



MemCCSea

Innovative membrane systems
for CO₂ capture and storage at sea

Deliverable D1.2

Report on membrane-based CO₂ capture technologies

WP1. Definition of process requirements and specifications

Authors: Akrivi Asimakopoulou¹, Theodoros Damartzis¹, Dimitrios Koutsonikolas¹, Michail Mouratidis¹, Georgios Skevis¹, Chara Georgopoulou², George Dimopoulos², Lampros Nikolopoulos³, Konstantinos Bougiouris³, Hannes Richter⁴, Udo Lubenau⁵, Solon Oikonomopoulos⁶, Christina Perinu⁶, David Hopkinson⁷ and Grigorios Panagakos^{7,8}

Affiliations: ¹Chemical Process & Energy Resources Institute (CPERI), Centre for Research and Technology Hellas (CERTH), 57001, Thessaloniki, Greece

²DNV GL Maritime Research and Development, Piraeus 18545, Greece

³Euronav Ship Management (Hellas) LTD, Athens 10447, Greece

⁴Fraunhofer IKTS, Institute for Ceramic Technologies and Systems, Michael-Faraday-Straße 1, 07629 Hermsdorf, Germany

⁵DBI GUT GmbH, Karl-Heine-Strasse 109/111, 04229 Leipzig, Germany

⁶Department of Chemistry, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway

⁷National Energy Technology Laboratory, 3610 Collins Ferry Road, Morgantown, WV 26507, USA

⁸Department of Chemical Engineering, Carnegie Mellon University, 5000 Forbes Ave, Pittsburgh, PA 15213, USA

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1 Introduction

Despite worldwide efforts to contain Greenhouse Gas Emissions (GHG) as a key measure to prevent excessive temperature rise, the latter are increasing at an alarming pace. In 2019 CO₂ emissions from fossil fuel combustion have reached 36.7 Gt with total GHG emissions approaching 50 Gt CO₂e¹ (an almost 40% increase compared to those of 1990). 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 tantamount². Power generation and transport together account for more than two thirds of the total GHG emissions (IEA, 2021, 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. Future projections bring this amount to almost 1.6 bt/y for 2050, see Fig. 1. (Malloupas and Yfantis, 2021, Balcombe et al., 2019) as world trade is expected to rise by almost 40% by 2050 (DNV, 2020).

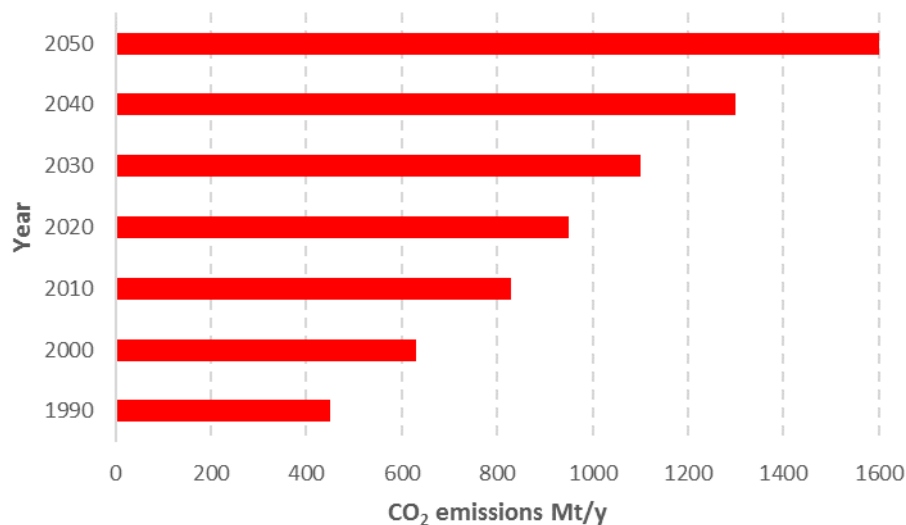



Figure 1. CO₂ emissions trend of the shipping sector.

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 IMO (International Maritime Organization)

¹ Greenhouse gas emissions – from carbon dioxide, methane, nitrous oxide, and fluorinated hydrocarbons – are expressed as carbon-dioxide equivalents (CO₂e), where “equivalent” means “having the same warming effect as CO₂ over a period of 100 years”.

