

Review

# Amine-Based Solvents and Additives to Improve the CO<sub>2</sub> Capture Processes: A Review

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**Abstract:** The use of amine-based solvents for carbon dioxide (CO<sub>2</sub>) capture has shown significant promise; however, operational challenges such as high energy requirements, solvent degradation, and equipment corrosion highlight the need for enhanced solutions. This review focuses on identifying amine-based solvents and additives that can improve CO<sub>2</sub> capture efficiency while minimizing costs and avoiding substantial modifications to existing industrial facilities. Specifically, the study emphasizes the development of a comprehensive database of additives to optimize CO<sub>2</sub> capture processes. A detailed analysis of recent advancements in amine-based solvents was conducted, with a focus on (i) process optimization strategies, (ii) sector-specific CO<sub>2</sub> emission profiles, and (iii) equipment issues associated with conventional chemical solvents. The study evaluates these solvents' kinetic and thermodynamic properties and their potential to address critical operational challenges, including reducing corrosion, solvent viscosity, and evaporation rates. The findings highlight the pivotal role of amino group-containing compounds, particularly alkanolamines, in enhancing CO<sub>2</sub> capture performance. The structural versatility of these compounds, characterized by the presence of hydroxyl groups, facilitates aqueous dissolution while offering kinetic and thermodynamic benefits. This review underscores the importance of continued innovation in solvent chemistry and the integration of amine-based solvents with emerging technologies to overcome current limitations and advance the implementation of efficient and sustainable CO<sub>2</sub> capture technologies.

**Keywords:** CO<sub>2</sub> capture; industrial processes; additives; alkanolamines; chemical solvents; review



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## 1. Introduction

Carbon dioxide (CO<sub>2</sub>) is one of the significant waste gases from factory exhaust and industrial activities, transportation, and electricity; these production sectors emit the most CO<sub>2</sub> by employing fossil fuels [1–3]. Most CO<sub>2</sub>-containing gases fall into typical gas mixtures, such as fuel gas (H<sub>2</sub> and CO<sub>2</sub>), flue gas (N<sub>2</sub> and CO<sub>2</sub>), and CO<sub>2</sub>-containing gas mixtures that comprise high CO<sub>2</sub> concentrations (>15 mole%), such as natural gas, biogas, landfill gas, and refinery gases [4–6]. As the concentration of greenhouse gases in the atmosphere increases, effective CO<sub>2</sub> emission reduction strategies, such as carbon capture, utilization, and storage (CCUS), are required to counter this trend [7–13]. Moreover, a carbon capture strategy is essential to prevent CO<sub>2</sub> emissions from all possible sources [14–18].

Emerging technologies focus on developing advanced materials and innovative techniques to enhance CO<sub>2</sub> capture efficiency and selectivity. Approaches such as metal–organic frameworks (MOFs) [19], solid sorbents (e.g., zeolites or clay/sand pellets) [20,21], covalent organic frameworks (COFs) [22], and covalent microporous polymers (CMPs) [23] have demonstrated potential due to their high porosity [24], structural stability, and tunable functionalities for CO<sub>2</sub> adsorption [25]. Electrochemical processes leveraging renewable electricity to integrate CO<sub>2</sub> capture with green hydrogen production [26] and membrane separation technologies that offer modular, solvent-free solutions for CO<sub>2</sub> capture are also

gaining traction [27,28]. Additionally, advanced porous materials, including polymeric and nanostructured adsorbents, are being developed to improve CO<sub>2</sub> selectivity and efficiency [29]. More ambitious methods, such as direct air capture (DAC) [30], aim to extract CO<sub>2</sub> directly from the atmosphere, promising net-negative emissions but facing challenges such as low CO<sub>2</sub> concentrations and high operational costs. Despite the significant advancements, the scalability, and economic feasibility remain critical hurdles for the industrial adoption of emerging technologies [31].

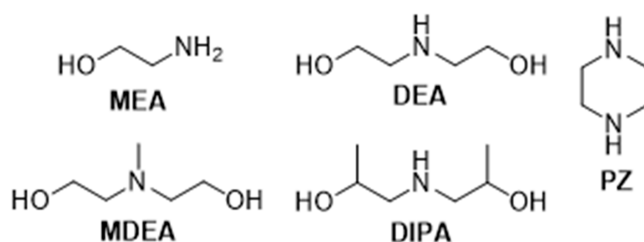
Conversely, mature technologies dominate industrial-scale CO<sub>2</sub> capture due to their reliability, scalability, and proven performance in diverse applications. Processes like amine-based solvent absorption [32], widely used for post-combustion capture, are favored for their high CO<sub>2</sub> capture efficiency despite drawbacks such as high energy requirements for regeneration and solvent degradation [33]. Pressure swing adsorption (PSA), temperature swing adsorption (TSA), and vacuum swing adsorption (VSA) are established methods for pre-combustion and high-purity CO<sub>2</sub> capture, with VSA offering lower energy requirements compared to TSA [34,35]. Cryogenic separation is suitable for streams with high CO<sub>2</sub> concentrations, while calcium looping provides high thermal efficiency for large-scale applications [34]. Additionally, oxy-fuel combustion produces concentrated CO<sub>2</sub> streams but faces challenges in retrofitting existing infrastructure due to high costs [36]. While these technologies are well-suited for current industrial needs, continued evolution aims to address energy intensity and integration challenges, creating opportunities for synergistic advancements with emerging approaches. Table A1 summarizes the main advantages and disadvantages of emerging and mature technologies for CO<sub>2</sub> capture processes.

Chemical absorption with aqueous solvents has been the most reliable and promising technology for CO<sub>2</sub> capture after large-scale combustion [37]. It consists of reversible reactions of CO<sub>2</sub> with chemical solvents to form weakly bonded intermediate compounds that can be regenerated by applying heat to the original solvent and CO<sub>2</sub> stream [38]. Two technological approaches usually reduce the energy used for CO<sub>2</sub> solvent regeneration [39–41]: (a) new solvent development, either using a selective CO<sub>2</sub> solvent or mixing various solvents or additives, and (b) process optimization. Amine-based, carbonate-based, aqueous ammonia, and ionic liquid-based systems are the standard systems for carbon dioxide capture [42–46]. Among these technological options, the amine-based solvents are the most mature technology and the most used worldwide [47–50].

