyamines [50, 51].

### 2.6.2. Biphasic solvents

In the last decades, it has been assumed that biphasic mixtures generation during CO<sub>2</sub> amine-based capture processes becomes an operation issue in terms of liquid circulation and homogeneity of the solvents, especially in the regeneration step. However, recent studies support the new idea that a decrease in the energy requirements using biphasic solvents would be possible.



**Figure 5.** Reaction of CO<sub>2</sub>-primary amines in the presence of a strong non-nucleophilic base. Note that gray balls represent C atoms; black big balls represent dimethyl groups; white balls represent H atoms; red/dark gray balls represent O atoms; dark blue/black balls represent N atoms.



Type	Absorbent	Absorption		Desorption	Stripping	Temp. (°C)
		Absorption rate (g/(Lh))	Rich loading (g/L)	Cyclic loading I (g/L)	Cyclic loading II (g/L)	
Primary solvent	DMCA	72	101	71	88	40–70
	MDEA	30	59	30	43	40–70
Activator	A1	130	124	86	101	40–80
	DPA	127	88	65	78	40–80
	MEA (30 wt%)	127	122	28	47	40–80
Blend 3:1	DMCA + DPA	89	90	80	86	40–75
	DMCA + A1	94	117	105	112	40–75
	MDEA + MEA	47	62	26	48	40–75

**Table 7.** Main properties of selected amines in 3 M aqueous solutions. Adapted from ref. [52].

This argument is based on the optimization of the solvent volume treated in regeneration step, stripping only the CO<sub>2</sub>-rich phase [52].

#### 2.6.2.1. TETA/ethanol blends

In recent years, polyamine compounds and blends have been studied in order to improve the CO<sub>2</sub> absorption capacity in CCS technologies. A higher amount of amine functional groups, using water as a dissolvent, provides the polyamines higher absorption rates, but in spite of that fact, regeneration penalties and solvent circulation costs due to the high viscosity of this kind of compounds made unfeasible its application in pilot plants. Triethylenetetramine (TETA) using ethanol as dissolvent was tested by Zheng et al. [53]. In this work, solid generation occurs after the CO<sub>2</sub> reaction with TETA. Solid phase generated and separated, containing a total of 81.8% of the captured CO<sub>2</sub>, allows a lower cost regeneration process due to the fact that liquid phase can be recycled back to the absorption process without energy consumption. The precipitate formed after CO<sub>2</sub> absorption can be regenerated heating to 90°C and returning to liquid phase TETA. This new solvent represents an alternative to the usual polyamine-water solvents although the high vapor pressure of ethanol must be considered in order minimize evaporation losses.

#### 2.6.2.2. Phase change amine blends

Recent studies showed that some types of blended amines have the property of forming two different liquid phases after reaction with CO<sub>2</sub> in capture process. This capacity of the solvent, provides the possibility of perform selective regeneration process, being only the rich amine treated inside the regeneration reboiler. 3-(methylamino)propylamine (MAPA) and 2-(diethylamino)ethanol (DEEA) blend was studied by Bruder and Svendsen showing a promising behavior in the CO<sub>2</sub> capture process compared with habitual solvents currently used for this proposal as, for example, 30 wt.% MEA [54].



### 2.6.2.3. Lipophilic-amine-based thermomorphic biphasic solvents

Lipophilic-amine-based thermomorphic biphasic solvents have shown potential advantages in CO<sub>2</sub> capture compared to conventional alkanolamines in terms of solvent regeneration and cyclic capacity. The improvements obtained using these types of solvent are based on its thermomorphic behavior. This phenomenon consists of the generation of two liquid phases after heating inside the reboiler. According to Zhang et al. [52], these systems can be regenerated at lower temperatures than the conventional alkanolamine blends. This temperature reduction in regeneration step allows a decrease of the energetic consumption in CO<sub>2</sub> capture processes. Amine blends used by Zhang were mostly composed of an absorption activator: A1, dipropylamine (DPA) and a regeneration promoter: N, N-dimethylcyclohexylamine (DMCA) and N-ethylpiperidine (EDP) (**Table 7**).