² A comprehensive and frequently updated database of GHG emissions is available in the Our World in Data website. (Hannah Ritchie and Max Roser (2020) - "CO₂ and Greenhouse Gas Emissions". Published online at OurWorldInData.org. Retrieved from: <https://ourworldindata.org/co2-and-other-greenhouse-gas-emissions> [Online Resource]). The United Nations Climate Change website also provides detailed inventories of GHG emissions worldwide.


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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, that targets the design phase of *new ships* through measures that affect hull hydrodynamics, propulsion and power systems, machinery technologies integration, and the use of alternative fuels and renewable energy sources (IRENA, 2021, DVN 2020). Compliance with the EEDI is mandatory. In 2018 IMO adopted the Initial Strategy on the reduction of 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 (Malloupas and Yfantis, 2021). 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. 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-mile³ and will provide the basis for a vessel energy efficiency rating system on a yearly basis thus assessing primarily operational efficiency.

The above regulations define 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 HFO (Heavy Fuel Oil) or MDO (Marine Diesel Oil). 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), Biofuels (including Bio-oils and Hydrotreated Vegetable Oils (HVO))
- (2) **Propulsion & Power System** (Engine efficiency improvement, Propulsion efficiency devices, Propeller optimization, Waste heat recovery, Wind and solar assistance technologies)
- (3) **Electrification** (On-board electricity production, Fuel cells, Battery storage, Hybrid systems, Cold ironing)
- (4) **Ship Design** (Hull hydrodynamics, Hull coatings, Air lubrication)
- (5) **Operational Measures** (Slow steaming, Weather routing, Route optimization, Ship energy management systems integration)

³ Gross tonnage (gt) is a measure of a vessel's internal volume. It is a dimensionless number that relates to the overall size of the ship. Deadweight tonnage (dwt) is a measure of the carrying capacity of a vessel, expressed in tonnes. It includes the weight of fuel, (ballast) water, cargo and passengers but not the empty weight of the ship (<https://safety4sea.com/cm-do-you-know-what-gt-and-dwt-measure-in-a-ship/>).


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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 emissions reduction potential and have identified limitations to their wide deployment. For example, Foretich et al. (2021) and Bouman et al. (2017) have concluded that the introduction of biofuels can, in principle, result in 100% reduction in GHG emissions. However, there are several technical and operational issues (such as engine compatibility, long-term storage, 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. (2019). 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 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 (CCS). CCS 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 (Bui et al, 2018). Multiple scenarios have been developed that attempt to predict the beneficial influence of CCS technologies in the global emissions map, including the Blue Scenario Map from the International Energy Agency (IEA). According to the IEA (IEA, 2017) CCS is crucial in the so-called B2DS scenario for limiting temperature rise below 2 °C by 2060. B2DS scenario sets out a rapid decarbonization pathway with CCS being the key driver and responsible for a massive 32% CO₂ emission reductions beyond the 2DS scenario. Currently only a small fraction (almost 230 Mt) of the carbon emitted is actually re-used in agriculture, oil and gas as well as food industries, with new routes of exploitation being developed for the build-ing, fuels and chemicals sectors (IEA, 2020). 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 in order 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. 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.

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

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chemical reaction promoted by the concentration difference. Subsequently, the CO₂ loaded solvent is usually driven to a regeneration process in which the opposite 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. Finally, membrane contactor-based systems can be employed to separate CO₂ from gaseous mixtures. Porous membranes are able to provide increased CO₂ capture efficiencies as a contactor mechanism for solvent-based CO₂ capture, mainly due to the high mass transfer area achieved as a result of their porous structure.

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 to inadequate efficiencies, mainly due to the small CO₂ concentrations (< 15%) found in conventional flue gas streams (Wilcox, 2012). Adsorption systems, on the other hand can 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 costs (McDowel et al, 2010).


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, 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 are compromised.

Considering the above, this paper analyzes 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 that will determine the suitability for use in a maritime environment. It is 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 is not accounted and the study will focus 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 technology for CO₂ separation is presented in Section 3. A comprehensive review of possible

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solvents for membranecontactor-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.

