

Review

Solvents for Membrane-Based Post-Combustion CO₂ Capture for Potential Application in the Marine Environment

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Abstract: Carbon capture on-board ships represents a powerful technological measure in order for the shipping industry to meet the very stringent GHG emission reduction requirements. Operation within the ship environment introduces a number of constraints associated mainly with space, energy supply, and safety which have to be addressed using compact yet efficient solutions. To this end, solvent-based membrane CO₂ capture offers several advantages and has the necessary technological maturity for on-board installation. Solvent choice remains a critical issue both for reasons associated with process efficiency as well as on-board safety. In this paper, we present an up-to-date comprehensive review of the different solvents that can be used for post-combustion CO₂ capture. Furthermore, we investigated the solvents' performance as determined by their inherent characteristics, properties, and behavior for a range of operating conditions against the strict shipping requirements. A preliminary qualitative comparative assessment was carried out based on appropriately selected key performance indicators (KPIs) pertinent to the requirements of the shipping industry. The identified solvent classes were compared using the most critical KPIs for system integration with the ship. It was concluded that at present, no solvent category can efficiently address all the requirements of the ship. However, widely used solvents such as secondary amines showed relatively good compatibility with the majority of the introduced KPIs. On the other hand, more recently developed molecules, such as phase change solvents and ionic liquids, can easily prevail over the vast majority of the identified solvents as long as they are brought to the same level of technological maturity with benchmark solvents. Such a conclusion points toward the need for accelerating research on more tailor-made and performance-targeted solvents.

Keywords: gas-liquid membrane contactor; carbon dioxide capture; solvent; absorption; modelling; maritime transport

1. Introduction

Despite worldwide efforts to contain greenhouse gas emissions (GHGs) as a key measure to prevent excessive temperature rise, they are increasing at an alarming pace. In 2019, CO₂ emissions from fossil fuel combustion reached 36.7 Gt with total GHG emissions approaching 50 Gt CO_{2,e}—an almost 40% increase compared to 1990 [1] (GHG emissions—from carbon dioxide, methane, nitrous oxide, and fluorinated hydrocarbons—are expressed as carbon dioxide equivalents (CO_{2,e}), where “equivalent” means “having the same warming effect as CO₂ over a period of 100 years”). Although there is some annual variation and a clear decrease in 2020 due to COVID-19, GHG emissions are on the rise and an intensification of reduction strategies in all sectors is tantamount. Power generation and transport sectors together account for more than two-thirds of the total GHG emissions [2] (2019 data) and have been responsible for almost all global growth since 2010. The transport sector alone produces roughly 25% of the total global emissions with the shipping industry being responsible for generating 12% of the transport emissions amounting to almost a billion metric tons per year [3]. As world trade is expected to rise by almost 40% by 2050 [4], future projections for maritime GHG emissions inevitably show similar trends. Estimates for 2050 vary significantly depending on the assumptions used in the calculations as well as on the projected global economic growth and assumed climate management strategy. For example, the most recent report of IMO [3] predicts significant emissions growth for maritime-attributed CO₂ emissions, ranging from 1100 to 1700 Mt/y. Depending on the scenario and assumptions used, the upper range can be shifted to even higher values approaching even 2350 Mt/y.

There is thus an increasing pressure from international and intra-national organizations and regulatory bodies on the maritime industry to reduce GHG emissions. This has resulted in the definition and implementation of several energy efficiency measures by the International Maritime Organization (IMO) designed to have a direct impact on GHG emissions from shipping. These include the energy efficiency design index (EEDI), implemented in 2013, expressed as gCO₂/tonne-mile, which targets the design phase of *new ships* through measures that affect hull hydrodynamics, propulsion and power systems, machinery technology integration, and the use of alternative fuels and renewable energy sources [4,5]. Compliance with the EEDI is mandatory. In 2018, IMO adopted the initial strategy for the reduction in GHG emissions from shipping, a policy framework which sets key ambitions, mainly to reduce GHG from international shipping by at least 50% by 2050 compared with their level in 2008, with the aim of phasing them out completely within this century, and to reduce the carbon intensity of international shipping by 40% by 2030 and by 70% by 2050 [6]. More recently, in June 2021, IMO adopted key short-term measures aimed at cutting the carbon intensity of all ships by at least 40% by 2030 [4]. In a marked change from the previous EEDI-based measures, the new initiative targets existing ships through the definition of metrics that reflect not only design but also operational strategies for energy efficiency and carbon reduction. The energy efficiency existing ship index (EEXI), equivalent to EEDI and also expressed as gCO₂/tonne-mile, will quantify the effects of energy efficiency improvements in existing ships compared to the original design. The carbon intensity indicator (CII) will be introduced for all large ships (with a gross tonnage of over 5000). CII is expressed in gCO₂/dwt-m and will provide the basis for a vessel energy efficiency rating system on a yearly basis, thus assessing primarily operational efficiency.

The above regulations present a new operating environment for the shipping industry where novel materials, processes, designs, and operational practices need to be defined, evaluated, and introduced in new and existing vessels at a fast pace. Proposed strategies can generally be classified in five broad categories:

1. Alternative fuels (the vast majority (>95%) of sea-going vessels is operated with either heavy fuel oil (HFO) or marine diesel oil (MDO). Liquefied natural gas (LNG) is mainly used as a fuel in LNG carriers. Potential alternative fuels being considered by

- the maritime industry include ammonia, methanol, liquefied petroleum gas (LPG), and biofuels (including bio-oils and hydrotreated vegetable oils (HVOs));
2. Propulsion and power system (engine efficiency improvement, propulsion efficiency devices, propeller optimization, waste heat recovery, and wind and solar assistance technologies);
 3. Electrification (on-board electricity production, fuel cells, battery storage, hybrid systems, and cold ironing);
 4. Ship design (hull hydrodynamics, hull coatings, and air lubrication);
 5. Operational measures (slow steaming, weather routing, route optimization, and ship energy management system integration).

Several recent studies in the open literature have attempted to assess the effect of the above measures and strategies on the overall ship energy efficiency and GHG emission reduction potential and have identified limitations to their wide deployment. For example, Foretich et al. [7] and Bouman et al. [8] have concluded that the introduction of biofuels can, in principle, result in a 100% reduction in GHG emissions. However, there are several technical and operational issues—such as engine compatibility, long-term storage, and bunkering infrastructure—that severely limit its applicability potential. Most stand-alone technical and operational measures, with the notable exemption of slow-steaming, can only achieve modest reductions in GHG emissions; see for example the comprehensive work of Balcombe et al. [9]. It is only through the optimized combination efficiency improvements, alternative fuels, and targeted operational measures that the IMO goals can be potentially met. This, however, will inevitably lead to increased system complexity and increased capital and operating costs.

An emerging alternative solution that can be both technically and financially feasible and offer a very high decarbonization potential is carbon capture utilization and storage (CCUS). CCUS offers the alternative of directly removing carbon emissions from an industrial process (or even directly from the atmosphere) and possibly reusing part of the captured carbon as valuable raw material for the synthesis of new fuels and/or chemicals [10]. Multiple scenarios have been developed that attempt to predict the beneficial influence of CCUS technologies in the global emissions map, including the Blue Scenario Map from the International Energy Agency (IEA). According to the IEA [11], CCUS is crucial in the so-called beyond 2 °C scenario (B2DS) for limiting temperature rise below 2 °C by 2060. The B2DS sets out a rapid decarbonization pathway with CCS being the key driver and responsible for a massive 32% CO₂ emission reduction beyond the 2DS scenario. Currently, only a small fraction (almost 230 Mt) of the carbon emitted is re-used in agriculture, oil, and gas as well as food industries, with new routes of exploitation being developed for the building, fuels, and chemicals sectors [12]. However, the demand of these sectors for CO₂ is not expected to meet the actual capacity of captured carbon, leading to the development of disposal and sequestration options to balance the carbon market.

Carbon capture relies predominantly on the successful separation and removal of CO₂ from a flue gas stream and is classified mainly as pre-combustion, post-combustion, and oxy-fuel combustion CO₂ capture [13]. Pre-combustion CO₂ capture refers to a pre-treatment of fuel (such as gasification or partial oxidation) to produce a gaseous stream (synthesis gas) relatively rich in CO₂ (typically 40% by volume) and hydrogen which can then easily be separated. Oxy-fuel combustion involves oxygen separation from air and combustion of a hydrocarbon fuel (or coal) with oxygen in a closed cycle producing an exhaust stream of almost pure CO₂ without need for further separation. Post-combustion CO₂ capture is the most versatile and well-established end-of-pipe option that involves the successful separation of CO₂ after combustion takes place. Although the process requires no significant engine or plant modifications, there are challenges related to the relatively low CO₂ levels (typically 5–15% by volume) and the variability of the exhaust stream [14].

The gaseous mixture can be separated using a number of diverse but well-established and technologically mature processes that include physical or chemical absorption, adsorption, membrane separation, or combinations of the above. Chemical absorption is by far

the most developed CO₂ capture method and is based on the selective reaction between a CO₂-containing gaseous mixture and a liquid solvent. In this way, the mass transfer following the dissolution of CO₂ in the liquid phase is further enhanced by the chemical reaction promoted by the concentration difference [14]. Subsequently, the CO₂-loaded solvent is usually driven to a regeneration process in which the reverse reaction occurs, releasing pure CO₂ and lean solvent. This process can either be temperature- or pressure-based, with the most prevalent one being the thermal regeneration in a fashion similar to distillation. Solvent regeneration ensures its recirculation in the system, thus minimizing liquid flowrates and solvent cost. On the other hand, chemical or physical adsorption systems are based on the binding of CO₂ on a solid adsorbent in a reactive or non-reactive step, respectively, and its subsequent release in a regeneration step similar to that of absorption-based systems. Adsorption systems primarily offer reduced energetic demands for sorbent regeneration; however, they involve solids handling which can prove challenging [15]. Finally, membrane-based systems (gas permeators or membrane contactors) can be employed to separate CO₂ from gaseous mixtures. Dense polymeric membranes can be used for selective CO₂ removal from the gaseous mixture (gas permeators), while porous membranes (either polymeric or ceramic) are able to provide very high specific mass transfer area (membrane contactors), resulting in increased CO₂ capture efficiencies in a membrane gas absorption mode of operation. However, it must be noted that the technology readiness level (TRL) of the membrane-based technologies is lower than the previously mentioned ones and their high application potential has to be demonstrated in an operating environment [16].

In general, solvent-based separation is often linked to somewhat increased energy demands for regeneration for the case of chemical absorption or generally admitted low efficiencies for physical absorption, while on the other hand, membrane-based separation alone results in inadequate efficiencies, mainly due to the small CO₂ concentrations (<15%) found in conventional flue gas streams [17]. Adsorption systems can instead easily benefit from the temperature or pressure control of the process. However, sorbent deactivation due to chemical degradation as well as sintering or attrition render them susceptible to high operating and maintenance costs [18].

Post-combustion carbon capture offers significant advantages as a decarbonization measure for the shipping industry. As mentioned earlier, it does not require significant engine or power plant modifications and it is largely fuel agnostic (provided that the separation process allows for the varying CO₂ levels in the flue gas stream). For these reasons, it is also very well-suited for retrofitting existing vessels. For maritime applications, the ship's operating environment poses a number of additional challenges such as increased needs for security in handling including hazard protection and increased needs for low toxicity due to the inability of rejecting chemicals into the open sea in times of operation, as well as the limiting demand for spacing in a finite volume. As such, the number of degrees of freedom for the choice of technology is compromised.