## 3. Physical absorption solvents

Physical absorption processes are highly recommended to separate CO<sub>2</sub> in pre-combustion processes that commonly operate at elevated CO<sub>2</sub> partial pressure. Physical solvents are able to selectively capture CO<sub>2</sub> in contact with a gas stream without a chemical reaction occurring. As it was indicated in the introduction section, the high partial pressures of CO<sub>2</sub> and low-temperatures are desirable to obtain an optimized performance of the physical absorption process in terms of absorption rates and solubility equilibrium of CO<sub>2</sub>. Then, the rich (CO<sub>2</sub> loaded) solvent is regenerated [55].

Focusing on the pre-combustion CO<sub>2</sub> capture process itself, seven processes using physical solvents are currently commercially available, which are discussed in the following section.

A summary of the most relevant physical properties of each solvent and the list of advantages and disadvantages can be found at the end of this chapter in **Table 8**.

### 3.1. Selexol™

The Selexol™ process has been widely used and effectively proven in the refinery industry, natural gas sweetening, syngas processing and fertilizer production since the 1960s. Recently, Selexol™ has also been used in IGCC for H<sub>2</sub>S, COS and CO<sub>2</sub> removal.

The Selexol™ process, licensed by Universal Oil Products (UOP), employs a mixture of different dimethyl ethers and polyethylene glycol, represented by the formulae (CH<sub>3</sub>O(C<sub>2</sub>H<sub>4</sub>O)<sub>n</sub>CH<sub>3</sub>), with n factor ranging from 3 to 9 [2]. This physical solvent was patented by DOW chemical [56]. Selexol™ provides a selective absorption of H<sub>2</sub>S, COS, mercaptans and CO<sub>2</sub> from a variety of natural and synthesis gas streams. It has shown a high performance under high-pressure, low-temperature and high acid gas process conditions.

In the Selexol™ process, the flue gas must be first dehydrated before being introduced in the absorption column. After that, the dehydrated flue gas enters the absorber at 30 atm and 0–5°C and the acid gas components are selectively absorbed into the solvent along the

Process	Advantages	Disadvantages
Selexol™	<ul style="list-style-type: none"><li>• Non-thermal solvent regeneration</li><li>• Non-corrosive solvent</li><li>• Dry gas leaves from the absorber</li></ul>	<ul style="list-style-type: none"><li>• Most efficient at elevated pressures</li></ul>
Rectisol™	<ul style="list-style-type: none"><li>• Non-foaming solvent</li></ul>	<ul style="list-style-type: none"><li>• High refrigeration costs</li></ul>
Ipexol-2™	<ul style="list-style-type: none"><li>• High chemical and thermal stability</li></ul>	<ul style="list-style-type: none"><li>• High capital costs</li></ul>
Fluor™	<ul style="list-style-type: none"><li>• Non-corrosive solvent</li><li>• High CO<sub>2</sub> solubility</li><li>• Non-thermal regeneration</li></ul>	<ul style="list-style-type: none"><li>• Amalgams formation at low T</li><li>• High solvent circulation rates</li><li>• Expensive solvent</li></ul>
Purisol™	<ul style="list-style-type: none"><li>• Simple operation</li><li>• Non-corrosive solvent</li><li>• Non-foaming solvent</li><li>• High chemical and thermal stability</li><li>• Non-corrosive solvent</li><li>• Low volatility</li></ul>	<ul style="list-style-type: none"><li>• High compression cost</li><li>• Most efficient at high-pressure</li></ul>
Sulfinol™	<ul style="list-style-type: none"><li>• High capacity</li><li>• Low solvent circulation rate</li></ul>	<ul style="list-style-type: none"><li>• Foaming issues</li><li>• Corrosive solvent</li><li>• Thermal regeneration</li></ul>
Morphysorb™	<ul style="list-style-type: none"><li>• High solvent loading capacity</li><li>• Low energy requirement</li><li>• Non-corrosive solvent</li><li>• Low capital and operating costs</li></ul>	<ul style="list-style-type: none"><li>• New process</li></ul>