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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 (DNV, 2011). 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 (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 (2017) 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 1.2MW. Luo and Wang (2017) 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. (2019) 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% capture 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, and 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 has been 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 will need to be effective within a range of variant operating conditions, including temperature, pressure, exhaust gas flow and CO ₂ content in the exhaust. The CO ₂ content in ship engine exhaust is about 4-6% when powered by LNG, 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.

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Energy penalty	Unlike land-based applications, the on-board ship environment has low availability of power, heat, and consumables' resources. Therefore, the energy demand for regenerating the solvent must be kept as low as possible.
Impurities	Some solvents may be sensitive to impurities, e.g. sulfur, particulate matter or methane traces, or their capture efficiency may degrade in the presence of such compounds in the flue gas. Any requirement for pre-treatment equipment would add complexity, risk, volume, and weight.
CO₂ product characteristics	The CO ₂ product form is important in accounting about on-board storage capacity and conditions (liquefied, compressed, etc.), thus affecting the on-board resources' requirements.
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 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, like 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 like high pressure or temperature impose additional design considerations related to safety.

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3 Membrane Contactors for Maritime CO₂ Capture

In general practice, post-combustion CO₂ capture is performed using either physical/chemical absorption or adsorption. Both processes rely on the contact of the flue gas with a liquid absorbent/ solid adsorbent and the selective transfer of CO₂ to it, either due to pure thermodynamics (i.e. vapor liquid equilibrium or Van der Waals forces) or due to the combined effect of thermodynamics and reaction kinetics 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 materials, positioned in appropriate configurations that act as a physical boundary between the gaseous and liquid phases. On the other side of the membrane, a CO₂ capture medium (i.e. a solvent) flows co-currently or counter-currently and chemically binds it, therefore enhancing its removal. The presence of the solvent is important for the enhancement of the transfer rate through the membrane due to the contribution of the chemical reactions to mass transfer. On the other hand, the membrane is responsible for increasing the contact area between the phases, also enhancing the mass transfer rate (Purwasasmita et al., 2015). The combination of these two factors leads to an intensified and compact process with increased efficiency when compared to membrane permeators and reduced volume compared to an absorption column. A typical contactor configuration can be seen in Figure 2.

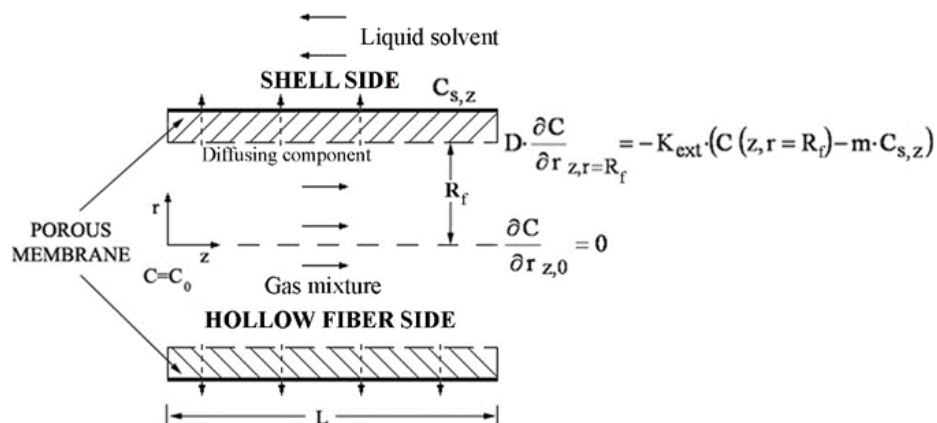



Figure 2. Schematic representation of a membrane contactor for CO₂ capture (adapted from Pantoleontos et al., 2017)


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 LNG ship engine operates at lean conditions with typical off-gas CO₂ molar concentrations in the order of 4-6 % and the remainder being mainly N₂ and water vapor. The use

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of membranes prior to the reaction zone (shell side - see Figure 2) can ensure that the liquid phase will come into contact with a very high concentration CO₂ vapor phase, further increasing the mass transfer rate between the two. 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, such as pore wetting and membrane degradation due to the solvent that have to be considered (Siagian et al., 2019).

The efficiency and applicability of membrane contactors as part of an absorption/desorption system has been studied by a number of researchers. Salmón et al. (2018) 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 > 5 times less volume. Additionally, the use of hollow fiber ceramic membranes instead of an absorption column in the conventional absorption/regeneration system results in lower pressure drop during the absorption step (Lee et al., 2020). Membrane contactors can be used to replace not only the absorption column but also the solvent regeneration column (Sohaib et al., 2020; Usman et al., 2018).