Considering the above, this paper analyzed the possibilities of on-board application of solvent-based CO₂ capture utilizing modular membrane contactors. It is then the different characteristics and performance behavior of the available solvents together with the specific requirements of the ship in the form of constraints that determine the suitability for use in a maritime environment. It has to be noted that the processing and use of the captured CO₂ is not within the scope of this work. As such, the dimension of CO₂ storage on-board was not accounted for and the study focused on the analysis of solvent properties and their compatibility with the maritime sector's requirements.

The paper is structured as follows. Section 2 summarizes work performed so far on maritime CCS technologies and defines appropriate key performance indicators (KPIs) that can be used to assess the suitability of solvents for on-board carbon capture. A brief outline of the key features and requirements of membrane contactor technology for CO₂ separation is presented in Section 3. A comprehensive review of possible solvents for membrane-based carbon capture is performed in Section 4 while Section 5 presents a critical assessment of the most promising solvents for on-board use based on the developed KPIs.

2. Integration of Carbon Capture Technologies in Ships: Status and Requirements

Several concepts on maritime CCS technologies have been proposed and analyzed through both academic research and joint industry projects. In 2009, DNV conducted the first study to demonstrate the technical feasibility of maritime CCS [19]. The study assessed a CCS design for 90% capture of the exhaust gas of a very large crude carrier (VLCC) fueled by heavy fuel marine oil (HFO), exploring candidate technologies including chemical absorption, adsorption, and membrane separation. Because of the increased capture rate and the conventional technology features (i.e., conventional solvents and auxiliary boiler use), the energy penalty was very high and could be reduced by 25 to 30% only by using improved solvents. Van den Akker [20] considered MEA absorption on-board an 8000 ton general cargo vessel with a 3000 kW LNG fueled engine. The system achieved 87% carbon abatement with a thermal demand of 1 to 1.2 MW. Luo and Wang [21] evaluated the cost impact of different solvent-based CO₂ capture integration options in a reference cargo ship with a propulsion system consisting of two 4-stroke engines of 17 MW power capacity and 3 generators of 1 MW each. The removal rate was 73%, at the expense of 21.4% additional energy demand on-board. Further, Feenstra et al. [22] demonstrated that amine-based CO₂ absorption is feasible for 2 cargo ships (1280 kW—inland ship and 3000 kW—8000 ton general cargo vessel) equipped with dual-fuel 4-stroke engines, with 60% efficiency.

CCS technologies are not directly transferrable from land- to sea-based applications without adaptation to the maritime environment. On-board the ship, certain technical, operational, safety, and value-chain constraints need to be satisfied, while the energy and space resources are limited. In this context, the suitability of CCS technologies for on-board use can be assessed by addressing a set of multidimensional specifications, including the following: technology maturity, compactness, endurance in saline environments, wide operability range, low energy penalty, effectiveness at low carbon content, endurance in impurities, low effect of ship motions, CO₂ product characteristics, health and safety performance, and capital and operational cost aspects. Among this list, a set of KPIs that can be used to assess the suitability of solvents for ship implementation was screened and is shown in Table 1.

Table 1. Key performance indicators for on-board solvent-based CO₂ capture.

KPI	Description
Maturity	Whilst land-based CCS is relatively mature, only limited demo cases are available for maritime CCS and at low capture rates.
Compactness	On-board space capacity is limited. The minimization of system dimensions and weight is important for on-board integration.
Operability range	The solvent needs to be effective within a range of variant operating conditions, including temperature, pressure, exhaust gas flow and CO ₂ content in the exhaust. When powered by LNG, the CO ₂ content in ship engine exhaust is about 4–6%, which is lower than that of land-based applications. Solvents need to be effective at such low CO ₂ content increasing the energy penalty for CO ₂ capture.
Energy penalty	Unlike land-based applications, the on-board ship environment has low availability of power, heat, and consumable resources. Therefore, the energy demand for regenerating the solvent must be kept as low as possible.
Impurity tolerance	Some solvents may be sensitive to impurities, e.g., sulfur, particulate matter, or methane traces, or their capture efficiency may be degraded in the presence of such compounds in the flue gas. Any requirement for pre-treatment equipment would add complexity, risk, volume, and weight.
CO ₂ product characteristics	The CO ₂ product form is important in accounting for on-board storage capacity and conditions (liquefied, compressed, etc.), thus affecting the on-board resource requirements.
CO ₂ loading	The molar ratio of CO ₂ over the pure solvent. It is often regarded as a measure of the solvent's capacity for CO ₂ capture (i.e., higher loading leads to more CO ₂ captured per unit of solvent) and can be correlated with solvent needs, regeneration demands, and the capture efficiency within the process.
OPEX	Costs are associated with large uncertainties and impact the uptake of technologies in the industry. Costs include maintenance and consumables, as well as any additional fuel costs as a result of the energy penalty. Degradation of solvent performance through use also plays important role in OPEX costs.
Other consumables	Depending on the solvent, other consumables may be needed, for example, water. Such demands increase the on-board requirements for energy and storage capacity.
Health and safety	The solvent physicochemical properties, e.g., flammability and toxicity, may impose health and safety hazards that require assessment, monitoring, and prevention measures. In addition, operational features such as high pressure or temperature impose additional design considerations related to safety as the key properties that determine the flammability of a material (such as lower-upper flammability limits, flash point, autoignition temperature, minimum ignition energy, and laminar flame speed, e.g., [23]) are strongly dependent on the temperature, pressure, and geometry of the container or reactor.

3. Membrane Contactors for Maritime CO₂ Capture

In general practice, post-combustion CO₂ capture is performed using either physical or chemical absorption or adsorption. Both processes rely on the contact of the flue gas with a liquid absorbent or solid adsorbent and the selective transfer of CO₂ to the latter, either due to purely thermodynamic (i.e., vapor liquid equilibrium or van der Waals forces), or due to the combined effect of thermodynamic and reaction kinetic phenomena. Among these methods, chemical absorption is the most prominent process used for CO₂ capture and is mainly associated with the use of packed separation columns for the absorption of CO₂ and subsequent regeneration of the solvent. The use of packing serves as a means to greatly increase the vapor-liquid contact area and thus to similarly increase the mass transfer fluxes along the column. Similar to absorption columns, membrane contactors have been used for the same purpose. These systems are comprised of membranes of suitable porous materials, positioned in appropriate configurations (hollow fibers) that selectively enable CO₂ to pass through them. A typical contactor configuration can be seen in Figure 1. On the one side of the hollow fiber membrane, the gas mixture is fed, while on the other (shell) side, a CO₂ capture medium (i.e., a solvent) flows co-currently or counter-currently and chemically binds it, therefore enabling its removal. The presence of the solvent is important for achieving high transfer rates through the membrane due to the contribution of the chemical reactions to mass transfer. On the other hand, the membrane is responsible for ensuring contact between the phases, while simultaneously preventing their mixing and thus enhancing the driving force and the overall mass transfer rate [24]. The combination of these two factors leads to an intensified and compact process with reduced volume compared to an absorption column. A detailed mathematical description of the membrane contactor system can be found in Pantoleonatos et al. [25].

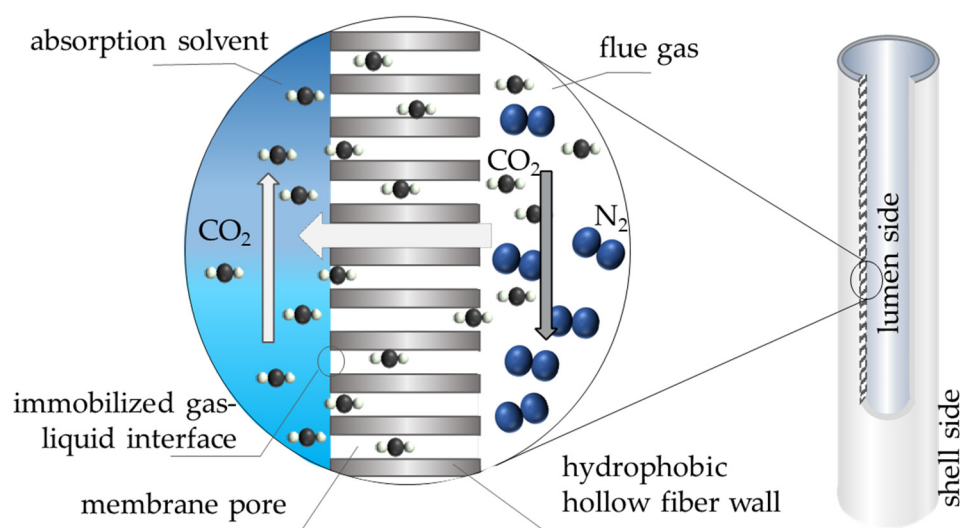


Figure 1. Schematic representation of a membrane contactor for CO₂ capture.

The use of membrane contactors for CO₂ absorption over packed columns offers the benefit of process flexibility by introducing the concept of modular units of smaller size in the system, in contrast to the bulkier design of a separation column. In the case of application within a ship environment with strict volume and weight restrictions, membrane contactors are expected to facilitate the efficient introduction of CO₂ capture. Moreover, a typical ship engine operates at lean conditions with typical off-gas CO₂ molar concentrations in the order of 4–6% with the remainder being mainly N₂ and water vapor.

Membrane contactors are usually less costly than absorption columns due to the lower expenses in fabrication of the membrane module. However, there are a number of operational challenges that are mainly associated with the pairing of the membrane and solvent. These include pore wetting and membrane degradation due to the solvent and have to be initially considered [26].

The efficiency and applicability of membrane contactors as part of an absorption and desorption system has been studied by a number of researchers. Salmón et al. [27] experimentally compared the solvent-based CO₂ capture in an absorption column and a membrane contactor. The main conclusion was that despite the fact that the absorption column offers increased mass transfer coefficients by an order of magnitude, membrane contactors can achieve similar results regarding the desired separation but with five times less volume. Additionally, the use of hollow fiber ceramic membranes instead of an absorption column in the conventional absorption and regeneration system results in a lower pressure drop during the absorption step [28]. Membrane contactors can be used to replace not only the absorption but also the solvent regeneration column [29,30].

Most of the commercially available membrane materials that are employed in membrane contactor devices are made of hydrophobic polymeric materials such as polypropylene (PP), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF). Polypropylene membranes are cheap and can be easily fabricated in large-area membrane modules, which have been commercialized by 3M™ Liqui-Cel™ even for industrial scale applications. However, they have relative limited thermal and chemical stability. On the other hand, PTFE membranes are much more thermally and chemically stable but they are more difficult to fabricate in small hollow fibers with high specific surface area and they also have significantly higher production costs. PVDF membranes lie somewhere between PP and PTFE in terms of stability and cost issues [31,32].