Namieśnik and Zygmunt [51] stated that amines are organic compounds derived from ammonia, like alcohols and ethers derived from water. Amines can be produced by decomposing larger molecules, i.e., amino acids and ammonia synthesis [52]. In addition, amines can be classified according to the number of alkyl (or aryl) groups attached to the nitrogen atom as primary amines (with only one radical bonded), secondary amines (with two radicals bonded), and tertiary amines (with three radicals bonded) [53]. Compared to tertiary amines, primary and secondary amines may have mobile hydrogen atoms on nitrogen, allowing for better performance [54]. Other amine-based solvents have also been proposed for CO<sub>2</sub> capture. Among these, heterocyclic amines stand out [55]. Heterocyclic amines are compounds with at least one heterocyclic ring, a cyclic chemical structure with two or more different elements [56]. Their reactivity in the capture process requires the absorption of the acid-free carbonic proton produced by the interaction between CO<sub>2</sub> and water. Owing to its basicity (in virtually all amines), the amine–water reaction interaction results in pH values higher than 8.5. Therefore, it facilitates faster CO<sub>2</sub> reactivity. Piperazine [57,58] and 3-piperidine-1,2-propanediol [59] are examples of heterocyclic amines used in CO<sub>2</sub> capture processes.

Alkanolamines originate from primary amines [60]. This group comprises three components: a hydroxyl group as the primary alcohol, an amino group as the primary amine, and an alkane backbone. Secondary and tertiary alkanolamines, each composed of secondary and tertiary amines, contain one or more hydroxyl groups in their backbones [59,61]. The –OH group in alkanolamines reduces instability and favors solubility in water [62]. Altway et al. [63] stated that different amine-based solvents have been extensively stud-

ied for CO<sub>2</sub> capture purposes. Figure 1 shows the chemical structure of the most commonly used amines for CO<sub>2</sub> capture—monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), piperazine (PZ), and diisopropanolamine (DIPA) [44,64]. The dominant mechanism for CO<sub>2</sub> capture by these amines involves the formation of carbamates through a nucleophilic attack of the amine nitrogen on the carbon of CO<sub>2</sub>, forming carbamic acid, which subsequently deprotonates to produce a carbamate ion. This reaction is prevalent in primary and secondary amines, such as MEA and DEA [65]. In contrast, tertiary amines like MDEA do not form carbamates directly, but promote CO<sub>2</sub> capture through the bicarbonate equilibrium by facilitating the conversion of dissolved CO<sub>2</sub> into bicarbonate ions [66]. Adding PZ as an activator in tertiary amine systems enhances the reaction kinetics, enabling faster absorption rates [67].



**Figure 1.** Chemical structures of the most common amine used in CO<sub>2</sub> capture.

A formulated amine can generally be defined as an amine specifically designed to carry out basic functions or simple tasks. Major solvent producers sell many patented solvents based on formulated amines with a high degree of secrecy about the chemical composition and the operational performance of these commercial solvents [68]. Nevertheless, formulated amines are versatile chemical solvents suitable for industrial applications [68,69]. According to Koehler and Claffey [70], polyisobuteneamine (PIBA) has been widely used for formulated amines. Chowdhury et al. [59] explored mixtures of amine sorbents, mainly primary and tertiary or secondary and tertiary amines, for example, MEA and MDEA or DEA and MDEA, respectively. These integrated components have higher reaction rates than the primary and secondary amine solvents proposed for industrial gas processing. Amines that are consumed in industrial processes have become impractical. Storage-deteriorated amines need to be cleaned before use, and they are too expensive owing to amine loss through oxidation and additional losses in cleaning processes.

Adding additives to chemical solvents could efficiently separate CO<sub>2</sub> gas, such as ionic liquids, surfactants, and physical and chemical absorbers [71,72]. Additives, such as aqueous amine solvents, contain either a single amine or several amines. While single-amine solvents are still commercially used, amine blends and formulated amines tend to be rational alternatives for gas separation. Newly produced high-performance solvents are also based on amine blends [66,68]. Several research studies have been focused on discovering new mixed amine solvents, primarily concentrating on the laboratory scale [66], and on conventional amine blends and/or additives to improve the capture processes of current industrial technologies [73]. Capturing and releasing CO<sub>2</sub> via a cyclical chemical absorption/regeneration mechanism is expected to result in more than half the cost of capturing absorbent regeneration and reducing the energy consumption of absorbent regeneration [59].

Several amine solvent solutions have been studied. However, an ideal solvent has not been found. One of the essential factors is implementing a closed process that allows solvents to be reused at minimal environmental and economic costs. Researchers must always consider the overall effect of the implementation of new technology and how it can be tested to provide solutions on a local or global scale [74]. Efforts by the scientific community have focused on finding additives that improve carbon dioxide capture processes [75]. This could be due to the increase in operational problems caused by conventional amines in their industrial use, such as technologies employed in natural gas, petroleum, coal-fuel-fired thermal power plants, and chemical process industrial units [76]. Furthermore, the high capital required to acquire permits and licenses for formulated amines is confidential [77].

Hence, this state-of-the-art review from the last 20 years focuses on scientific articles, proceedings, and patents to identify chemical solvents and additives to improve the CO<sub>2</sub> capture process in mainly amine-based solutions. The identification and classification of chemical solvents and additives reduce typical problems related to amine usage, such as volatility and corrosion of equipment and pipes, as well as reduce unscheduled downtime as much as possible, high regeneration temperatures, and high energy consumption. An extensive and in-depth study of chemical additives employed to enhance and improve CO<sub>2</sub> capture is carried out to establish the most effective options for choosing possible additives for future studies. The chemical solvents and additives obtained are then classified according to technical aspects, such as their performance and viability. Moreover, we identify some characteristics when choosing different additives (as their efficiency might come from kinetics or thermodynamic enhancement) and analyze the actual tendencies within this field of investigation.