Material compatibility (how solvent affects membrane operational properties e.g. reaction between membrane/solvent, hydrophobicity, corrosion, clogging etc.)

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4 Solvents for CO₂ Capture


Solvent-based separations are perhaps the most deeply studied field in CO₂ separation. The principle behind the separation of CO₂ using a solvent depends on the binding mechanism with CO₂. To this end, solvents are mainly separated into physical and chemical. Table 2 summarizes the main 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.

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 pressure, making the typical flue gas streams difficult to separate. According to NETL (2003), 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 that is proportional to gas pressure. Thus far, physical absorption has been used in a number of industrial off-shore power plants (Olajire, 2010) demonstrating adequate CO₂ capture efficiencies with rather small energy penalties (Owens et al., 2000). However, one of the problems associated with physical absorption is poor gas pair selectivity 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 (Mumford et al., 2015). 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 (Gainar and Anitescu, 1995). Mumford et al. (2015) 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 in order to further enhance the rate of separation. In practice, the solvent is an effective molecule, mainly an amine, with which the flue gas is brought in contact either in a separation column or in a membrane module. A very large number of CO₂ capture solvents have already been developed and used broadly 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

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solvents (PCS) and aminated ionic liquids (IL). 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 cyclic CO₂ 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 bound by thermodynamics in the form of the vapor-liquid equilibrium (VLE) as well as the kinetics of the chemical system. Vapor pressure and viscosity play a major role for the assessment of chemical solvents as they indirectly affect the regeneration strategy and associated required energy. Finally, 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 to 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 (Kohl and Nielsen, 1997), 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 and are relatively cheap, and also achieve fast reaction rates with high selectivity towards CO₂. They are usually classified as primary, secondary or tertiary depending on the degree of substitution on the nitrogen atom. The existing amine group serves as a promoter of the reaction with acid gases meaning that highly substituted molecules tend to exhibit higher capture capacities. On the other hand, the hydroxyl group contributes to reduction of the amine's vapor pressure (and in most cases also the viscosity) (Vega et al., 2017).

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 towards 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 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) 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 (Sharif Dashti et al., 2015). 3-amino-1-propanol (MPA) 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 % (Damartzis et al., 2016).

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/cyclic capacity. Similar to primary amines, these solvents follow the zwitterion mechanism but they are more resistant to degradation and less corrosive (Vega et al, 2017).


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Another widely used secondary amine solvent is piperazine (PZ). PZ has a high absorption rate, good stability, low viscosity, and high capacity (Chen et al., 2017), but is prone to form solid precipitates (Chen and Rochelle, 2011), thus it is rarely used as a standalone solvent. Secondary amines also generally offer the benefit of decreased energy demand for their thermal regeneration due to their lower volatility and lower circulation rates as compared with primary amines.

On the other hand, tertiary amines such as triethanolamine (TEA) and methyldiethanolamine (MDEA) are more stable molecules with comparable heat of absorption with the secondary amines, however, the large number of carbon atoms in their chains causes an 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 (Vaidya and Kenig, 2009).

Sterically hindered amines, such as 2-amino-2-methyl-1-propanol (AMP) or 2-piperidinethanol (PE) are branched molecules where the amino group is linked to a tertiary carbon atom. Due to this, the stability of the resulting product from the CO₂-amine reaction is significantly lower than in the case of linear amines. In turn, this means that a significant reduction regeneration energy is possible Hüsser et al. (2017). Furthermore, the overall reaction between a sterically hindered amine and CO₂ requires one mole of amine per mole CO₂, in contrast to linear primary and secondary amine solvents where there is a requirement for 2 moles of amine, meaning 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 (Buvik, 2021), making sterically hindered solvents a better choice when oxidative environments are present. However, oxidative stability is not correlated with thermal stability. Moreover this class of amines tend to form solid precipitates at process conditions (Bruder and Svendsen, 2012).