For the last few years, ceramic membranes have also been studied as membrane contactors for CO₂ capture applications, due to their inherently higher thermal and chemical stability. However, the hydroxide groups that are typically present on their surface render them hydrophilic which is typically associated with decreased mass transfer rates in gas separation applications. Thus, ceramic membranes need to be modified in order to become hydrophobic before their application. Moreover, they cannot be easily processed in high specific surface area hollow fibers and they have much higher cost than the polymeric materials (more than an order of magnitude higher). For all these reasons, they are still in a lower technology readiness level (TRL) than polymeric membranes for CO₂ capture applications [33,34].

The membrane–solvent compatibility is a crucial factor that needs to be seriously taken into account because it significantly affects process performance. Even if the membrane material is not significantly degraded due to the presence of a solvent, the process performance may be compromised due to membrane wetting. Membrane wetting is the phenomenon of partial liquid penetration in the pores of a hydrophobic membrane. In this case, the gas–liquid interface can be shifted with time from the pore mouth to some (variable) location inside the membrane pores, resulting in increased membrane mass transfer resistance and absorption's flux deterioration with time. The exact mechanism of membrane wetting has not been fully clarified yet, due to the complex nature of membrane–solvent interaction phenomena. Some potential causes can be attributed to: (i) chemical reactions between the membranes and the solvent which can change the hydrophobic characteristics of the system, (ii) physical interactions between the membrane pores and solvents (e.g., swelling), and (iii) changes in membrane surface hydrophobicity by trace impurities of the solvent. In any case, the membrane wetting phenomenon depends on membrane material and solvent type, as well as on process conditions (e.g., temperature, pressure, flow rates, etc.). Partial membrane wetting by the solvent is something expected, at least to some extent, for any membrane–solvent pair. The partial performance loss can many times be counterbalanced by the much higher specific membrane area of membrane contactors with respect to the conventional packed columns. However, there are also references for dramatic performance losses during the first hours of operation, which apparently inhibits the applicability of the process [35]. Some general conclusions that have been derived regarding membrane wetting by different solvents are [36–41]:

1. Inorganic solvents such as H₂O, NaOH, K₂CO₃, etc. have high surface tension and do not easily wet the common hydrophobic polymeric membranes. However, they are typically less efficient than conventional amines.
2. Amines have high CO₂ capture efficiency but they have typically lower surface tension compared with inorganic solvents and they tend to more easily wet the common hydrophobic polymeric membranes. Among the different types of amines that are typically used, MEA has the highest wetting potential and typically leads to significant flux declines in all commercial hydrophobic membranes. DEA and MDEA tend to have milder effects on membrane performance.
3. Novel solvents, such as the amino acid salts (e.g., potassium glycinate) or composite solutions with an amino acid salt, typically combine the high performance with a very low wetting potential.
4. Ionic liquids typically require high operating temperatures, which can be tolerated only by PTFE or ceramic membranes.

4. Solvents for CO₂ Capture

Solvent-based technology for CO₂ separation is one of the most deeply studied fields in CO₂ capture. Whether it is for application in absorption, adsorption, or membrane-based separation processes, solvents are used to enhance the driving force between the gaseous and liquid phases, facilitating the selective transport of CO₂ to the liquid side. The principle behind the separation of CO₂ using a solvent depends on the binding mechanism of the latter with CO₂. To this end, solvents are mainly separated into physical and chemical.

4.1. Physical Solvents

Solvents based on physical absorption rely on the exploitation of Henry's law, expressing the solubility of CO₂ in the liquid phase. This solubility is favored by high pressures, making the typical flue gas streams difficult to separate. Such solvents can be typically used when the CO₂ partial pressure is more than 10 bar. The principle of dissolution of CO₂ and the absorption in the liquid phase creates a weak bond between the dissolved molecules and as such, solvent regeneration can be achieved by a simple reduction in pressure. This family of solvents is also able to achieve absorption capacity proportional to the gas pressure. Thus far, physical absorption has been used in a number of industrial off-shore power plants [42] demonstrating adequate CO₂ capture efficiencies with rather small energy penalties [43]. However, one of the problems associated with physical absorption is the lack of control in the selectivity of the solvents for mixed gas feed streams—which is the case with post-combustion flue gases. The most common representative methods using this solvent class are the Rectisol and the Selexol processes. The Rectisol process employs chilled ammonia and utilizes significantly lower operating temperatures than the other processes, with capture efficiencies that can reach up to 90–95%. However, severe problems exist with the selectivity of this process when used for CO₂ in the presence of sulfur-based compounds [44]. Selexol, on the other hand, utilizes dimethyl ether of polyethylene glycol (DPEG) and exhibits very high solubility, a large range of operating temperatures, and low cost compared to similar processes. On the downside, however, the higher viscosity of the employed solvent inhibits the use at low temperatures as the mass transfer rate is lowered [45]. Mumford et al. [44] present a detailed review on the properties, advantages, and disadvantages of these solvents and processes.

4.2. Chemical Solvents

In contrast to the physical solvents that rely solely on the solubility of CO₂ in the liquid phase, chemical solvents exploit the selective reaction between CO₂ and the solvent molecule, either in a separation column or in a membrane module, to further enhance the rate of separation. The flue gas is brought into contact with the solvent and the different reactions taking place in the liquid phase determine the efficiency of the chemical absorption of CO₂. Aqueous amine solvents for chemical absorption of CO₂ are considered to be a robust technology. A very large number of CO₂ capture solvents has already been

developed and used routinely in both industrial and pilot scales, while research is still ongoing for the identification of new molecules with targeted optimal properties. Such molecules range from the more mature amines to the more recently developed phase change solvents (PCSs) and ionic liquids (ILs). In all cases, certain performance indicators need to be maximized for the consideration of each solvent according to the application. One of the most important indices is the CO₂ cyclic capacity, commonly referred to as the working capacity, which is the difference in the amount of CO₂ captured per mol of solvent before and after the reaction has taken place. Such a property is linked to thermodynamics in the form of the vapor–liquid equilibrium (VLE) as well as to the kinetics of the chemical system. Vapor pressure and viscosity play an important role for the assessment of chemical solvents as they indirectly affect the regeneration strategy and associated required energy. In addition, the solvent's resistance to thermal and oxidative degradation, in cases where oxygen is also present in the inlet stream, represents a measure of the process viability as it is directly associated with the need of replacement or the use of make-up streams in order to maintain steady state conditions.

4.2.1. Single Amine Solvents

Linear or branched alkanolamines of the general form R₁R₂R₃N, with the different organic groups R_i defining the nature of the amine, are the most common CO₂ capture solvents. The benchmark solvent monoethanolamine (MEA—R₁ = CH₃CH₂OH, R₂ = R₃ = H) has been used for capturing CO₂ from industrial flue gases since the 1950s [46], mainly in chemical processing, making it the most developed solvent for CO₂ capture applications. In general, alkanolamines are compounds with variable (low to moderate) volatility, are relatively cheap, and also achieve fast reaction rates with high selectivity toward CO₂. They are usually classified as primary, secondary, and tertiary depending on the number of carbon atoms bound to the nitrogen atom. The amine group serves as a promoter of the reaction with acid gases, meaning that highly substituted molecules tend to exhibit higher capture capacities, while the hydroxyl group mainly contributes to the reduction in the amine's vapor pressure (and in most cases, also the viscosity) and the subsequent increase in solubility [47].

Primary alkanolamines, such as the widely used MEA, have fast kinetics and acceptable absorption capacity with a thermodynamic maximum in the range of 0.5 moles CO₂ per mole of solvent. The mechanism of CO₂ binding onto the amine molecule follows the dissolution of CO₂ to form carbonate and bicarbonate ions and their reaction with the amine toward a more stable carbamate ion through a fast chemical reaction that follows the zwitterion mechanism. However, they appear to show a highly corrosive behavior in high concentrations; hence, the concentration of the amine in the solution must be always kept to a low value. Moreover, they have high enthalpy of reaction which leads to high energy requirements during the thermal regeneration of the solvent. Another primary amine, diglycolamine (DGA, R₁ = R₂ = CH₂CH₂OCH₂CH₂OH), shows similar behavior with MEA, although higher concentrations in the liquid phase could be allowed due to the lower vapor pressure, allowing for higher CO₂ loadings in the system [48]. 3-amino-1-propanol (MPA, R₁ = CH₂CH₂CH₂OH) contains one more methylene group compared to the conventional MEA, allowing for denser solutions and equally fast kinetics but lower volatility and thus lower regeneration energy demand by almost 10% [49].

Secondary amines such as diethanolamine (DEA) and diisopropanolamine (DIPA) have two of their hydrogens in the nitrogen atom substituted by ethoxy-groups. This enables them to perform better than primary amines in terms of loading and cyclic capacity. Similar to primary amines, these solvents follow the zwitterion mechanism but they are more resistant to degradation and less corrosive [47]. In addition to DEA, a widely used secondary cyclic amine solvent is piperazine (PZ). PZ has a high absorption rate, good stability, low viscosity, and high capacity [50], but is prone to form solid precipitates [51] and it is therefore rarely used as a standalone solvent. Secondary amines also generally

offer the benefit of decreased energy demand for their thermal regeneration than primary amines due to their lower volatility and lower circulation rates.

On the other hand, tertiary amines such as triethanolamine (TEA) and methyldiethanolamine (MDEA), which have three carbon chains linked to the nitrogen atom, are more stable molecules with comparable heat of absorption with the secondary amines. However, the increase in carbon atoms in their structure causes an overall increase in the molecular weight which in turn leads to higher viscosities and slower kinetics. In contrast to primary and secondary amines, carbamate ions are not formed with tertiary amines, leading to slower reaction rates due to the kinetically limited hydration of CO₂ [52].

Sterically hindered amines, such as 2-amino-2-methyl-1-propanol (AMP) or 2-piperidinoethanol (PE), are branched molecules where the primary or secondary amino group is linked to a tertiary carbon atom. Due to this, the stability of the resulting product from the direct CO₂-amine reaction (i.e., carbamate formation) is significantly lower than in the case of linear amines. In turn, this means that significant savings in the energy for breaking the bond during the regeneration step is possible [53]. Furthermore, the overall reaction between a sterically hindered amine and CO₂ requires one mole of amine per mole of CO₂, in contrast to linear primary and secondary amine solvents where there is a requirement for two moles of amine per mole of captured CO₂. This means that higher loadings can be achieved or equivalently less solvent has to be used for the same capture performance. Steric hindrance effects and high atom substitution have been observed to increase the oxidative stability of amines [54], making sterically hindered solvents a better choice when oxidative environments are present. However, oxidative stability has not been yet successfully correlated with thermal stability. Moreover, this class of amines should be treated with care as due to their thermodynamics, they tend to form solid precipitates at process conditions [55].

An extensive number of simulation and optimization studies has been performed to assess the behavior and performance of different amine solvents for CO₂ capture. Although most of the studies refer to chemical absorption in packed columns, the idea of CO₂ capture and regeneration is similar for membrane systems as well. Cavaignac et al. [56] performed a techno-economic study comparing the use of DGA and a mixture of DEA-MDEA, concluding that the DGA yielded better economic results and absorption capacity for a biogas upgrade plant in the given plant. Damartzis et al. [49] compared the behavior of MEA, DEA, AMP, and MPA in terms of energetic demand and process economics, showing that for both indices, the ranking AMP > MPA > DEA > MEA holds. The superiority of AMP was presented, which exhibited a decrease in the required energy by 55% compared to MEA. Mathias et al. [57] attempted to identify the thermodynamically "optimum" solvent by assessing the performance of several commercial and non-commercial solvents. Kim et al. [58] also compared the performance of aqueous MEA, DEA, TEA, and AMP solutions. Dubuis et al. [59] compared the performance of PZ and its mixtures with MDEA with that of MEA showing energy savings in the order of 35% when PZ or PZ/MDEA was used. Finally, Damartzis et al. [60] went one step further, linking the thermodynamics and VLE behavior of MEA, DEA, and MPA with process dynamics.