**Table 8.** Main advantages and disadvantages of physical absorption technologies available for CO<sub>2</sub> capture [58, 59].

column. A pre-treatment absorption column can be used to accomplish the sulfur compound removal prior to CO<sub>2</sub> separation. The CO<sub>2</sub> loaded solvent is then sent to the regeneration process from which the solvent recovers its original capacity by either reducing the pressure or inert gas stripping. The recovered (lean) solvent is recycled back into the absorber, whereas the high purity CO<sub>2</sub> exits the regeneration stages to be compressed and stored.

### 3.2. Rectisol™

The Rectisol™ process is applied in H<sub>2</sub>S and CO<sub>2</sub> removal from syngas streams, mainly from heavy oil and coal gasification. The CO<sub>2</sub> stream obtained can be used in urea, methanol and ammonia production, but it is not applied for the food and beverage industry. It has a high selectivity for H<sub>2</sub>S, CO<sub>2</sub> and COS and can be configured to accomplish the separation of synthesis gas into various components depending on the final product specifications and process objectives.

Rectisol™ is licensed by Lurgi AG, which is an affiliated company of Air Liquide. This technology employs chilled methanol as solvent and can be applied for low and moderate CO<sub>2</sub> concentrated gas streams. Due to the high vapor pressure of the solvent, the absorption stage must be carried out at very low-temperatures to reduce solvent losses [57].

In the Rectisol™ process, the raw syngas is cooled before being introduced into the absorption process. The sulfur compounds must be firstly removed using a CO<sub>2</sub> loaded solvent. After that, the sulfur exempt syngas contacts with the chilled methanol in the absorber, operating at 50 atm and temperatures in the range of [−100°C, −30°C]. The rich solvent is then sent to the regeneration stage where CO<sub>2</sub> is released by flash desorption, reducing the pressure up to 1 bar. The lean solvent is recycled back to the absorber [2, 57].

### 3.3. Ifpexol™

The Ifpexol™ process introduced in 1991 can be used for natural gas applications. This process is based on two steps as follows: Ifpex-1™ removes condensable hydrocarbons and water and Ifpex-2™ removes acid gas [58]. Ifpexol™ is licensed by Prosernat and uses refrigerated methanol as physical solvent.

The Ifpexol-2™ process for acid gas removal is similar to an amine-based chemical absorption process except for the operating temperatures. The absorber operates below −29°C to minimize methanol losses, and the regenerator operates at about 6 bar. Cooling is required on the regenerator condenser to recover the methanol releasing during the regeneration step. This process usually follows the Ifpexol-1™ process so excessive hydrocarbon absorption is not as great a problem [59].

### 3.4. Fluor™

Fluor™ process is the most suitable physical absorption process to be applied for high CO<sub>2</sub> partial pressure syngas streams and has been in use since the late 1950s. Fluor™ is licensed by Fluor Daniel, Inc. and employs propylene carbonate (C<sub>4</sub>H<sub>6</sub>O<sub>3</sub>) as solvent (available as JEFFSOL™ PC solvent), which has a lower vapor pressure than those used by Rectisol™ and Selexol™. The solvent requires neither a low nor no presence of H<sub>2</sub>S and can be applied in large CO<sub>2</sub> removal applications [60, 61].

In the Fluor™ process, physical absorption occurs at moderate to high-pressure, ranging between 30 and 80 bar, and at ambient temperature. The flue gas must be dehydrated before the gas enters into the absorption column to prevent water build-up in the solvent. As indicated before, H<sub>2</sub>S must also be removed before the CO<sub>2</sub> absorption occurs. After CO<sub>2</sub> is absorbed, the CO<sub>2</sub> loaded solvent is flashed to release CO<sub>2</sub> and recovers its original capacity. The lean solvent is recycled back to the absorber, whereas the high purity CO<sub>2</sub> exits the regeneration stages to be compressed and stored [62].