An extensive number of simulation/optimization studies has been performed to assess the behavior and performance of different amine solvents for CO₂ capture. Although the majority 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. (2021) 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. (2016) 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 of the required energy by 55% compared to MEA. Mathias et al. (2013) attempted to identify the thermodynamically “optimum” solvent by assessing the performance of several commercial and non-commercial solvents. Kim et al. (2013) also compared the performance of aqueous MEA, DEA, TEA and AMP solutions. Dubuis et al. (2018) compared the performance of PZ and its mixtures with MDEA with that of MEA showing energy savings on the order of 35% when PZ or PZ/MDEA was used. Finally, Damartzis et al. (2018) went one step further, linking the thermodynamics and VLE behavior of MEA, DEA and MPA with process dynamics.

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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 (Nwaoha et al., 2017). The combination of 2 or more amines in a single solution offers the advantage of utilizing the different reaction mechanisms inherent to each type of amine, towards maximizing CO₂ capacity 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 (Idem et al, 2006). The mixture of AMP and PZ has been tested by (Mangalapally and Hasse, 2011), leading to 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 (Mudhasakul et al, 2013; Adeosun and Abu-Zahra, 2013). In many cases, mixtures of AMP have shown great potential (Dash et al, 2014; Choi et al, 2009). According to Bruder et al, (2011) a bi-solvent blend of AMP and PZ in a molar ratio 2:1 showed a 20% increase in the CO₂ working 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 (Bruder and Svendsen, 2012). 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 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 (2014) 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. (2016) 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 (Nwaoha, 2015). 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 equivalently. The two phases can be mechanically separated resulting in significantly reduced thermal regeneration costs due to the avoidance of water vaporization (Papadopoulos et al.,

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2021). 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 (Papadopoulos et al., 2019). Zhang et al. (2019) presents a comprehensive review on phase change solvents analyzing their potential as well as drawbacks. Lipophilic amines were considered initially by Zhang (2007) 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 (Pinto et al., 2014). As such, CO₂, water and MAPA remain in the organic, CO₂ rich phase, while DEEA is mostly found in the aqueous phase (Arshad et al., 2013). Shavaliyeva et al. (2021) 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 show significantly reduced thermal requirements compared to the base case CO₂ absorption with MEA. Regeneration of both solvents is also performed at lower temperatures in the range of 85-105 °C. Tzirakis et al. (2019) 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. (2021) used an optimal design framework to design of an absorption-desorption process using a mixture of S1N-DMCA. They report a minimized thermal requirement on 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) are molten salts which are in liquid phase 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 (Friess et al., 2021), 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, high thermal stability that generally leads to reduced requirements for their regeneration as well as tunable CO₂ capacity (Aghaie et al., 2018; hang et al., 2012; Sarmad et al., 2017). On the other hand though, their typically 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

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capture one such property is evidently centered on the rate of reaction. To this end, imidazolium carboxylate ILs are the most prominent ones (Stevanovic et al., 2013; Tian et al., 2015). Such ILs follow a 1:2 stoichiometry when reacting with CO₂ (Cabaço et al., 2012) and their heats of reaction are in the range of -35 to -39 kJ/mol, less than half of that of MEA (Mota-Martinez et al., 2017). However, they show a high viscosity (Almeida, 2012) and decompose at temperatures higher than 100 °C (Williams et al., 2018). 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 (Chen et al., 2016; Sistla and Khanna, 2015). 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 modification in the form of support or encapsulation is recommended (Santiago et al., 2018). Similar to AA-ILs, aprotic heterocyclic ionic liquids (AHA-ILs) have shown promising properties for CO₂ capture. These include their high reaction rates, high CO₂ solubility as well as high thermal stability (Wu et al., 2019; Hong et al., 2016; Seo et al., 2014). 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 (Seo et al., 2014). Such issues may be partially alleviated by supporting or encapsulating AHA-ILs using co-solvents (Moya et al., 2018; Filion et al., 2017). A number of process simulation studies exist for assessing the performance of ILs, evaluating the cost of the overall CO₂ capture process as well as operating parameters like the regeneration demands. Oko et al. (2008) 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. This energy has been estimated at 3.6 GJ/t CO₂ by Zhai and Rubin (2014). Shiflett et al. (2010) 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 of can be as low as 1.4 GJ/t CO₂ according to de Riva et al. (2018) 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. 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 (Borhani and Wang, 2019). 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 (Sartori and Savage, 1983). However, aside from their slow kinetics, these solvents have low selectivity and promote deposition and corrosion of the equipment (Asif et al., 2018). Borhani et al. (2015) 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 amino-acid with a base group such as KOH (Song et al., 2012) or NH₃ (Yang et al., 2014). Potassium salts of taurine and glycine (Kumar et al., 2003) and sarcosine (Aronu et al., 2011) are deemed to be promising solvents for CO₂ capture. Nakjiri et al. (2018) tested numerically the absorption performance of three absorbents in a PVDF hollow fiber membrane contactor, namely potassium glycinate (PG), potassium arginate (PA)