4.2.2. Solvent Blends

The idea behind the use of blended solvents is to exploit the beneficial properties of single solvents in a synergistic way while reducing bottlenecks. Such bottlenecks include the high cost of regeneration expressed usually as increased thermal needs as well as the resistance of the solvent to thermal and oxidative degradation [61]. The combination of two or more amines in a single solution offers the advantage of utilizing the different reaction mechanisms, inherent to each type of amine, toward maximizing CO₂ capture efficiency or minimizing the heat of reaction. Combinations of MEA and MDEA have been used in pilot plants, showing that the addition of MDEA at a 5:1 ratio can achieve large reductions in thermal energy for solvent regeneration [62]. The mixture of AMP and PZ has been tested by Mangalapally and Hasse [63], leading to a great reduction in the liquid flowrate as well as the regeneration energy. Numerous studies exist confirming that solvent blends of MDEA-PZ or MDEA-DEA show improved CO₂ capture behavior [64,65]. In many cases,

mixtures of AMP have shown great potential [66,67]. According to Bruder et al. [68] a bi-solvent blend of AMP and PZ in a molar ratio 2:1 showed a 20% increase in the CO₂ cyclic capacity compared to the benchmark solvent MEA. However, the use of AMP should be done with caution due to the tendency of this solvent to form precipitates [55]. Despite the advantages that bi-solvent blends offer for CO₂ capture, one must not forget that the design of a process involving a mixture of two solvents introduces a severe complexity in the control of the solvent concentration as the balance between the mixture components can easily be disturbed. Furthermore, each solvent component may require different conditions for absorption and desorption, leading to process challenges. In turn, this would lead to changes in the process's capture efficiency.

Going one step further into solvent development, mixtures of more than two amines can be used. Haghtalab et al. [69] investigated the use of an AMP-PZ-DIPA tri-solvent blend concluding that the presence of AMP-PZ improved the ability of DIPA to capture CO₂, thus increasing the absorption capacity. Moreover, Liu et al. [70] showed that the addition of AMP into a bi-solvent blend of MEA-MDEA greatly improves the kinetics of the amine–CO₂ reaction. When AMP is used, tri-solvent blends can be used to moderate its concentration offering a much better control over precipitate formation [71]. The existence of more than two amine solvents usually signifies increased concentration, leading to increased CO₂ absorption, provided that unwanted interactions between the base molecules of the solvent blend are averted. As with bi-solvent blends, the use of three solvents further increases the complexity in maintaining the concentration within a desired range. However, as long as robust control schemes are present, the careful design of multi-solvent blends often leads to better performance.

4.2.3. Phase Change Solvents

Phase change solvents are mixtures that under certain thermodynamic conditions can undergo reversible phase separation forming two distinct liquid phases of different concentrations. When such mixtures are used in CO₂ capture, the resulting two phases, namely an organic and an aqueous one, or a solvent rich and a solvent lean, respectively, can be mechanically separated resulting in significantly reduced thermal regeneration costs due to the avoidance of water vaporization [72]. A phase change solvent can comprise one base component (e.g., aqueous solution of an amine) or a mixture of components (e.g., amine blend). This way, the thermodynamic conditions of phase splitting can also be controlled using the initial concentration or the molar ratio as a parameter [73]. Zhang et al. [74] present a comprehensive review on benchmark and novel phase change solvents analyzing their potential as well as drawbacks. Lipophilic amines were considered initially by Zhang [75] and subsequently received great attention in the years after. Such solvents exhibit liquid–liquid (LL) phase split within the temperature range of 60–90 °C, considering aqueous solutions with concentrations between 10–30% *w/w*. In a capture process where the reaction of CO₂ is favored by low temperatures, the importance of the LL split temperature plays a crucial part. However, as the reaction temperature is outside the LL split temperature range, a better control of the process can be achieved as the phase splitting can be induced after the reaction takes place without compromising the concentration of the reacting mixture. Mixtures of DEEA (N,N-diethylethanolamine) and MAPA (3-(methylamino)propylamine) have been extensively studied as a candidate solvent for efficient CO₂ capture and simultaneous energy reduction. This mixture exhibits LL split at low temperatures around 40 °C, which coincide with the absorption temperature [76]. As such, CO₂, water and MAPA remain in the organic, CO₂-rich phase, while DEEA is mostly found in the aqueous phase [77]. Shavaliyeva et al. [78] studied a novel mixture of S1N (cyclohexylpropane-1,3-diamine) and DMCA (dimethylcyclohexylamine) as well the known phase change solvent MCA (methylcyclohexylamine). Both S1N-DMCA and MCA solvents showed significantly reduced thermal requirements compared to the base case CO₂ absorption with MEA. Regeneration of both solvents was also performed at lower temperatures in the range of 85–105 °C. The impact of MCA was studied using

an environmental, health, and safety (EHS) analysis by Shavaliyeva et al. [79], showing that additional hazard-countermeasures could be needed for its use; however, the environmental impact is expected to be lower than that of conventional systems. Tzirakis et al. [80] experimentally investigated a ternary phase change solvent, an aqueous solution of DMCA-MCA-AMP. Such solvent exhibits phase splitting at temperatures greater than 40 °C where the absorption of CO₂ takes place and is able to achieve a rich loading of more than 0.7, far surpassing the thermodynamic limitations of MEA. Kazepidis et al. [81] used an optimal design framework to design an absorption-desorption process using a mixture of S1N-DMCA. They reported a minimized thermal requirement in the order of 2.1. GJ/t CO₂ as well as a CO₂ loading in the organic-rich phase far surpassing 1 (i.e., $\alpha = 1.35$).

4.2.4. Ionic Liquids

Ionic liquids (ILs) often refer to compounds resembling the structure of molten salts which are found as liquids at temperatures below 100 °C. In contrast to amine solvents, ILs are composed of two parts, an anion and a cation which can either be of organic or inorganic nature. With a large number of available ionic species that act as “synthesis blocks” to choose from, the number of potential synthesized ILs is vast [82], with the most common ions being the tetrafluoroborate ([BF₄][−]) and acetate ([Ac][−]) as well as the imidazolium ([R₁R₂R₃Im]) and phosphonium ([P]) cations. ILs have very low vapor pressure, resulting in negligible losses due to thermodynamic equilibrium mandates and high thermal stability that generally leads to reduced requirements for their regeneration as well as tunable CO₂ capacity [83–85]. On the other hand, their fabrication as a combination of bulky ions creates large molecules that result in highly viscous fluids which increase pumping energy requirements. Their production cost is also higher than that of conventional solvents and their toxicity and environmental impact is still obscure due to being relatively new. All of the above properties are directly dependent on the nature of the ionic groups comprising the IL and as such, they can be tailored according to the needs of a given process. For solvent-based CO₂ capture, one such property is evidently centered on the rate of reaction. To this end, imidazolium carboxylate ILs are the most prominent ones [86,87]. Such ILs follow a 1:2 stoichiometry when reacting with CO₂ [88] and their heats of reaction are in the range of −35 to −39 kJ/mol, less than half of that of MEA [89]. However, they show a high viscosity [90] and decompose at temperatures higher than 100 °C [91]. Another IL category that has received attention is the amino acid ILs (AA-ILs) which show reduced toxicity and have been reported as good CO₂ capture candidate solvents [92,93]. These ILs are believed to react with CO₂ with a mechanism similar to the zwitterion mechanism of primary and secondary alkanolamines and show very low heats of absorption in the range of −15 to −35 kJ/mol. However, their very high viscosity leads to low reactions rates and thus the need for modification in the form of support or encapsulation is recommended [94]. Similar to AA-ILs, aprotic heterocyclic ionic liquids (AHA-ILs) have shown promising properties for CO₂ capture. These include their high reaction rates and high CO₂ solubility as well as high thermal stability [95–97]. Unlike carboxylate or AA-ILs, AHA-ILs follow a 1:1 stoichiometry and have high decomposition temperatures. However, they have relatively high heats of absorption (−37 to −54 kJ/mol) and medium to high viscosity [96]. Such issues may be partially alleviated by supporting or encapsulating AHA-ILs using co-solvents [98]. A number of process simulation studies exist for assessing the performance of ILs and evaluating the cost of the overall CO₂ capture process as well as operating parameters such as the regeneration demands. Oko et al. [99] compared a mixed aqueous solution of MEA and six different ILs, concluding that ILs based on the 2-cyanopyrrole anion showed the lowest circulation rate and lowest regeneration energy requirements. This energy was estimated at 3.6 GJ/t CO₂ by Zhai and Rubin [100]. Shiflett et al. [101] studied CO₂ capture using the imidazolium-based [BMIM]Ac, which showed a better performance (−20% energy requirements for regeneration) compared to the benchmark amine solvent MEA. The energy requirements could be as low as 1.4 GJ/t CO₂ according to de Riva et al. [102] for mixtures of tetraglyme and AHA-ILs.

4.2.5. Other Solvents

Aside from amines and ionic liquids, a few other solvents have been used for capturing CO₂ from flue gas streams. Salt solutions have been widely used thus far due to their abundance in the chemical industry and their relatively low cost compared to amines or ILs. These systems are mainly based on sodium or potassium carbonates which show low degradation as well as high stability and absorption capacity [103]. Carbonate systems can be classified as conventional or precipitating depending on the chemistry of the system, usually employing promoters due to the slow kinetics of the reaction with CO₂ [104]. However, aside from their slow kinetics, these solvents have low selectivity and promote deposition and corrosion of the equipment [105]. Borhani et al. [106] present a comprehensive review on potassium carbonate solutions. Amino acids can also be used as CO₂ absorbents. They are most commonly used in their salt form, resulting from the reaction of an amino acid with a base group such as KOH [107] or NH₃ [108]. Potassium salts of taurine and glycine [109] and sarcosine [110] are deemed to be promising solvents for CO₂ capture. Nakjiri et al. [111] numerically tested the absorption performance of three absorbents, namely potassium glycinate (PG), potassium arginate (PA), and sodium hydroxide (NaOH), concluding that PA was the best candidate absorbent, followed by PG and NaOH. Ammonia systems offer advantages compared to amine ones, including high cyclic capacity, high efficiency, lower rate of solvent circulation, lower regeneration demands, and no corrosion issues [112]. Such solutions also offer the benefit of simultaneous removal of NO_x and SO_x in addition to CO₂ [113]. They are, however, much more volatile, resulting in high solvent losses and often linked with irritations in the human body and toxicity [114]. Finally, the capture of CO₂ using seawater of variable salinity was studied by Li et al. [115]. They showed that salinity and CO₂ solubility are inversely related and that the addition of inorganic substances that promote precipitation, such as CaO, can enhance the solubility by up to 79%. One such solution can be the addition of steel slag which has been proven to be quite effective [116]. Usually, such systems operate as full capture, utilization, and sequestration systems and may seem favorable for use in maritime systems; however, further studies are needed in order to determine if seawater can be a viable solution for CO₂ capture. Table 2 summarizes the main identified advantages and drawbacks of each class of solvent addressed in this work. An upward (downward) facing arrow signifies a high (low) value for the corresponding property; very high (low) values merit a double arrow.