## 2. Methodology

A systematic search was conducted in several databases to ensure a comprehensive review of amine-based solvents and additives that could improve CO<sub>2</sub> capture, using keywords aligned with the study's objectives. First, the most effective characteristics for choosing amine-based compounds as chemical solvents to enhance and improve CO<sub>2</sub> capture were established. Second, the solvents and additives identified were classified according to their technical aspects, such as their performance and feasibility. Finally, some physicochemical characteristics of the kinetic and thermodynamic types were identified as related to the stability of the derivatives formed by the interaction between CO<sub>2</sub> and the compounds. At the beginning of the study, the search focused on keywords and databases centered on the study's objectives, as indicated in Table 1. Therefore, the selection was based on common words plus compound terms, and one more was added to the above results to narrow down the search criteria. This study was based on a literature review focused on the last 20 years consulting scientific articles, proceedings, and patents on databases and search engines such as Scopus, Web of Science, Crossref, Google Patents, SciFinder, and OnePetro.

**Table 1.** The establishment of keywords employed for the search in the search-motor database was consulted.

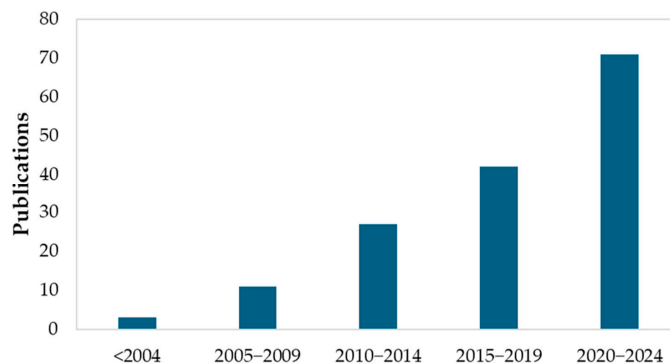
Establishment	Specific Words	Variable Words
Amine-based solvents Additives improvements	CO <sub>2</sub> capture amine	Classification; mechanism; kinetics; formulated amines; amine mixtures; solvents; industrial problems; processes; improvements; conventional; renewable

### Research Approach

More than 150 research articles were found, starting at the beginning of the 21st century to 2024, where a clear tendency to increase research on amine-base compounds as chemical solvents for CO<sub>2</sub> capture exponentially was observed (Figure 2), with than 70% of the publications in the period 2015–2014.

The scientific community's effort to find additives that improve CO<sub>2</sub> capture tends to increase. This could be due to the increase in operational problems that conventional amines cause in their industrial use, such as technologies employed in natural gas, petroleum, coal-fuel thermal power plants, and chemical process industrial units [41]. Furthermore, the high capital required to acquire permits and licenses for formulated amines is confidential [42]. There might be many cases that solve and prove this trend, but this study proposes one by assuming that a chemical capture process undergoes amine-based blends composed of additives. In that case, the capture process rate might increase, helping industrial operation

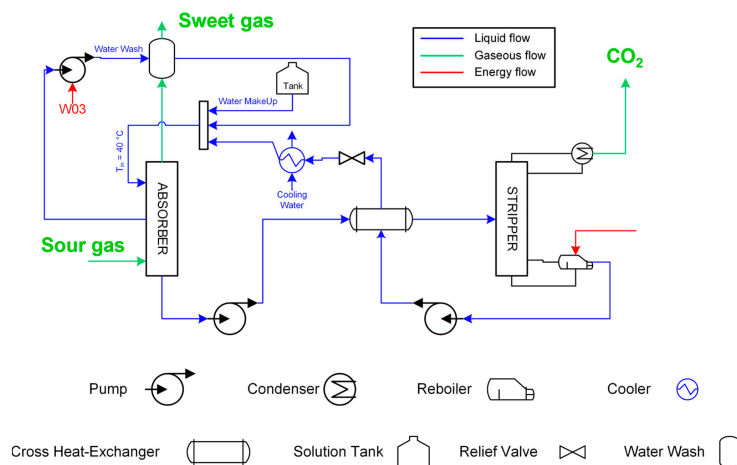
units prevent their main problems like corrosion and reducing maintenance and energetic costs, especially in countries that base their economies on oil and gas production.



**Figure 2.** Publication's trend of amine-based solvents and additives to improve CO<sub>2</sub> capture.

### 3. Challenges in Amine-Based Solvents Used in CO<sub>2</sub> Capture Processes

Typically, the capture process that uses aqueous amines includes two units (Figure 3): The first column, labeled the absorber, is where absorption occurs due to contact between the sour gas and the chemical solvent in a countercurrent arrangement. The second column, labeled the stripper, releases the previously absorbed CO<sub>2</sub> and regenerates the chemical solvent, which can be used again to promote absorption in the first column [78,79]. Additional equipment, like pumps, condensers, and reboilers, must perform well in gas-processing quantities and reduce energy consumption. The sweet gas must meet quality specifications depending on downstream natural gas usage [80]. The CO<sub>2</sub> content must be <1–2 mole% if used as fuel gas [81].



**Figure 3.** Typical process flow diagram of the CO<sub>2</sub> capture process using amine-based solvents. (Adapted from [79]). © 2023 by the authors.

CO<sub>2</sub> capture processes using aqueous amines as chemical solvents employ amine-based compounds that have been thoroughly tested on laboratory and pilot scales to study their ability to achieve high absorption potential, cyclic loading and cyclic capacity, improved absorption rate, low solvent regeneration energy, decreased corrosion, and thermal degradation [82]. The effectiveness of several chemical solvents depends not only on their CO<sub>2</sub> absorption capacity and efficiency, particularly the role of the thermodynamic solution, but also on their kinetics [83–85]. It has been shown that using amines as additives, the most widely used chemical solvents to capture and sequester carbon dioxide, is an exciting option for improving the overall performance [72,86].

Most amine-based chemical compounds and blends have been employed as 10–65 wt.% solutions in deionized or distilled water [40,60,82,87,88]. However, it is essential to mention

that in various processes, amines can vary their concentrations as a function of the desired grade of capture, operational arrangements of the industrial plant, or even the characteristics of the gas current employed due to corrosion problems [89]. Higher concentrations can reduce the circulation of amines and increase absorption temperature and corrosion rate. Amine units can usually meet performance promises and have no operational issues during early service. However, device efficiency typically deteriorates with time, primarily due to the build-up of pollutants and impurities and lack of maintenance [40].