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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 (Dave et al., 2009). Such solutions also offer the benefit of simultaneous removal of NO_x and SO_x in addition to CO₂ (Resnik and Pennline, 2013). They are however much more volatile, resulting in high solvent losses and often linked with irritations in the human body and toxicity (Zhang and Guo, 2013). Finally, the capture of CO₂ using seawater of variable salinity was studied by Li et al. (2018). 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 (Li et al., 2022). 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 media for CO₂ capture.

Table 2. Characteristics of different solvents for CO₂ capture.

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

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


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5 Solvents Evaluation

Selecting the most suitable solvent for post-combustion CO₂ capture in a maritime environment 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 the KPIs defined in Section 2.

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 technology readiness level (TRL) land-based technological applications. Process compactness can be achieved in a number of ways i.e. low density solvents or lower liquid flowrates (equivalently, high working 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. Solvent regeneration energy is strongly correlated to the overall energy penalty for integration of the process within the ship. On the downside, however, immediate applicability of phase change and IL systems is limited due to their increased complexity. Operability range characteristics of the examined solvent classes, including their selectivity to CO₂ over other gaseous components, 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. Finally, 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.

Based on the qualitative assessment of the considered solvent classes it seems that traditional solvents such as amines have the 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 towards 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, as they are still under continuous development, creating risk for usage in an environment characterized by stringent specifications like 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 is a human health hazard. 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 increased footprint and cost of capture.

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At this stage it would be premature to provide an absolute or 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, lack of real application data of solvent-based CO₂ capture in ships leads creates a subsequent experience gap which prevents the formulation of purely on-board CO₂ capture technology-based KPIs.

As each of this criteria can be associated with more than one thermodynamic and/or thermochemical properties of a given solvent,

qualitative findings of this work. Primarily, this would require an XXX which is currently not possible given the absence of application data.



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

KPI	Physical solvents	Primary amines	Secondary amines	Tertiary amines	Sterically hindered amines	Amine Blends	Phase-change solvents	Ionic Liquids	Salts	Ammonia	Seawater
Maturity	Light green	Light green	Light green	Light green	Light green	Light green	Red	Red	Light green	Light green	Red
Compactness	Yellow	Yellow	Yellow	Yellow	Yellow	Light green	Light green	Light green	Yellow	Yellow	Orange
Operability range	Light green	Light green	Light green	Light green	Orange	Light green	Yellow	Light green	Light green	Light green	Yellow
Energy penalty	Yellow	Red	Orange	Orange	Orange	Light green	Light green	Light green	Yellow	Light green	Yellow
Impurities	Orange	Light green	Light green	Light green	Light green	Light green	Light green	Light green	Light green	Light green	Light green
CO₂ product characteristics	Light green	Light green	Light green	Light green	Light green	Light green	Light green	Light green	Orange	Light green	Orange
OPEX	Light green	Orange	Orange	Light green	Light green	Orange	Orange	Orange	Light green	Light green	Light green
Other consumables	Light green	Light green	Light green	Light green	Light green	Light green	Light green	Light green	Orange	Light green	Orange
Health and safety	Yellow	Light green	Light green	Light green	Light green	Light green	Light green	Light green	Light green	Orange	Light green

(*) Color coding is a qualitative assessment of each KPI. Green: favorable, Light green: somewhat favorable, Yellow: medium, Orange: somewhat unfavorable, Red: unfavorable.