Table 2. Characteristics of different solvents for CO₂ capture.

Class	Type	Advantages	Disadvantages
Physical	Methanol	Solvent cost ↓ Toxicity ↓ Vapor pressure ↓	Vapor pressure ↑ Process complexity ↑
	Selexol DPEG	Temperature range ↑ Selectivity for H ₂ S ↑	Viscosity ↑
	Rectisol/NH ₃	Temperature ↓	Selectivity for CO ₂ ↓ Vapor pressure ↑
Amines	Primary	Solvent cost ↓ Reaction rate ↑	Stability ↓ Corrosiveness ↑ Regeneration energy ↑
		Vapor pressure ↓ Regeneration energy ↓	Reaction rate ↓ Corrosiveness ↑
	Secondary	Vapor pressure ↓ Regeneration energy ↓	Reaction rate ↓ Corrosiveness ↑
		Tertiary	Stability ↑ CO ₂ loading ↑ Stability ↑
	Sterically hindered	CO ₂ loading ↑ Corrosiveness ↓	Reaction rate ↓

Table 2. Cont.

Class	Type	Advantages	Disadvantages
Ionic Liquids	Bi-Blends	Reaction rate ↑ CO ₂ loading ↑ Regeneration energy ↓	Process complexity ↑
	Tri-Blends	Reaction rate ↑ CO ₂ loading ↑↑ Regeneration energy ↓	Process complexity ↑↑
	Phase change	CO ₂ loading ↑ Regeneration energy ↓ Operating Temperature ↓	Solvent cost ↑ Process complexity ↑
	Imidazolium	Vapor pressure ↓↓ Regeneration energy ↓	Viscosity ↑ Solvent cost ↑↑
	Amino acid (AA)	Reaction rate ↑ Vapor pressure ↓↓ Regeneration energy ↓↓	Viscosity ↑↑ Solvent cost ↑↑
	Aprotic-heterocyclic (AHA)	Reaction rate ↑ Stability ↑ Vapor pressure ↓↓ Regeneration energy ↓	Viscosity ↑ Solvent cost ↑↑
Salts	Carbonate	Solvent cost ↓ Stability ↑ High temperature ↑	Reaction rate ↓ Precipitation chance ↑
	Amino acids	Stability ↑ Vapor Pressure ↓ Solvent cost ↓	Regeneration energy ↑ Precipitation chance ↑
Ammonia		Stability ↑ CO ₂ loading ↑ Regeneration energy ↓ Solvent cost ↓	Vapor pressure ↑↑ Reaction rate ↓ Process complexity ↑
Seawater		Stability ↑ Potential for CCUS ↑	CO ₂ loading ↓ Process complexity ↑↑

5. Solvent Evaluation

Selecting the most suitable solvent for post-combustion CO₂ capture in a maritime environment from a list of potential candidates can prove to be a strenuous task. This is mainly due to the interaction of multiple on-board constraints with the different characteristics of each solvent class. Table 3 shows a qualitative assessment of the different identified CO₂ capture solvents using most KPIs defined in Section 2. It has to be noted that the KPI related to the end-use of the captured CO₂ was not accounted for in Table 3 as it is directly related to the on-board storage strategy, a feature which was not considered in this paper due to its largely complex nature.

Each criterion for each addressed solvent in Table 3 was given a score on a scale from one to five which corresponds to its *degree of positive impact* (five being the best). Another aspect is the *degree of criticality*, an index representing the importance of the particular KPI during maritime application. Performance indicator sorting was performed using two different categories—namely I and II—with I being KPIs that pose critical boundaries for real-time applications. A characteristic example would be, for instance, the health and safety criterion, with solvents scoring low in this particular KPI likely being excluded from consideration during ship design.

Table 3. Comparative assessment of the different solvent classes for CO₂ capture using on board KPIs *.

	Physical Solvents	Primary Amines	Secondary Amines	Tertiary Amines	Sterically Hindered Amines	Amine Blends	Phase Change Solvents	Ionic Liquids	Salts	Ammonia	Seawater	Degree of Criticality
Maturity	5	5	5	4	4	3	1	1	4	4	1	I
Compactness	3	3	3	3	3	4	4	4	3	3	2	I
Energy Penalty	3	2	3	3	3	4	5	5	4	4	4	I
CO₂ Loading	2	3	3	4	4	5	5	5	3	3	1	I
Health and Safety	3	3	3	3	3	3	3	4	4	2	5	I
Operability Range	4	4	4	3	2	4	3	4	4	3	3	II
Impurity Tolerance	2	3	3	3	4	3	3	4	4	4	4	II
OPEX	4	2	2	3	3	2	2	2	4	4	5	II
Other Consumables	4	4	4	4	4	4	4	4	2	4	2	II

(*) Color coding is a measure of the quality of the KPI. Green (5): good, light green (4): medium-good, yellow (3): medium, orange (2): medium-bad, red (1): bad.

It can easily be seen that no solvent class excels in all categories. On the contrary, there is a large distribution of advantages and disadvantages for almost all solvent types in the different ship requirements. Technological maturity, perhaps one of the most important constraints for direct on-board application of solvent-based membrane CO₂ capture, is ensured by only a few solvent categories that have been extensively tested in different scales and high TRL land-based technological applications. For a given capture target, process compactness can be achieved in a number of ways, i.e., low-density solvents or lower liquid flowrates (equivalently, high cyclic capacity) mostly associated with recently developed solvents such as phase change solvents and ionic liquids. These solvents are being designed to minimize a number of technological constraints, including the process cost per unit of captured CO₂ and the requirements for solvent regeneration, alternatively, the energy penalty coming from the energy integration of the process within the ship. On the downside, however, immediate applicability of PCM and IL systems is limited due to their increased complexity and property uncertainties. On-board safety needs to be addressed with utmost care. Solvent toxicity combined with higher presence in the vapor phase due to their high vapor pressure is a factor that needs to be carefully considered. Operational characteristics of the examined solvent classes, including the sensitivity of their selectivity to CO₂ over other gaseous components and their oxidative stability in the presence of impurities as well as the range of process parameters in which the system maintains acceptable operating levels (e.g., avoidance of thermal decomposition, unfavorable precipitation, etc.) are assessed in Table 3. Cost-related KPIs are mainly associated with the market price of the raw solvent together with the necessary flowrate within the process. The latter is directly or indirectly determined by solvent properties such as vapor pressure, cyclic capacity, chemical kinetics, and degradation behavior. Moreover, for certain solvent classes, additives or promoters in the form of inorganic solids or additional solvents are necessary to enhance the performance of the CO₂ capture system, necessitating extra room for consumables storage.

Based on the qualitative assessment of the considered solvent classes, it seems that traditional solvents such as amines have the crucial advantage of maturity as they have been extensively used up to now. During on-board application, their increased energy penalty can be compensated by an efficient energy integration with the ship's energy system. On the other hand, physical solvents suffer from lack of selectivity toward CO₂ and their operation is susceptible to impurities in the feed stream. Newly developed solvents such as phase change solvents and ionic liquids are promising candidates; however, they are still under continuous development, creating risk for usage in an environment characterized by stringent specifications such as the shipping sector. Ammonia-based solvents, despite their maturity, suffer from the fact that ammonia can easily escape in the vapor phase due to its high vapor pressure and can cause redness and inflammation when in contact with the human body. Seawater would be an ideal solvent for on-board application due to its abundance and low cost. However, seawater systems offer very limited CO₂ capture efficiency, which in turn leads to reduced compactness and increased carbon footprint and of capture.

In order to better understand the multi-dimensional problem of solvent selection for maritime applications, a multi-objective assessment method was applied, consisting only of KPIs which were attributed a criticality degree of I from Table 3. Table 4 provides an initial comparative view of the considered solvents. In Table 4, if a solvent outmatches the performance of another solvent (see scoring in Table 3) in all considered KPIs, it is given a point. Otherwise, the value of the entry in the table is set to zero. For example, ionic liquids outperform phase change solvents in all KPIs with a criticality degree I, thus the respective entry in Table 4 is one. From all the considered solvent classes, it can be seen that only one, namely the secondary amines, received two points using this method. This means that they dominate two other solvent types in all of the above discussed and assessed criteria. On the other hand, four solvent types, namely tertiary amines, sterically hindered amines,

ionic liquids, and salts, received a score of one, showing a somewhat promising behavior in terms of potential application in maritime environments.

It has to be noted that this method assumes that all performance indicators of the same criticality degree are equally important. In real-life applications however, this is not 100% certain as in practice, widely tested solutions are more likely to be adopted in order for the degree of uncertainty to be minimized. In the hypothetical scenario where all assessed solvents have the same ranking in maturity, Table 5 shows again the scores using the same multi-objective assessment methodology. Evidently, should all solvents reach the same technological maturity, conventional solvents such as primary and secondary amines receive very low scores. On the other hand, ionic liquids seem to surpass almost all but one solvent type in all KPIs at the same time, having a score of nine and followed by phase change solvents with a score of seven. This is further supported by the fact that such advanced solvents have been recently developed to tackle the problems of conventional capture media such as primary amines, meaning that they are indeed expected to perform better. The main results of this qualitative analysis showed that if the maturity of the solvents is neglected, recent and more advanced solvents should be used in maritime applications. In other words, this means that additional research needs to be focused onto these solvent classes in order to enable their use in commercial, large-scale systems.

Notably, the above analysis and Tables 3–5 can be used as a qualitative guide to assess the correlation between the different identified solvent classes and the ship requirements as expressed through the formulated KPIs. At this stage, it would be premature to provide an absolute or even a more quantitative ranking of the above solvents based on the analysis performed. Primarily, this would somehow require the direct quantification of the criteria used in Table 3. In turn, this means that appropriate weighting factors would have to be applied to each of the identified KPIs in order to highlight the specific importance of each requirement. On the other hand, this is a difficult task as the lack of real application data of solvent-based CO₂ capture on ships creates a subsequent knowledge gap which hinders the formulation of purely on-board CO₂ capture technology-based KPIs.

6. Conclusions and Outlook

Carbon capture on ships during maritime operation is an emerging measure in order to achieve the necessary CO₂ emissions reduction in a key carbon-intensive sector. The constraints imposed by the ship environment such as the available volume, energy supply and most importantly, on-board safety, constitute a difficult to tackle combination of process limitations that need to be countered using compact but efficient solutions. Post-combustion CO₂ capture using modular membrane contactors offers a number of advantages together with the necessary technological maturity for direct on-board application. However, the true bottleneck of such a system remains the choice of the solvent for reasons directly associated with both process efficiency as well as on-board safety. In this work, a comprehensive review of the various classes of CO₂ capture solvents, based on their operational, thermodynamic, and kinetic characteristics, was carried out, utilizing appropriately selected KPIs targeted to the shipping industry's demands.