A single method cannot be selected based only on the solution flow rate when employing amine-based compounds as chemical solvents. Consequently, it is essential to point out the typical characteristics of conventional amines. Chemical solvents employed as aqueous amines have advantages and disadvantages [90], as illustrated in Table 2.

**Table 2.** Advantages and disadvantages of amine-based technology for CO<sub>2</sub> capture.

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>• Less volatile</li> <li>• Good stability of absorbent</li> <li>• Enhancement role used as additives</li> <li>• Mature technology</li> </ul>	<ul style="list-style-type: none"> <li>• Low carbon dioxide loading capacity</li> <li>• The high corrosion rate of the equipment</li> <li>• Amine oxidation by SO<sub>2</sub>, NO<sub>2</sub>, HCl, and HF, and the presence of oxygen in the natural gas stream</li> <li>• High energy consumption during high-temperature absorbent regeneration</li> <li>• Toxicity and environmental issues</li> <li>• High capital costs (CAPEX) and operational costs (OPEX)</li> </ul>

Amine solvents can cause operational problems in absorption units [91], which can be mitigated by maintaining a temperature approach between the lean amine and feed gas, skimming hydrocarbons from rich amine flash drums and reflux drums, and improving particulate filters and carbon filters [37,40,92,93]. The drawbacks of the most common amines employed in the capture process are as follows [64,94–96]:

1. *Low carbon dioxide loading capacity.* The solubility of CO<sub>2</sub> in the liquid phase is essential for adequately measuring the absorption effectiveness. As a result, replacing water in amine solvents with organic co-solvents such as alcohols will also increase the physical solubility of CO<sub>2</sub> in solutions, enhance solvent regeneration performance, and reduce regeneration costs. However, the elevated volatility of co-solvents is a drawback for industrial applications. In addition, the higher viscosity of organic solvents such as amines may harm the heat exchanger efficiency, absorption kinetics, and pumping costs [91].
2. *High corrosion rate of the equipment.* CO<sub>2</sub> capture systems as amine-based chemical solvents are used in industrial processes, which may corrode lines and equipment owing to their chemical nature, leading to bicarbonate and carbamate species [97,98]. Some techniques have been implemented, such as incorporating corrosion inhibitors or introducing alternate absorption liquids [99–101]. Electrochemical tests must be performed to clarify the potential harm incurred by the preceding evidence [102]. Other operational problems include solvent chemical instability, which is more prone to using primary and secondary amines than tertiary amines [103].
3. *Amine oxidation by SO<sub>2</sub>, NO<sub>2</sub>, HCl, and HF, and the presence of oxygen in the natural gas stream.* Oxidative degradation of amine solutions reduces CO<sub>2</sub> capacity absorption and can increase corrosion in natural gas treatment facilities [104,105]. Vega et al. [106] summarized the main degradation products of the common amine-based solvents.
4. *High energy consumption during high-temperature absorbent regeneration.* In comparison, mixed amine solvents can lead to a lower circulation flow rate, which means smaller equipment sizes and lower capital and operational costs [91]. Using an alkanolamine, such as a liquid absorbent, causes variable debris and operative problems such as

corrosion, volatility, and thermal degradation at 100–150 °C, making it difficult to control. Therefore, the use of power and cost is high and may increase in each absorption process [107]. Thus, developing improved chemical methods for CO<sub>2</sub> capture processes is required to prevent high temperatures and mitigate their adverse effects [108,109]. The amine degradation activity can result in the loss of solvents, accumulation of byproducts, foaming, and corrosion, significantly affecting the CO<sub>2</sub> capture efficiency [110]. Moreover, as is well known in industrial applications, a high-grade amine vaporization loss arises in the absorber when the sweet gas escapes and is saturated with water at a higher temperature.

5. *Toxicity and environmental issues.* Solvent emissions are a severe problem in the industrialization of the amine-based CO<sub>2</sub> capture process [111]. Amine-based solvent degradation during operation, driven by thermal and oxidative stresses, generates harmful byproducts such as nitrosamines, nitramines, and aldehydes, which can pose risks to human health and ecosystems. Nitrosamines, in particular, are classified as potential carcinogens and have strict regulatory limits in many jurisdictions [112]. Additionally, amines and their degradation products can leach into water systems if they are not properly managed, leading to contamination and ecological harm [113]. The corrosive nature of amine solutions also contributes to increased maintenance and material costs, potentially exacerbating waste management issues, as corroded materials require disposal [114]. Advanced solvent formulations with improved thermal and oxidative stability can reduce the formation of hazardous byproducts. In contrast, process design improvements such as effective byproduct removal and closed-loop systems can minimize environmental release.
6. *High capital costs (CAPEX) and operational costs (OPEX).* CAPEX is associated with the equipment required for CO<sub>2</sub> absorption and amine-based solvent regeneration. Developing new equipment materials and process optimization could help reduce the capital cost for existing and new industrial facilities [115–117]. For its part, OPEX is associated with plant operation and maintenance issues; these costs can be minimized by reducing the viscosity and foaming of the aqueous solution, reducing the amine loss through evaporation, lowering energy consumption in the solvent regeneration unit, and reducing the corrosion rate. Some additives have been tested to improve the operational performance of amine-based solvents, e.g., imidazolium-based ionic liquids can reduce the viscosity [118], piperazine and bicine control the foam formation [119], and ionic surfactants can reduce the energy requirement in the amine regeneration processes [120]. Blending two or more amines has been recognized as an efficient strategy to formulate competitive liquid sorbents, as it allows one to benefit from the advantages of each individual amine, improving the CO<sub>2</sub> absorption and desorption rates and energy consumption during the regeneration process [73].