MemCCSea

Innovative membrane systems
for CO₂ capture and storage at sea

6 Conclusions and Outlook

Carbon capture and storage on-board commercial ships represents a powerful technological tool for the shipping industry to meet the very stringent GHG emission reduction requirements. Given the space and energy constraints of ships, compact membrane solvent contactor-based CO₂ capture offers several advantages for on-board installation. A critical issue, both for operating and safety reasons, is the choice of solvent. The deliverable presents an up-to-date comprehensive review of XXX. A preliminary qualitative comparative assessment has been performed based on appropriately selected KPIs pertinent to the requirements of the shipping industry. It is concluded that XXX.

Further work will have to focus on (a) more data on the performance of solvent-membrane pairs (b) on a more inclusive process-focused definition of KPIs.

The fate of captured CO₂ is not considered here.

7 References

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.

Aghaie, M.; Rezaei, N.; Zندهboudi, S. A systematic review on CO₂ capture with ionic liquids: current status and future prospects. *Renew. Sustain. Energy Rev.*, **2018**, *96*, 502-525.

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.

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.

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.

Asif, M.; Suleman, M.; Haq, I.; Jamal, S.A. Post-combustion CO₂ capture with chemical absorption and hybrid system: current status and challenges, *Greenhouse Gas. Sci. Technol.*, **2018**, *8*, 998-1031.


Balcombe, P.; Brierley, J.; Lewis, Ch.; 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.

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.



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		Version Final

Borhani, T.N.G.; Wang, M. Role of solvents in CO₂ capture processes: The review of selection and design methods. *Renew. Sust. Energ. Rev.*, **2019**, *114*, 109299.

Bouman

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.

Bruder, P.; Svendsen, H.F. Capacity and kinetics of solvents for post-combustion CO₂ capture. *Energy Procedia*, **2012**, *23*, 45-54.

Bui, M.; Adjiman, C.S.; Bardow A.; Anthony, E.J.; Boston, A.; Brown S.; et al. Carbon capture and storage (CCS): The way forward. *Energy Environ. Sci.* **2018**, *11*, 1062–176.

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.

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.

Cavaignac, R.S.; Ferreira, N.L.; Guardani, R. Techno-economic and environmental process evaluation of biogas upgrading via amine scrubbing. *Renewable Energy*, **2021**, *171*, 868-880.

Chen, E.; Zhang, Y.; Lin, Y.; Nielsen, P.; Rochelle, G. Review of recent pilot plant activities with concentrated piperazine. *Energy Procedia*, **2017**, *114*, 1110-1127.

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.

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.

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.

Damartzis, Th.; 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.


Damartzis, Th.; 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.

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.

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*, 709–15.

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.

DNV 2011

	<p style="text-align: center;">Title</p> <p style="text-align: center;">Report on membrane-based CO₂ capture technologies</p>	Deliverable number D1.2
		Version Final

DVN 2020

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, 14th International Conference on Greenhouse Gas Control Technologies, GHGT-14, **2018**, Melbourne, Australia.

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.

Foretich et al. (2021)

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.

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.

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-

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.

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.

IEA (2021) Greenhouse Gas Emissions from Energy: Overview, IEA, Paris <https://www.iea.org/reports/greenhouse-gas-emissions-from-energy-overview>.

IEA. Energy Technology Perspectives 2020 - Special Report on Carbon Capture Utilisation and Storage. Paris, France: International Energy Agency; 2020.


IEA. IEA Energy technology perspectives 2010-scenarios and strategies to 2050. Paris, France. International Energy Agency.

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.

IRENA 2021

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.

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.

	<p style="text-align: center;">Title</p> <p style="text-align: center;">Report on membrane-based CO₂ capture technologies</p>	Deliverable number D1.2
		Version Final

Kohl, A.L.; Nielsen, R.B. Alkanolamines for Hydrogen Sulfide and Carbon Dioxide Removal. In *Gas Purification* 5th ed.; Gulf Publication Company: Houston, Texas, USA, 1997; pp. 40-186.

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.

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.

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.

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.

Luo, X.; Wang, M. Study of solvent-based carbon capture for cargo ships through process modelling and simulation. *Applied Energy*, **2017**, *195*, 402-413.

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.

Malloupas & Yfantis 2021

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.

Monteiro, J.; van den Akker, J.T.; Sommer, K.; Verhoeff, C.J. CO₂ASTS – carbon capture, storage and transfer in shipping. A technical and economic feasibility study: Public Concise Report. Available Online: [200513-CO₂ASTS-Public-Concise-Report.pdf \(mariko-leer.de\)](https://www.mariko-leer.de/200513-CO2ASTS-Public-Concise-Report.pdf), (assessed on 30/3/2022).