A qualitative analysis of solvent performance, performed on the basis of the selected KPIs in order to assess their compliance with the maritime industry requirements, revealed that presently, no solvent is able to fully satisfy all the conflicting objectives of an "ideal" on-board operation. Benchmark solvents such as primary and secondary amines appear to adequately serve the shipping needs, showing good compatibility with the majority of the selected KPIs and moreover have the advantage of maturity, resulting from their extensive on-shore operation. On the other hand, recently developed solvents, such as phase change solvents and ionic liquids, which excel in operational performance, simply lack the maturity to be safely considered as CO₂ capture candidates in ships. A multi-objective analysis among the solvents with respect to the most crucial KPIs showed exactly this; under present operating conditions and protocols, secondary amines showed an overall superior performance being the only solvent type that outperformed two other solvent classes. However, if the bottleneck of maturity is removed, ionic liquids clearly prevailed by excelling in all considered KPIs over almost all other types of solvents. The latter directly points toward the need to accelerate research on new and on-demand solvents such as ILs in order to allow their efficient penetration in large-scale industrial applications like the maritime environment.

Safe results regarding a direct and detailed quantitative ranking are difficult to extract based on the present knowledge due to the lack of experience from real-time operation of on-board solvent-based membrane CO₂ capture systems. Furthermore, the large catalogue of solvents presented here has been so far used mainly in configurations with separation columns. As such, data on the potential interactions of the chemical solvent with the employed membrane and their effect on the operation on the compact contactor system need to be enriched through targeted solvent–membrane pair studies. Finally, the present study focused on using KPIs which are mostly ship-oriented. However, the evaluation of the overall system performance has to account for indices that equally comprise the effects of both solvent characteristics (e.g., thermodynamic, thermochemical, and hydrodynamic performance) together with the prerequisites for efficient on-board operation. To this end, future studies that target the formulation of appropriate indices correlating the solvent properties with the desired on-board operating characteristics may greatly facilitate the assessment and subsequent penetration of solvent-based membrane CO₂ capture systems on ships.

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References

1. Ritchie, H.; Roser, M. CO₂ and Greenhouse Gas Emissions. 2020. Available online: <https://ourworldindata.org/co2-and-other-greenhouse-gas-emissions> (accessed on 16 March 2022).
2. IEA. *Greenhouse Gas Emissions from Energy: Overview*, International Energy Agency; IEA: Paris, France, 2021. Available online: <https://www.iea.org/reports/greenhouse-gas-emissions-from-energy-overview> (accessed on 16 March 2022).
3. IMO. *Fourth IMO Greenhouse Gas Study*; International Maritime Organization: London, UK, 2021.
4. DNV. *Maritime Forecast to 2050, Energy Transition Outlook 2021*; DNV: Bærum, Norway, 2021.
5. IRENA. *A Pathway to Decarbonise the Shipping Sector by 2050*; International Renewable Energy Agency: Abu Dhabi, United Arab Emirates, 2021.
6. Mallouppas, G.; Yfantis, E.A. Decarbonization in shipping industry: A review of research, technology development, and innovation proposals. *J. Mar. Sci. Eng.* **2021**, *9*, 415. [[CrossRef](#)]
7. Foretich, A.; Zaimes, G.G.; Hawkins, T.R.; Newes, E. Challenges and opportunities for alternative fuels in the maritime sector. *Marit. Transp. Res.* **2021**, *2*, 100033. [[CrossRef](#)]
8. Bouman, E.A.; Lindstad, E.; Riialand, A.I.; Stromman, A.H. State-of-the-art technologies, measures, and potential for reducing GHG emissions from shipping—A review. *Transport. Res. Part D Transp. Environ.* **2017**, *52*, 408–421. [[CrossRef](#)]
9. Balcombe, P.; Brierley, J.; Lewis, C.; Skatvedt, L.; Speirs, J.; Hawkes, A.; Staffell, I. How to decarbonise international shipping: Options for fuels, technologies and policies. *Energy Convers. Manag.* **2019**, *182*, 72–88. [[CrossRef](#)]
10. Bui, M.; Adjiman, C.S.; Bardow, A.; Anthony, E.J.; Boston, A.; Brown, S.; Fenell, P.S.; Fuss, S.; Galindo, A.; Hackett, L.A.; et al. Carbon capture and storage (CCS): The way forward. *Energy Environ. Sci.* **2018**, *11*, 1062–1176. [[CrossRef](#)]
11. IEA. *Energy Technology Perspectives 2017*; International Energy Agency: Paris, France, 2017.
12. IEA. *Energy Technology Perspectives 2020—Special Report on Carbon Capture Utilisation and Storage*; International Energy Agency: Paris, France, 2020.
13. Madejski, P.; Chmiel, K.; Subramanian, N.; Kus, T. Methods and techniques for CO₂ capture: Review of potential solutions and applications in modern energy technologies. *Energies* **2022**, *15*, 887. [[CrossRef](#)]
14. Chao, C.; Deng, Y.; Dewil, R.; Baeyens, J.; Fan, X. Post-combustion CO₂ capture. *Renew. Sustain. Energy Rev.* **2021**, *138*, 110490. [[CrossRef](#)]
15. Raganati, F.; Miccio, F.; Ammendola, P. Adsorption of carbon dioxide for post-combustion capture: A review. *Energy Fuels* **2021**, *35*, 12845–12868. [[CrossRef](#)]
16. Vaz, S., Jr.; de Souza, A.P.R.; Baeta, B.E.L. Technologies for carbon dioxide capture: A review applied to energy sectors. *Clean Eng Technol.* **2022**, *8*, 100456. [[CrossRef](#)]
17. Wilcox, J. *Carbon Capture*, 1st ed.; Springer: New York, NY, USA, 2012.
18. Mc Dowell, N.; Florin, N.; Buchard, A.; Hallett, J.; Galindo, A.; Jackson, G.; Adjiman, C.S.; Williams, C.K.; Shah, N.; Fennell, P. An overview of CO₂ capture technologies. *Energy Environ. Sci.* **2010**, *3*, 1645–1669. [[CrossRef](#)]
19. DNV. Maritime CCS Project. 2011. Available online: <https://www.era-learn.eu/network-information/networks/eurostars/eurostars-cut-off-2/novel-process-designs-forreduction-of-maritime-carbon-emissions> (accessed on 1 May 2022).
20. Van den Akker, J.T. Carbon Capture on-Board LNG-Fuelled Vessels. Master's Thesis, TU Delft, Delft, The Netherlands, 2017.
21. Luo, X.; Wang, M. Study of solvent-based carbon capture for cargo ships through process modelling and simulation. *Appl. Energy* **2017**, *195*, 402–413. [[CrossRef](#)]
22. Feenstra, M.; Monteiro, J.; Gilling, E.; Goetheer, E.; van den Akker, J.; Abu-Zahra, M. Ship-based carbon capture on-board of diesel or LNG-fuelled ships. *Int. J. Greenh. Gas Contr.* **2019**, *85*, 1–10. [[CrossRef](#)]
23. Ragland, K.W.; Bryden, K.M. *Combustion Engineering 2011*, 2nd ed.; CRC Press: Boca Raton, FL, USA, 2011.
24. Purwasmita, M.; Nabu, E.B.P.; Khoiruddin, K.; Wenten, I.G. Non dispersive chemical deacidification of crude palm oil in hollow fiber membrane contactor. *J. Eng. Technol. Sci.* **2015**, *47*, 426–446. [[CrossRef](#)]
25. Pantoleontos, G.; Theodoridis, T.; Mavroudi, M.; Kikkinides, E.S.; Koutsonikolas, D.; Kaldis, S.P.; Pagana, A.E. Modelling, simulation, and membrane wetting estimation in gas-liquid contacting processes. *Canadian J. Chem. Eng.* **2017**, *95*, 1352–1363. [[CrossRef](#)]
26. Siagian, U.W.R.; Raksajati, A.; Himma, N.F.; Khoiruddin, K.; Wenten, I.G. Membrane-based carbon capture technologies: Membrane gas separation vs. membrane contactor. *J. Nat. Gas Sci. Eng.* **2019**, *67*, 172–195. [[CrossRef](#)]
27. Salmon, I.R.; Cambier, N.; Luis, P. CO₂ capture by alkaline solution for carbonate production: A comparison between a packed column and a membrane contactor. *Appl. Sci.* **2018**, *8*, 996. [[CrossRef](#)]