#### 4. Amine-Based Solvents and Additives to Improve the CO<sub>2</sub> Capture Process

##### 4.1. Classification According to Their Chemical Nature

A classification based on the origin of the compounds was performed, focusing on their chemical nature, as shown in Table 3. Extensive research has been conducted on chemical solvents, additives, and promoters to improve CO<sub>2</sub> absorption. According to their chemical nature and engineering aspects, the criteria for classification are conventionally named products employed in the CO<sub>2</sub> capture process. The additives were grouped into primary, secondary, and tertiary amine categories. Additional classifications correspond to other amine compounds with structures different from those of primary, secondary, and tertiary amino acids (containing a mixture). Some other compounds that do not contain amines in their chemical structures but remain as chemical solvents are also classified as other chemical compounds. The chemical compounds were classified into families because it is necessary to manage the information efficiently. However, this study found that additives are not just close to kinetic or thermodynamic improvements. Additives can also control foaming production or protect the available equipment to avoid corrosion.

Hence, chemical solvents as additives/promoters to improve chemical absorption are at the forefront of investigative applications. The main benefit comes from the existence of these chemical additive (purchasable) compounds. Its utilization is being tested, and the current infrastructure does not need to be transformed or adapted for its implementation. Details of each compound identified in this study can be found in the Supplementary Materials.

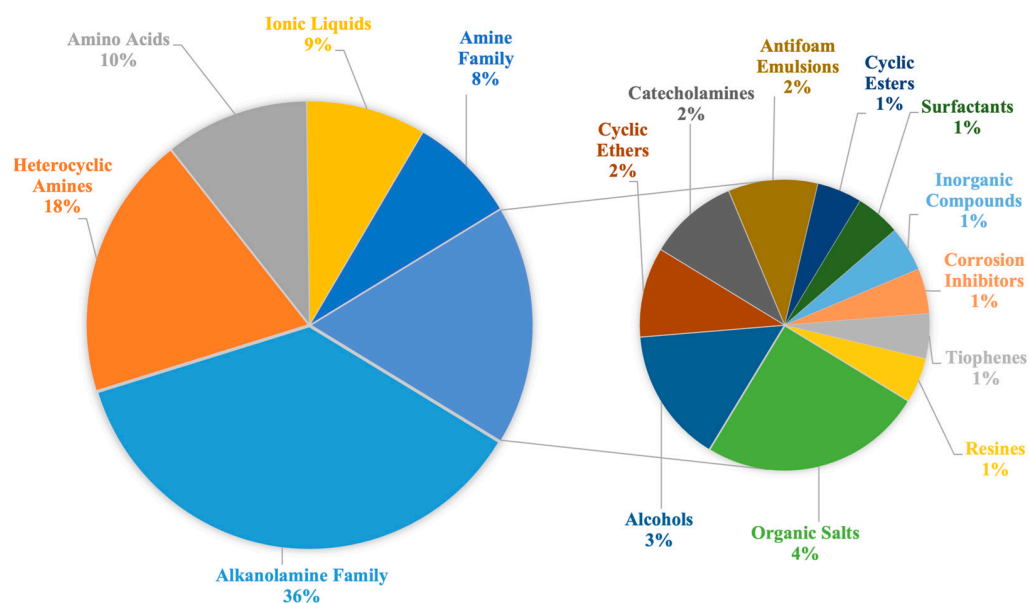
**Table 3.** Abbreviations in the classification of amine-based solvents and additives.

Chemical Nature (Abbreviation)	Compounds Identified	Compounds [References]
Alkanolamine Family (AAM)	43	AMP [85,121–126]; AMPD [121]; AEDP [121,124]; THAM [121,127]; MEA [78,85,96,122–126,128–134]; DEEA [59,60,87,108,134–138]; AEEA [122,126,131,136]; AEP [122]; DMEA [59,60,108,126,137]; DMA-1P [59,60]; DEA-1P [59,60]; DMA-2P [59,60]; DEA-2P [59,60]; DIPAE [59]; DMA-2M-1P [59,60]; DMA-2,2-DM-1P [59]; 4EMA-2B [59]; EDEA [59,135]; IPDEA [59,123]; tBDEA [59]; DMA-1,2-PD [59,60]; DEA-1,2-PD [59,60]; TEA [59,139]; MDEA [59,60,78,85,88,96,123,124,126,129,137,139–145]; DEAB [60]; DEA [78,96,123,124,126,131,145]; MAMP [123]; EAMP [123]; IPAE [123]; IBAE [123]; SBAE [123]; MMEA [124,126]; NBMEA [124]; TBMEA [124]; EMEA [124,135]; DIPA [124]; AMPDI [124]; MAPA [87,129]; TEPA [129]; DGA [85]; TIPA [137,139]; triMEA [126]
Heterocyclic Amines (HCA)	21	PZ [78,85,122,124,131,146,147]; NMP [146,148]; IMI [146]; 4-A1MPD [134]; 1-(2HE)PRLD [59]; PRLD-1,2-PD [59]; 1-(2HE)PP [59]; 3PP-1,2-PD [59]; 1M-2PPE [59,123]; 3H-1MPP [59]; 1E-3HPP [59]; AEPI [88,143,149]; BTA [140]; H [149]; SRT [149]; 2-PMA [149]; 2-2-AEP [149]; 4-2-AEM [149]; NFM [148]; PYR [139]; DMP [126]
Amino Acids (AmA)	12	Arg [142,150]; L-His [149]; D-His [149]; L-Phe [149]; D-Phe [149]; L-DOPA [149]; D-DOPA [149]; L-Trp [149]; D-Trp [149]; L-Tyr [149]; D-Tyr [149]; 4-A-L-Phe [149]
Amine Family (AF)	10	BEHA [78]; N,N-DM13PDA [134]; N,N-DM12EDA [126,134]; TMEDA [110,126]; TMPDA [110]; TMBDA [110]; EDA [43,78,135]; DETA [129,141]; TETA [88,129,141]; TELA [78,85]
Ionic Liquids (IL)	10	[EMIM]BF <sub>4</sub> [71]; [EtOHMim][PF <sub>6</sub> ] [151]; [EtOHMim][BF <sub>4</sub> ] [151]; [EtOHMim]Cl [151]; [Choline][PF <sub>6</sub> ] [151]; [Choline][BF <sub>4</sub> ] [151]; [Choline]Cl [151]; 2-PHEN [152]; 3-PHEN [152]; 4-PHEN [152]
Organic Salts (OS)	5	TBAB [71,153,154]; TBAF [155]; TBAC [153]; TBPB [152,153]; TBPC [153]
Alcohols (Al)	3	TEG [146]; MeOH [131,156]; PHEN [152]
Antifoam Emulsions (AE)	2	SAG 7133 [140]; VP 5371 [140]
Catecholamines (Cam)	2	DA [149]; ADR [149]
Cyclic Esters (CEs)	2	PC [71,148]
Cyclic Ethers (CEt)	2	PEGDME [148]; THF [153,154]
Corrosion Inhibitors (CI)	1	CRO27005 [140]
Inorganic Compounds (IC)	1	AM [121,151]
Resines (R)	1	Amberlite IRA-402 [108]
Surfactants (S)	1	SDBS [71]
Thiophenes (TF)	1	SUF [146,148]