### 3.5. Purisol™

The Purisol™ process is particularly suited to treat high-pressure, high CO<sub>2</sub> synthesis gas from IGCC systems because of the high selectivity for H<sub>2</sub>S. This technology is licensed by Lurgi AG and employs N-methyl pyrrolidone.

In the Purisol™ process, H<sub>2</sub>S removal is not required prior to CO<sub>2</sub> absorption occurring. The process can be operated at 50 bar and either at ambient temperature or with refrigeration down to about −15°C. The CO<sub>2</sub> desorption is accomplished by stripping with an inert gas [63].

### 3.6. Sulfinol™

The Sulfinol™ process can remove H<sub>2</sub>S, CO<sub>2</sub>, carbonyl sulfide, mercaptans and organic sulfur components from natural and synthesis gas from coal or oil gasifiers and steam reformers. This process accomplishes H<sub>2</sub>S and CO<sub>2</sub> separation in a wide variety of compositions up to around 50%v/v H<sub>2</sub>S and above 20%v/v CO<sub>2</sub>. The principle of this process aims at combining the high absorption potential of alkanolamine (chemical absorption) and the low regeneration energy requirement of the physical solvent (physical absorption).

Sulfinol™ is licensed by Shell Oil Company and employs mixtures of diisopropylamine (DIPA) or methyldiethanolamine (MDEA) and tetrahydrothiophene dioxide (SULFOLANE) in different blends. The physical solvent used (DIPA or MDEA) has a higher absorption capacity and a low energy requirement for regeneration, thus increasing the carrying capacity due to lower solvent recycled requirements. The absorber is operated at 40°C and a pressure around 60–70 bar. The rich solvent is then sent to the stripping column where CO<sub>2</sub> is released at temperatures over 110°C and vacuum pressure. It should be noted that addition of anti-foam is needed in the absorber and solvent degrades due to the presence of oxygen and stripper temperatures [64].

### 3.7. Morphysorb™

The Morphysorb™ process is applied for selective removal of H<sub>2</sub>S, CO<sub>2</sub>, COS, CS<sub>2</sub>, mercaptans and other components from coal/oil gasification syngas at IGCC facilities. This process is particularly effective for high-pressure and high acid gas applications and offers substantial savings in investment and operating cost compared to the competitive physical solvent-based processes. The operational cost is 30–40% lower than that for Selexol™ Process [65, 66].

This technology is developed by Krupp Uhde GmbH in cooperation with the Institute of Gas Technology (GTI), and employs N-formyl morpholine (NFM) and N-acetyl morpholine (NAM) mixtures as solvent (manufactured by BASF AG). In comparison with other physical solvents, the Morphysorb solvent co-absorbs fewer heavier hydrocarbons and is also suited for simultaneous water removal from the feed gas [67]. In this process, the acid gases are removed from the absorbent by flashing and the regenerated absorbent is recycled to the absorber. The physical absorption occurs at temperatures between −20 and +40°C and at pressure of 10–150 bar [67]. The key advantage of the Morphysorb™ technology is the high acid gas capacity together with the low solubility of C1–C3 hydrocarbons, resulting in a higher product yield and a lower recycle flash stream [68].

## 4. Conclusions

Physical and chemical CO<sub>2</sub> absorption are mature technologies that can be applied to CO<sub>2</sub> emission mitigation at large scale, mainly focused on fossil-fuel power plants, cement production and steel manufacturing. This chapter summarizes the cutting-edge of the knowledge about absorbents developed for this proposal. The most relevant aspect of conventional physical and chemical solvents applied to CO<sub>2</sub> capture was summarized and their physical properties, absorption mechanisms and kinetics were further discussed. Based on the current state-of-art in the field of CO<sub>2</sub> absorption, the novel solvents and blends were also reported and new applications such as ionic liquids have been deeply discussed along the manuscript from the specific literature available on this topic.

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