28. Lee, H.J.; Kim, M.K.; Park, J.H.; Magnone, E. Temperature and pressure dependence of the CO₂ absorption through a ceramic hollow fiber membrane contactor module. *Chem. Eng. Process.* **2020**, *150*, 107871. [[CrossRef](#)]
29. Sohaib, Q.; Vadillo, J.M.; Gómez-Coma, L.; Albo, J.; Druon-Bocquet, S.; Irabien, A.; Sanchez-Marcano, J. CO₂ capture with room temperature ionic liquids; coupled absorption/desorption and single module absorption in membrane contactor. *Chem. Eng. Sci.* **2020**, *223*, 115719. [[CrossRef](#)]
30. Usman, M.; Hillestad, M.; Deng, L. Assessment of a membrane contactor process for pre-combustion CO₂ capture by modelling and integrated process simulation. *Int. J. Greenh. Gas Control* **2018**, *71*, 95–103. [[CrossRef](#)]
31. Khaisri, S.; Montigny, D.; Tontiwachwuthikul, P.; Jiratananon, R. Comparing membrane resistance and absorption performance of three different membranes in a gas absorption membrane contactor. *Sep. Purif. Technol.* **2009**, *65*, 290–297. [[CrossRef](#)]
32. Chuah, C.Y.; Kim, K.; Lee, J.; Koh, D.-Y.; Bae, T.-H. CO₂ absorption using membrane contactors: Recent progress and future perspective. *Ind. Eng. Chem. Res.* **2020**, *59*, 6773–6794. [[CrossRef](#)]
33. An, L.; Yu, X.; Yang, J.; Tu, S.-T.; Yan, J. CO₂ capture using a superhydrophobic ceramic membrane contactor. *Energ. Procedia* **2015**, *75*, 2287–2292. [[CrossRef](#)]
34. Nogalska, A.; Trojanowska, A.; Garcia-Valls, R. Membrane contactors for CO₂ capture processes—Critical review. *Phys. Sci. Rev.* **2017**, *2*, 1–7. [[CrossRef](#)]
35. Xu, Y.; Malde, C.; Wang, R. Correlating Physicochemical Properties of Commercial Membranes with CO₂ Absorption Performance in Gas-Liquid Membrane Contactor. *J. Membrane Sci.* **2020**, *6*, 630–639.
36. Mavroudi, M.; Kaldis, S.P.; Sakellariopoulos, G.P. A study of mass transfer resistance in membrane gas-liquid contacting processes. *J. Membrane Sci.* **2006**, *272*, 103–115. [[CrossRef](#)]
37. Cui, Z.; deMontigny, D. Part 7: A review of CO₂ capture using hollow fiber membrane contactors. *Carbon Manag.* **2013**, *4*, 69–89. [[CrossRef](#)]
38. Mosadegh-Sedghi, S.; Rodrigue, D.; Brisson, J.; Iliuta, M.C. Wetting phenomenon in membrane contactors—Causes and prevention. *J. Membrane Sci.* **2014**, *452*, 332–353. [[CrossRef](#)]
39. Dai, Z.; Ansaloni, L.; Deng, L. Precombustion CO₂ Capture in Polymeric Hollow Fiber Membrane Contactors Using Ionic Liquids: Porous Membrane versus Nonporous Composite Membrane. *Ind. Eng. Chem. Res.* **2016**, *55*, 5983–5992. [[CrossRef](#)]
40. Ibrahim, M.H.; El-Naas, M.H.; Zhang, Z.; Van der Bruggen, B. CO₂ Capture using Hollow Fiber Membranes: A review of membrane wetting. *Energ. Fuel.* **2018**, *32*, 963–978. [[CrossRef](#)]
41. Yan, X.; Anguille, S.; Bendahan, M.; Moulin, P. Ionic liquids combined with membrane separation processes: A review. *Sep. Purif. Technol.* **2019**, *222*, 230–253. [[CrossRef](#)]
42. Olajire, A.A. CO₂ capture and separation technologies for end-of pipe applications—A review. *Energy* **2010**, *35*, 2610–2628. [[CrossRef](#)]
43. Owens, W.; Buchanan, T.; DeLallo, M.; Schoff, R.; White, J.; Wolk, R. *Evaluation of Innovative Fossil Fuel Power Plants with CO₂ Removal*; EPRI: Palo Alto, CA, USA, 2000.
44. Mumford, K.A.; Wu, Y.; Smith, K.H.; Stevens, G.W. Review of solvent based carbon-dioxide capture technologies. *Front. Chem. Sci. Eng.* **2015**, *9*, 125–141. [[CrossRef](#)]
45. Gainar, I.; Anitescu, G. The solubility of CO₂, N₂ and H₂ in a mixture of dimethylether polyethylene glycols at high pressures. *Fluid Phase Equilibria* **1995**, *109*, 281–289. [[CrossRef](#)]
46. Kohl, A.L.; Nielsen, R.B. Alkanolamines for Hydrogen Sulfide and Carbon Dioxide Removal. In *Gas Purification*, 5th ed.; Gulf Publication Company: Houston, TX, USA, 1997; pp. 40–186.
47. Vega, F.; Cano, M.; Camino, S.; Gallego Fernandez, L.M.; Portillo, E.; Navarrete, B. Solvents for CO₂ capture. In *Carbon Dioxide Chemistry, Capture and Oil Recovery*; Karamé, I., Shaya, J., Srour, H., Eds.; IntechOpen: London, UK, 2018. [[CrossRef](#)]
48. Dashti, S.S.; Shariati, A.; Nikou, M.R.K. Sensitivity analysis for selection of an optimum amine gas sweetening process with minimum cost requirement. *Asia-Pacific J. Chem. Eng.* **2015**, *10*, 709–715. [[CrossRef](#)]
49. Damartzis, T.; Papadopoulos, A.I.; Seferlis, P. Process flowsheet design optimization for various amine-based solvents in post-combustion CO₂ capture plants. *J. Clean. Prod.* **2016**, *111*, 204–216. [[CrossRef](#)]
50. Chen, E.; Zhang, Y.; Lin, Y.; Nielsen, P.; Rochelle, G. Review of recent pilot plant activities with concentrated piperazine. *Energ. Procedia* **2017**, *114*, 1110–1127. [[CrossRef](#)]
51. Chen, X.; Rochelle, G.T. Aqueous piperazine derivatives for CO₂ capture: Accurate screening by a wetted wall column. *Chem. Eng. Res. Des.* **2011**, *89*, 1693–1710. [[CrossRef](#)]
52. Vaidya, P.D.; Kenig, E.Y. CO₂-alkanolamine reaction kinetics: A review of recent studies. *Chem. Eng. Technol.* **2007**, *30*, 1467–1474. [[CrossRef](#)]
53. Hüser, N.; Schmitz, O.; Kenig, E.Y. A comparative study of different amine-based solvents for CO₂-capture using the rate-based approach. *Chem. Eng. Sci.* **2017**, *157*, 221–231. [[CrossRef](#)]
54. Buvik, V.; Vevelstad, S.J.; Brakstad, O.G.; Knuutila, H.K. Stability of structurally varied aqueous amines for CO₂ capture. *Ind. Eng. Chem. Res.* **2021**, *60*, 5627–5638. [[CrossRef](#)]
55. Bruder, P.; Svendsen, H.F. Capacity and kinetics of solvents for post-combustion CO₂ capture. *Energ. Procedia* **2012**, *23*, 45–54. [[CrossRef](#)]
56. Cavaignac, R.S.; Ferreira, N.L.; Guardani, R. Techno-economic and environmental process evaluation of biogas upgrading via amine scrubbing. *Renew. Energy* **2021**, *171*, 868–880. [[CrossRef](#)]

57. Mathias, P.M.; Reddy, S.; Smith, A.; Afshar, K. Thermodynamic analysis of CO₂ capture solvents. *Int. J. Greenh. Gas Control* **2013**, *19*, 262–270. [[CrossRef](#)]
58. Kim, Y.E.; Kim, J.A.; Jeong, S.K.; Yoon, Y.I.; Bae, S.T.; Nam, S.C. Comparison of carbon dioxide absorption in aqueous MEA, DEA, TEA and AMP solutions. *Bull. Korean Chem. Soc.* **2013**, *34*, 783–787. [[CrossRef](#)]
59. Dubuis, L.; Thomas, D. Optimization of the post-combustion CO₂ capture applied to cement plant flue gases: Parametric study with different solvents and configurations combined with intercooling. In Proceedings of the 14th International Conference on Greenhouse Gas Control Technologies, GHGT-14, Melbourne, Australia, 21–25 October 2018.
60. Damartzis, T.; Papadopoulos, A.I.; Seferlis, P. Solvent effects on design with operability considerations in post-combustion CO₂ capture plants. *Chem. Eng. Res. Des.* **2018**, *131*, 414–429. [[CrossRef](#)]
61. Nwaoha, C.; Supap, T.; Idem, R.; Saiwan, C.; Tontiwachwuthikul, P.; Al-Marri, M.J.; Benamor, A. Advancement and new perspectives of using formulated reactive amine blends for post-combustion carbon dioxide (CO₂) capture technologies. *Petroleum* **2017**, *3*, 10–36. [[CrossRef](#)]
62. Idem, R.; Wilson, M.; Tontiwachwuthikul, P.; Chakma, A.; Veawab, A.; Aroonwilas, A.; Gelowitz, D. Pilot plant studies of the CO₂ capture performance of aqueous MEA and mixed MEA/MDEA solvents at the University of Regina CO₂ capture technology development plant and the boundary dam CO₂ capture demonstration plant. *Ind. Eng. Chem. Res.* **2006**, *45*, 2414–2420. [[CrossRef](#)]
63. Mangalapally, H.P.; Hasse, H. Pilot plant experiments for post combustion carbon dioxide capture by reactive absorption with novel solvents. *Energy Procedia* **2011**, *4*, 1–8. [[CrossRef](#)]
64. Mudhasakul, S.; Ku, H.; Douglas, P.L. A simulation model of a CO₂ absorption process with methyldiethanolamine solvent and piperazine as an activator. *Int. J. Greenh. Gas Control* **2013**, *15*, 134–141. [[CrossRef](#)]
65. Adeosun, A.; Abu-Zahra, M.R.M. Evaluation of amine-blend solvent systems for CO₂ post-combustion capture applications. *Energy Procedia* **2013**, *37*, 211–218. [[CrossRef](#)]
66. Dash, S.K.; Samanta, A.N.; Bandyopadhyay, S.S. Simulation and parametric study of post combustion CO₂ capture process using (AMP + PZ) blended solvent. *Int. J. Greenh. Gas Contr.* **2014**, *21*, 130–139. [[CrossRef](#)]
67. Choi, W.-J.; Seo, J.-B.; Jang, S.-Y.; Jung, J.-H.; Oh, K.-J. Removal characteristics of CO₂ using aqueous MEA/AMP solutions in the absorption and regeneration process. *J. Environ. Sci.* **2009**, *21*, 907–913. [[CrossRef](#)]
68. Bruder, P.; Grimstedt, A.; Mejdell, T.; Svendsen, H.F. CO₂ capture into aqueous solutions of piperazine activated 2-amino-2-methyl-1-propanol. *Chem. Eng. Sci.* **2011**, *66*, 6193–6198. [[CrossRef](#)]
69. Haghtalab, A.; Eghbali, H.; Shojaeian, A. Experiment and modeling solubility of CO₂ in aqueous solutions of diisopropanolamine + 2-amino-2-methyl-1-propanol + piperazine at high pressures. *J. Chem. Thermodyn.* **2014**, *71*, 71–83. [[CrossRef](#)]
70. Liu, Y.; Fan, W.; Wang, K.; Wang, J. Studies of CO₂ absorption/regeneration performances of novel aqueous monoethanolamine (MEA)—based solution. *J. Clean. Prod.* **2016**, *112*, 4012–4021. [[CrossRef](#)]
71. Nwaoha, C. CO₂ Absorption: Solubility of CO₂ in 2-amino-2-methyl-1-Propanol Solvent Promoted by Piperazine and Monoethanolamine Blends. Master's Thesis, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand, 2015.
72. Papadopoulos, A.I.; Perdomo, F.A.; Tzirakis, F.; Shavaliyeva, G.; Tsivintzelis, I.; Kazepidis, P.; Nessi, E.; Papadokostantakis, S.; Seferlis, P.; Galindo, A.; et al. Molecular engineering of sustainable phase-change solvents: From digital design to scaling-up for CO₂ capture. *Chem. Eng. J.* **2021**, *420*, 127624. [[CrossRef](#)]
73. Papadopoulos, A.I.; Tzirakis, F.; Tsivintzelis, I.; Seferlis, P. Phase-change solvents and processes for post-combustion CO₂ capture: A detailed review. *Ind. Eng. Chem. Res.* **2019**, *58*, 5088–5111. [[CrossRef](#)]
74. Zhang, S.; Shen, Y.; Wang, L.; Chen, J.; Lu, Y. Phase change solvents for post-combustion CO₂ capture: Principle, advances and challenges. *Applied Energy* **2019**, *239*, 876–897. [[CrossRef](#)]
75. Zhang, X. Studies on Multiphase CO₂ Capture Systems. Ph.D. Thesis, TU-Dortmund, Dortmund, Germany, 2007.
76. Pinto, D.D.D.; Zaidy, S.A.H.; Hartono, A.; Svendsen, H.F. Evaluation of a phase change solvent for CO₂ capture: Absorption and desorption tests. *Int. J. Greenh. Gas Control* **2014**, *28*, 318–327. [[CrossRef](#)]
77. Arshad, M.W.; Von Solms, N.; Thomsen, K.; Svendsen, H.F. Heat of absorption of CO₂ in aqueous solutions of DEEA, MAPA and their mixture. *Energy Procedia* **2013**, *37*, 1532–1542. [[CrossRef](#)]
78. Shavaliyeva, G.; Kazepidis, P.; Papadopoulos, A.I.; Seferlis, P.; Papadokostantakis, S. Environmental, health and safety assessment of post-combustion CO₂ capture processes with phase-change solvents. *Sustain. Prod. Consum.* **2021**, *25*, 60–76. [[CrossRef](#)]
79. Shavaliyeva, G.; Papadokostantakis, S.; Kazepidis, P.; Papadopoulos, A.I.; Seferlis, P. Sustainability analysis of phase-change solvents for post-combustion CO₂ capture. *Chem Eng Transact* **2019**, *76*, 1045–1050.
80. Tzirakis, F.; Tsivintzelis, I.; Papadopoulos, A.I.; Seferlis, P. Experimental measurement and assessment of equilibrium behaviour for phase change solvents used in CO₂ capture. *Chem. Eng. Sci.* **2019**, *18*, 20–27. [[CrossRef](#)]
81. Kazepidis, P.; Papadopoulos, A.I.; Tzirakis, F.; Seferlis, P. Optimum design of industrial post-combustion CO₂ capture processes using phase-change solvents. *Chem. Eng. Res. Des.* **2021**, *175*, 209–222. [[CrossRef](#)]
82. Friess, K.; Izák, P.; Kárásova, M.; Pasichnyk, M.; Lanc, M.; Nikolaeva, D.; Luis, P.; Jansen, J.C. A review on ionic liquid gas separation membranes. *Membranes* **2021**, *11*, 97. [[CrossRef](#)]
83. Aghaie, M.; Rezaei, N.; Zendejboudi, S. A systematic review on CO₂ capture with ionic liquids: Current status and future prospects. *Renew. Sustain. Energy Rev.* **2018**, *96*, 502–525. [[CrossRef](#)]