Note: The full names and CAS registry numbers of all additives listed above are available in the Supplementary Materials.



Figure 4 shows the percentage of additives being used as promoters in the chemical absorption of carbon dioxide. The compounds with amines in their structure are separated into four groups because of their nature; the remnant components are described as each one's chemical family. It is also important to clarify that the compounds described in Figure 4 are mainly used as promoters, considering the employment of a base solution (unrelated to basicity) as the support or template of the chemical experiments and how the promoters show their improvements. Regarding additives, compounds containing amine groups in their structure are the most commonly employed in carbon dioxide capture, representing 74% of the total compounds.



**Figure 4.** Amine-based solvents and additives employed to improve CO<sub>2</sub> capture.

The primary group of compounds used in CO<sub>2</sub> capture processes is the alkanolamine family, which is formed mainly by primary alkanolamines (composed of primary amines and alcohols). Other groups are secondary and tertiary alkanolamines, formed by secondary and tertiary amines and one or more hydroxyl groups. To unite all alkanolamine groups, an alkanolamine family was established. These are the most frequent additives that enhance the capture process because the alcohol group increases their solubility, avoiding the blend's major viscosity problems. Reciprocal alkanolamines are widely developed as promoters because of their availability at purchase and use; they are the most commonly employed chemical solvents in industrial applications. Here lies the most typical amine MEA. This group's most typical secondary and tertiary amines are DEA and MDEA, respectively. These amines are also considered base solutions because of their current industrial applications. Many types of research have commonly evaluated their possible improvements, such as Liu et al. [60] and You et al. [121], who stated that low-energy regeneration has drawn a great deal of interest in absorption compared to other traditional amine absorbents.

The second group consists of amine-cyclic-based additives and heterocyclic amines. Their names reveal their forms and importance, mainly as kinetic promoters, which will be explained below. The most studied additive in this category has been piperazine (PZ), which consists of a six-membered ring, four carbons, and two nitrogens in opposite positions. PZ can be considered a new standard for CO<sub>2</sub> capture technology [147] due to its "high absorption rate, good stability, low viscosity, and high capacity" [146].

The third group corresponds to amino acids that have appeared in recent years. Many studies have been conducted to justify their new importance as additives in the capture process. According to Bavoh et al. [157], amino acids have chemically more robust interactions with water through zwitterion mechanisms and can be more environmentally

friendly. The next group is ionic liquids (IL); these compounds have the same characteristics as amino acids, i.e., the strong electronic interaction between the compounds and CO<sub>2</sub> [46]. Their stability is also higher than that of the conventional additives. However, it is challenging to synthesize ionic compounds as they require specific ambient conditions and are among the most expensive compounds to investigate [158]. Additionally, the use of IL has been proposed to increase exponentially over time, as stated in the investigation by Haider et al. [158].

In addition, one of the major groups is the amine family. This group is composed of smaller families that contain only amine groups. The four smaller ones are monoamines, consisting of compounds with only one amine group; diamines, consisting of two amine groups; triamines, consisting of three amine groups; and tetramines, consisting of four amine groups, depicting the presence of primary, secondary, or tertiary amines.

As seen in Figure 4, the alkanolamine family, heterocyclic amine, amino acid, ionic liquid, and amine family comprise the top five employed additives. These compounds are called the big five compounds because they represent 83% of the total additives considered in this study. Smaller percentages are compounds with no amine groups, which might cause their use. They include organic salts, alcohols, surfactants, catecholamines, antifoam emulsions, inorganic compounds, cyclic esters, cyclic ethers, corrosion inhibitors, thiophenes, and resins. Most of them can be related to additives. Their efficiency is not focused on improving the in situ capture process itself, but instead on improving the technical aspects of capture, such as foam formation or one of the process's significant problems, such as corrosion.