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.


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.

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.

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.

National Energy Technology Laboratory, U.S. Department of Energy. DOE/NETL Advanced Carbon Dioxide Capture R&D Program: Technology Update. 2013.

Nwaoha, C. CO₂ Absorption: Solubility of CO₂ in 2-amino-2-methyl-1-propanol solvent promoted by Piperazine and Monoethanolamine blends, MSc Thesis, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand, 2015.

	<p style="text-align: center;">Title</p> <p style="text-align: center;">Report on membrane-based CO₂ capture technologies</p>	Deliverable number D1.2
		Version Final

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.

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.

Olajire, A.A. CO₂ capture and separation technologies for end-of pipe applications—A review. *Energy*, **2010**, *35*, 2610–2628.

Owens, W.; Buchanan, T.; DeLallo, M.; Schoff, R.; White, J. Evaluation of innovative fossil fuel power plants with CO₂ removal. 2000

Pantoleonos, 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.

Papadopoulos, A.I.; Perdomo, F.A.; Tzirakis, F.; Shavaliyeva, G.; Tsvintzelis, I.; Kazepidis, P.; Nessi, E.; Papadokonstantakis, S.; Seferlis, P.; Galindo, A.; Jackson, G.; Adjiman, C.; Molecular engineering of sustainable phase-change solvents: From digital design to scaling-up for CO₂ capture. *Chem. Eng. J.*, **2021**, *420*, 127624.

Papadopoulos, A.I.; Tzirakis, F.; Tsvintzelis, I.; Seferlis, P. Phase-change solvents and processes for post-combustion CO₂ capture: A detailed review. *Ind. Eng. Chem. Res.*, **2019**, *58*, 5088-5111.

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.

Purwasasmita, 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.

Resnik, K.P.; Pennline, H.W. Study of an ammonia-based wet scrubbing process in a continuous flow system. *Fuel*, **2013**, *105*, 184–191.


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.

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.

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

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.

Sartori, G.; Savage D.W. Sterically hindered amines for carbon dioxide removal from gases. *Ind Eng Chem Fundam*, **1983**, *22*, 239-249.

	<p style="text-align: center;">Title</p> <p style="text-align: center;">Report on membrane-based CO₂ capture technologies</p>	Deliverable number
		Version
		D1.2
		Final

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.

Shavaliyeva, G.; Kazepidis, P.; Papadopoulos, A.I.; Seferlis, P.; Papadokonstantakis, S. Environmental, health and safety assessment of post-combustion CO₂ capture processes with phase-change solvents. *Sustain. Prod. Consum.*, **2021**, *25*, 60-76.

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.

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.

Sistla, Y.S.; Khanna, A. CO₂ absorption studies in amino acid-anion based ionic liquids. *Chem. Eng. J.*, **2015**, *273*, 268-276.

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.

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.

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.

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.

Tzirakis, F.; Tzivintzelis, 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.

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.


Vaidya, P.D.; Kenig, E.Y. CO₂-alkanolamine reaction kinetics: A review of recent studies. *Chem. Eng. Technol.*, **2007**, *30*, 1467-1474.

Van den Akker, J.T. Carbon capture on-board LNG-fuelled vessels, MSc Thesis, TU Delft, 2017.

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*, eds. Karamé, I., Shaya, J., Srour. H. IntechOpen, London. 10.5772/intechopen.71443.

J. Wilcox, Carbon Capture, 1st Edition, 2012, Springer, New York, NY, USA.

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.

	<p style="text-align: center;">Title</p> <p style="text-align: center;">Report on membrane-based CO₂ capture technologies</p>	<p style="text-align: center;">Deliverable number</p> <p style="text-align: center;">D1.2</p>
		<p style="text-align: center;">Version</p> <p style="text-align: center;">Final</p>

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.

Yang, N.; Yu, H.; Xu, D.; 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.

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.

Zhang, X. Studies on Multiphase CO₂ Capture Systems. Ph.D. Thesis, TU-Dortmund, 2007.,

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.

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.

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.

The successful completion and submission of DX.X (Title of Deliverable) provides the necessary means of verification for Milestone MX (Title of Milestone).