84. Zhang, X.; Zhang, X.; Dong, H.; Zhao, Z.; Zhang, S.; Huang, Y. Carbon capture with ionic liquids: Overview and progress. *Energy Environ. Sci.* **2012**, *5*, 6668–6681. [[CrossRef](#)]
85. Sarmad, S.; Mikkola, J.-P.; Ji, X. Carbon dioxide capture with ionic liquids and deep eutectic solvents: A new generation of sorbents. *ChemSusChem* **2017**, *10*, 324–352. [[CrossRef](#)]
86. Stevanovic, S.; Podgorsek, A.; Moura, L.; Santini, C.C.; Padua, A.A.H.; Costa Gomes, M.F. Absorption of carbon dioxide by ionic liquids with carboxylate anions. *Int. J. Greenh. Gas Control* **2013**, *17*, 78–88. [[CrossRef](#)]
87. Tian, Q.; Li, R.; Sun, H.; Xue, Z.; Mu, T. Theoretical and experimental study on the interaction between 1-butyl-3-methylimidazolium acetate and CO₂. *J. Mol. Liq.* **2015**, *208*, 259–268. [[CrossRef](#)]
88. Cabaço, M.I.; Besnard, M.; Danten, Y.; Coutinho, J.A.P. Carbon dioxide in 1-Butyl-3-methylimidazolium acetate. I. Unusual solubility investigated by Raman Spectroscopy and DFT calculations. *J. Phys. Chem. A* **2012**, *116*, 1605–1620. [[CrossRef](#)] [[PubMed](#)]
89. Mota-Martinez, M.T.; Hallett, J.P.; Mc Dowell, N. Solvent selection and design for CO₂ capture—how we might have been missing the point. *Sustain. Energy Fuels* **2017**, *1*, 2078–2090. [[CrossRef](#)]
90. Almeida, H.F.D.; Passos, H.; Lopes-da-Silva, J.A.; Fernandes, A.M.; Freire, M.G.; Coutinho, J.A.P. Thermophysical properties of five acetate-based ionic liquids. *J. Chem. Eng. Data* **2012**, *57*, 3005–3013. [[CrossRef](#)]
91. Williams, M.L.; Holahan, S.P.; McCorkill, M.E.; Dickmann, J.S.; Kiran, E. Thermal and spectral characterization and stability of mixtures of ionic liquids [EMIM]Ac and [BMIM]Ac with ethanol, methanol, and water at ambient conditions and at elevated temperatures and pressures. *Thermochim. Acta* **2018**, *669*, 126–139. [[CrossRef](#)]
92. Chen, F.F.; Huang, K.; Zhou, Y.; Tian, Z.Q.; Zhu, X.; Tao, D.J.; Jiang, D.E.; Dai, S. Multi-molar absorption of CO₂ by the activation of carboxylate groups in amino acid ionic liquids. *Angew. Chem.* **2016**, *55*, 7166–7170. [[CrossRef](#)]
93. Sistla, Y.S.; Khanna, A. CO₂ absorption studies in amino acid-anion based ionic liquids. *Chem. Eng. J.* **2015**, *273*, 268–276. [[CrossRef](#)]
94. Santiago, R.; Lemus, J.; Moya, C.; Moreno, D.; Alonso-Morales, N.; Palomar, J. Encapsulated ionic liquids to enable the practical application of amino acid-based ionic liquids in CO₂ capture. *ACS Sustain. Chem. Eng.* **2018**, *6*, 14178–14187. [[CrossRef](#)]
95. Wu, J.; Lv, B.; Wu, X.; Zhou, Z.; Jing, G. Aprotic heterocyclic anion-based dual-functionalized ionic liquid solutions for efficient CO₂ uptake: Quantum chemistry calculation and experimental research. *ACS Sustain. Chem. Eng.* **2019**, *7*, 7312–7323. [[CrossRef](#)]
96. Hong, B.; Simoni, L.D.; Bennett, J.E.; Brennecke, J.F.; Stadtherr, M.A. Simultaneous process and material design for aprotic N-heterocyclic anion ionic liquids in post-combustion CO₂ capture. *Ind. Eng. Chem. Res.* **2016**, *55*, 8432–8449. [[CrossRef](#)]
97. Seo, S.; Quiroz-Guzman, M.; DeSilva, M.A.; Lee, T.B.; Huang, Y.; Goodrich, B.F.; Schneider, W.F.; Brennecke, J.F. Chemically tunable ionic liquids with aprotic heterocyclic anion (AHA) for CO₂ capture. *J. Phys. Chem. B* **2014**, *118*, 5740–5751. [[CrossRef](#)]
98. Fillion, J.J.; Bennett, J.E.; Brennecke, J.F. The viscosity and density of ionic liquid + tetraglyme mixtures and the effect of tetraglyme on CO₂ solubility. *J. Chem. Eng. Data* **2017**, *62*, 608–622. [[CrossRef](#)]
99. Oko, E.; Zacchello, B.; Wang, M.; Fethi, A. Process analysis and economic evaluation of mixed aqueous ionic liquid and monoethanolamine (MEA) solvent for CO₂ capture from a coke oven plant. *Greenhouse Gas. Sci. Technol.* **2018**, *8*, 686–700. [[CrossRef](#)]
100. Zhai, H.; Rubin, E.S. Systems analysis of ionic liquids for post-combustion CO₂ capture at coal-fired power plants. *Energy Procedia* **2014**, *63*, 1321–1328. [[CrossRef](#)]
101. Shiflett, M.B.; Drew, D.W.; Cantini, R.A.; Yokozeki, A. Carbon dioxide capture using ionic liquid 1-Butyl-3-methylimidazolium acetate. *Energy Fuels* **2010**, *24*, 5781–5789. [[CrossRef](#)]
102. De Riva, J.; Ferro, V.; Moya, C.; Stadtherr, M.A.; Brennecke, J.F.; Palomar, J. Aspen Plus supported analysis of the post-combustion CO₂ capture by chemical absorption using the P-2228 CNPyr and P-66614 CNPyr AHA Ionic Liquids. *Int. J. Greenh. Gas Control* **2018**, *78*, 94–102. [[CrossRef](#)]
103. Borhani, T.N.G.; Wang, M. Role of solvents in CO₂ capture processes: The review of selection and design methods. *Renew. Sustain. Energy Rev.* **2019**, *114*, 109299. [[CrossRef](#)]
104. Sartori, G.; Savage, D.W. Sterically hindered amines for carbon dioxide removal from gases. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 239–249. [[CrossRef](#)]
105. Asif, M.; Suleman, M.; Haq, I.; Jamal, S.A. Post-combustion CO₂ capture with chemical absorption and hybrid system: Current status and challenges. *Greenh. Gases Sci. Technol* **2018**, *8*, 998–1031.
106. Borhani, T.N.G.; Azarpour, A.; Akbari, V.; Wan Alwi, S.R.; Manan, Z.A. CO₂ capture with potassium carbonate solutions: A state-of-the-art review. *Int. J. Greenh. Gas Contr.* **2015**, *41*, 142–162. [[CrossRef](#)]
107. Song, H.-J.; Park, S.; Kim, H.; Gaur, A.; Park, J.-W.; Lee, S.-J. Carbon dioxide absorption characteristics of aqueous amino acid salt solutions. *Int. J. Greenh. Gas Control* **2012**, *11*, 64–72. [[CrossRef](#)]
108. Yang, N.; Yu, H.; Xu, D.Y.; Conway, W.; Maeder, M.; Feron, P. Amino acids/NH₃ mixtures for CO₂ capture: Effect of neutralization methods on CO₂ mass transfer and NH₃ vapour loss. *Energy Procedia* **2014**, *63*, 773–780. [[CrossRef](#)]
109. Kumar, P.S.; Hogendoorn, J.A.; Versteeg, G.F.; Feron, P.H.M. Kinetics of the reaction of CO₂ with aqueous potassium salt of taurine and glycine. *AIChE J* **2003**, *49*, 203–213. [[CrossRef](#)]
110. Aronu, U.E.; Hartono, A.; Hoff, K.A.; Svendsen, H.F. Kinetics of carbon dioxide absorption into aqueous amino acid salt: Potassium salt of sarcosine solution. *Ind. Eng. Chem. Res.* **2011**, *50*, 10465–10475. [[CrossRef](#)]

111. Nakjiri, A.T.; Heydarinasab, A.; Bakhtiari, O.; Mohammadi, T. Modeling and simulation of CO₂ separation from CO₂/CH₄ gaseous mixture using potassium glycinate, potassium arginate and sodium hydroxide liquid absorbents in the hollow fiber membrane contactor. *J. Environ. Chem. Eng.* **2018**, *6*, 1500–1511. [[CrossRef](#)]
112. Dave, N.; Do, T.; Puxty, G.; Rowland, R.; Feron, P.H.M.; Attalla, M.I. CO₂ capture by aqueous amines and aqueous ammonia—A comparison. *Energy Procedia* **2009**, *1*, 949–954. [[CrossRef](#)]
113. Resnik, K.P.; Pennline, H.W. Study of an ammonia-based wet scrubbing process in a continuous flow system. *Fuel* **2013**, *105*, 184–191. [[CrossRef](#)]
114. Zhang, M.; Guo, Y. Process simulations of NH₃ abatement system for large-scale CO₂ capture using aqueous ammonia solution. *Int. J. Greenh. Gas Control* **2013**, *18*, 114–127. [[CrossRef](#)]
115. Li, H.; Tang, Z.; Xing, X.; Guo, D.; Cui, L.; Mao, X.-Z. Study of CO₂ capture by seawater and its reinforcement. *Energy* **2018**, *104*, 1135–1144. [[CrossRef](#)]
116. Li, H.; Zhang, R.; Wang, T.; Wu, Y.; Xu, R.; Wang, Q.; Tang, Z. Performance evaluation and environment risk assessment of steel slag enhancement for seawater to capture CO₂. *Energy* **2022**, *238B*, 121861. [[CrossRef](#)]