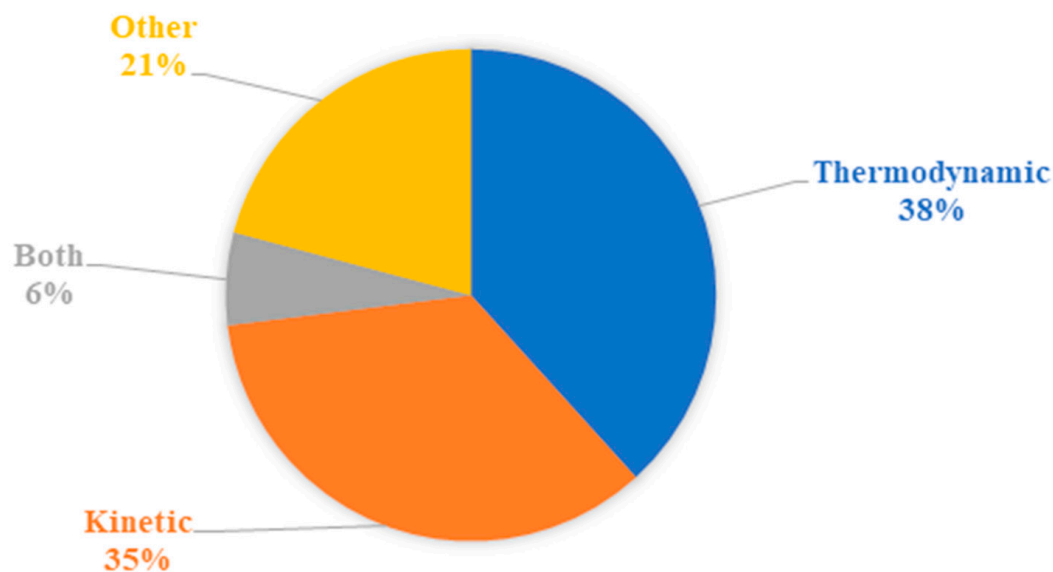
Blended solvents, composed of an amine blend and some chemical additives, have been proposed to overcome the limitations of chemical absorption with amine-based solvents. The benefits of amine blends are also limited to individual amines on the market [123]. Gómez-Díaz et al. [84] studied the effect of primary amines (MEAs), secondary amines (DEAs), and tertiary amines (TEAs) on absorption with and without the addition of CO<sub>2</sub> with a purity of 99.99%. They demonstrated that the primary reaction was carbamate formation when MEA and DEA were employed. The stability of DEA-carbamate was lower than that of MEA-carbamate because of the higher steric hindrance of DEA. Therefore, it reduced the overall rate and lowered the absorption value. Because TEA reacts differently with CO<sub>2</sub> and water, it has a different absorption value. If an additive is added to amines, their properties change. Gómez-Díaz et al. [84] concluded that the absorption efficiency of amines can be disposed of according to the following scale: DEA < MEA < TEA. This scale can be modified by incorporating various additives, with the primary objective being the investigation of kinetic or thermodynamic additives to enhance its properties. An example of kinetic and thermodynamic promoters occurs in MEA in the presence of sodium dodecyl sulfate (SDS); tetra-*n*-butylammonium bromide (TBAB) can increase the mass transfer rate and solubility in the presence of the additive, respectively [159].

Another study of conventional MDEA was conducted by Wang et al. [88]: A mixture of simulated carbon dioxide and nitrogen flue gas was combined to perform this experiment, with no further purification (99.99%) and distilled water. It was prepared under two conditions: absorption and desorption. The amine additives were triethylenetetramine (TETA) and 1,3-Diamino-2-propanol (AEP), each employed with different compositions at vol%, one with the conventional amine and distilled water; the other with the amine additive TETA and distilled water; and the final with MDEA, TETA, AEP, and distilled water at different compositions. The experiment was conducted at 25 °C with 1 bar of absorption and 100 °C with 1 bar for desorption. It was observed that the viscosity and concentration of the amine blend increased with the addition of additives. The results indicate that the absorption capacity increased with the addition of additives to the amine base solution. These results also recalled that the activation effect of the chemical solvents was much better than expected, as MDEA < MDEA + TETA < MDEA + TETA + AEP. Similarly, the desorption efficiency of the additives also improved as solvents were added. However, the negative effect reflected in the experiment was the increase in viscosity; thus, it was confirmed that there was a noticeable increase in viscosity with an increasing

volume fraction of additives. Even though the experiment revealed no direct relationship between the absorption performance and viscosity, an additional negative effect was the low desorption efficiency.

#### 4.2. Improvements in the CO<sub>2</sub> Capture Process

According to the additive classification, the analysis proposed in this study reveals the different improvements of the additives' different families. The results are shown in Figure 5. The final classification of additives can be divided into enhancements that directly affect the capture process per se and others that involve enhancements that prevent specific problems in the equipment and around the process.



**Figure 5.** Type of additives' enhancements.

Thermodynamic enhancements are related to those that affect the solubility, viscosity, evaporation, and physicochemical properties of the additives in the blends. For example, You et al. [121] employed different alkanolamines as additives, such as AMP (2-amino-2-methyl-1-propanol), AMPD (2-amino-2-methyl-1,3-propanediol), AEDP (2-amino-2-ethyl-1,3-propanediol), and THAM (tri(hydroxymethyl) aminomethane), to test their efficiency as thermodynamic promoters to avoid evaporation in the experiment, demonstrate it in different graphs of removal efficiency, and quantify the results at the scale of weight loss. In addition, Xu et al. [151] used different ionic liquids to test their efficiency. The results are shown as the variation in CO<sub>2</sub> concentration for the different additives in the treated gas, the variation in the blend concentration in the process, and a comparative table of the total CO<sub>2</sub> capacity in blended solutions. This gives the final result of the improvement in both experiments; thus, the thermodynamic improvement is confirmed. Kinetic enhancements are based on the reaction mechanism that can be macroscopically observed during the tests and at the absorption–desorption rate. Xiao et al. [134] tested different amine compounds, an alkanolamine, two diamines, and one heterocyclic amine, such as DEEA (diethylethanolamine), N,N-DM13PDA (N,N-dimethyl-1,3-propanediamine), N,N-DM12EDA (N,N-dimethyl-1,2-ethanediamine); and 4-A1MPD (4-amino-1-methylpiperidine), respectively. The evaluation was performed to observe the absorption curves versus carbamate formation rate data of carbamate bicarbonate concentrations versus CO<sub>2</sub> loading. Wang et al. [86] studied the influence of TETA and AEP in MDEA. The CO<sub>2</sub> absorption capacity, average CO<sub>2</sub> absorption rate, and absorption and desorption rates were quantified as a function of time. Both experiments resulted in an improvement in absorption rates, which confirmed the improvement in kinetic efficiency.

At this point, a few compounds may reflect both improvements, as suggested by the analysis of different studies that or many not contain dual information. Yuan and Rochelle [146] investigated the effects of piperazine (PZ) with different additives. The results reflected an improvement in viscosity and solubility with piperazine usage, which can be categorized as a thermodynamic improvement according to the present study's classification. On the other hand, piperazine blends also exhibited an increase in the CO<sub>2</sub> absorption rate capacity, cyclic capacity, and average absorption rate, which in this study can be reflected as a kinetic improvement. Finally, the other enhancements were strongly related to the surroundings of the capture process, as foam can be produced during this process. Antifoam emulsions were then added to control this formation. Mota-Martínez et al. [140] investigated it and studied the effect of corrosion inhibitors on the blends. Vullo et al. [149] studied the effect of additives, such as amines and amino acids, which slightly improved the kinetic parameters of the blends. This category is located within others because the effects have been proven in the catalytic processes of carbon anhydrases when analyzing the investigation results. Thus, this process can be stigmatized at a much smaller scale than that proposed in this study. Additionally, the first study can reduce the maintenance frequency of the absorption–desorption equipment.

## 5. Final Remarks and Perspectives

This extensive research review of different articles and their subsequent classifications according to the characteristics of the additives made it possible to classify them according to their chemical nature. It has been shown that amine compounds, specifically alkanolamines, are the primary group and the most employed additives because of their high percentage of use to improve CO<sub>2</sub> capture. Few additives enhance industrial operability compared to those that can improve kinetic and thermodynamic conditions. Both are the most desirable because they are the source of the most significant improvements, such as reducing additive volatility, decreasing viscosity, or increasing capture rate. Likewise, avoiding changes in current capture units by considering new additives does not affect the economy of industries or the environment. It is suggested that the selection or design of tertiary alkanolamines should be made with linear alkanol chains instead of branched ones for better CO<sub>2</sub> capture performance in industrial applications.

Amine-based solvents remain a cornerstone of CO<sub>2</sub> capture technology due to their high capture efficiency and seamless integration with existing infrastructure, particularly in post-combustion applications. Despite their widespread adoption, these solvents are hindered by several challenges, including substantial energy requirements for solvent regeneration, chemical degradation leading to byproduct formation, equipment corrosion, and environmental concerns associated with waste management [64]. To address these limitations, ongoing research is advancing the development of next-generation amine-based solvents. Innovations such as blended amine formulations and novel solvent chemistries are being explored to reduce energy consumption, enhance thermal and oxidative stability, and minimize corrosivity [160]. Complementary process optimization strategies, including advanced heat integration techniques, intercooling, and energy recovery systems, aim to improve overall operational efficiency [118]. Furthermore, integrating renewable energy sources into the regeneration process presents an opportunity to significantly reduce the carbon footprint of these systems [161].

The integration of amine-based solvents with emerging technologies also holds considerable promise. Hybrid systems that combine amine solvents with technologies such as membranes or solid sorbents could capitalize on the strengths of each approach, potentially achieving greater efficiency and flexibility in CO<sub>2</sub> capture [162]. These advancements highlight the enduring relevance of amine-based solvent technologies. However, their future success depends on continued innovation to mitigate environmental and economic impacts while maintaining scalability and reliability for industrial applications [163].

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/chemengineering8060129/s1>, Table S1. Additive classification: alkanolamine family; Table S2. Heterocyclic amines; Table S3. Amino acids; Table S4. Amine family; Table S5. Ionic liquids; Table S6. Organic salts; Table S7. Chemical compounds with other functional groups.

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## Appendix A

**Table A1.** Advantages and disadvantages of emerging and mature technologies for CO<sub>2</sub> capture.

Category	Technology	Advantages	Disadvantages
Emerging technologies	Metal-Organic Frameworks (MOFs)	High selectivity and tunable structures; low regeneration energy; potential for direct air capture.	Limited scalability; high material costs; stability challenges under industrial conditions.
	Solid sorbents (e.g., zeolites)	Reusable; reduced energy requirements; lower environmental impact compared to liquid solvents.	Sensitivity to humidity; performance degradation over multiple cycles; limited CO <sub>2</sub> loading capacity compared to liquid systems.
	Covalent Organic Frameworks (COFs)	High porosity and structural stability; tunable functionality for CO <sub>2</sub> selectivity; low regeneration costs.	Limited scalability; challenging synthesis methods; potential degradation in industrial environments.
	Covalent Microporous Polymers (CMPs)	High surface area and CO <sub>2</sub> affinity; lightweight and chemically robust; customizable functionality.	Expensive synthesis; lower CO <sub>2</sub> capture capacity compared to some MOFs; potential difficulty in scaling production.
	Electrochemical processes	Low-temperature operation; direct utilization of renewable electricity; integration with green hydrogen.	High operational costs; limited industrial deployment; lower capture rates in current designs.
	Membrane separation	Compact design; no chemical solvents required; modular scalability.	Low CO <sub>2</sub> purity for some applications; susceptibility to fouling; energy-intensive compression required for high-pressure streams.
	Direct Air Capture (DAC)	Captures CO <sub>2</sub> directly from ambient air; potential for net-negative emissions.	High energy and cost demands; low CO <sub>2</sub> concentrations in air require large processing volumes.

Table A1. Cont.

Category	Technology	Advantages	Disadvantages
Mature Technologies	Chemical solvents (e.g., Amine-based solvents)	High capture efficiency; proven scalability; compatibility with existing infrastructure.	High energy consumption for regeneration; solvent degradation and corrosivity; high capital and operational costs.
	Pressure Swing Adsorption (PSA)	Well-suited for pre-combustion capture; rapid cycle times; no chemical solvents required.	Requires high-pressure gas streams; limited effectiveness for low-concentration CO <sub>2</sub> sources; energy-intensive compression.
	Temperature Swing Adsorption (TSA)	High selectivity for CO <sub>2</sub> ; effective for low-pressure or dilute gas streams; simple regeneration.	High energy requirements due to heating; slower cycle times because of thermal inertia.
	Vacuum Swing Adsorption (VSA)	Lower energy requirements compared to TSA; faster cycle times; effective for high-concentration streams.	Requires robust vacuum equipment; less effective for dilute or very low-pressure gas streams; higher capital and maintenance costs.
	Cryogenic separation	Produces high-purity CO <sub>2</sub> ; well-suited for gas streams with high CO <sub>2</sub> concentrations.	Very energy-intensive due to cooling requirements; high capital costs; limited viability for dilute CO <sub>2</sub> sources.
	Calcium looping	High thermal efficiency; suitable for large-scale applications; regenerable sorbents.	High-temperature operation; potential for sorbent attrition; requires integration with existing industrial processes.
	Oxy-fuel Combustion	Produces a concentrated CO <sub>2</sub> stream, simplifying capture; integrates with power generation.	Requires oxygen separation, which is energy-intensive; retrofitting existing systems is complex and costly.

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