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# The potential of carbon capture technologies for shipboard application

A review of carbon capture technologies and their feasibility for the application onboard vessels

Master's thesis in Mechanics and Maritime Sciences

Jonas Georg Havenstein Maximilian Weidenhammer

Department of Mechanics and Maritime Sciences CHALMERS UNIVERSITY OF TECHNOLOGY Gothenburg, Sweden 2021

MASTER'S THESIS 2021

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Supervisor: Julia Hansson, IVL Swedish Environmental Research Institute Co-Supervisor: Maria Grahn, Chalmers University of Technology Examiner: Selma Brynolf, Chalmers University of Technology

Master's Thesis 2021 Department of Mechanics and Maritime Sciences Chalmers University of Technology SE-412 96 Gothenburg Telephone + 46 (0)31-772 1000

Cover: Schematic drawing of a post-combustion carbon capture process using aqueous ammonia as solvent for absorption of  $CO_2$ . The system has been proposed by Awoyomi et al. (2020) for carbon capture onboard of  $CO_2$ -carriers. For further information refer to section 4.1.1.6.

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## Abstract

The IMO's Initial strategy on reduction of GHG emissions from ships defined the goal to reduce the total emissions from international shipping by 50 % in 2050, compared to the emissions of 2008. The majority of ships being built today and up to 2030 are expected to be equipped with combustion engines running on fossil fuels. The fact that vessels have an average scrappage age of 28 years, further highlights the problematical long-time dependence of shipping on fossil fuels. Therefore, carbon capture technology is considered as an option allowing the combustion of fossil fuels and still being able to reduce the emission of GHGs. This thesis is taking a top-down approach to identify carbon capture technologies which have been researched until today. The conducted literature review identifies several post- and pre-combustion capture systems as well as oxyfuel combustion as technologies to capture CO<sub>2</sub> from fossil fuel combustion exhausts. Based on the knowledge retrieved from literature and expert interviews, a broad spectrum of carbon capture technologies is presented, including information on the process setup, current applications, costs, space requirements as well as specific advantages and drawbacks of each technology. Furthermore, the research conducted for the application of the identified technologies onboard has been reviewed and the findings are presented in a summarised form. To decide which of the identified technologies is the most promising for the application onboard, a comparative assessment is conducted, with specific regards to the constraints determined by the particulars of the onboard environment. The technology found to perform best in newbuilding as well as retrofit applications, is post-combustion absorption with aqueous ammonia as solvent. Although post-combustion carbon capture technology in general is found to be feasible for all ships, implications on the transport capacity and economy-of-scale factors show, that carbon capture technology might be more feasible for larger vessels.

Keywords: maritime carbon capture, post-combustion carbon capture, onboard, ship, assessment, ICE

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## Abbreviations

| A3C    | Advanced Cryogenic Carbon Capture                            |
|--------|--|
| AIS    | Automatic Identification System                              |
| ASU    | Air Separation Unit  |
| BECCS  | Bioenergy with Carbon Capture and Storage                    |
| CAPEX  | Capital Expenses   |
| CC     | Carbon Capture   |
| CCC    | Cryogenic Carbon Capture                                     |
| CCS    | Carbon Capture and Storage                                   |
| CCU    | Carbon Capture and Utilisation                               |
| CFG    | Compressed Flue Gas  |
| CRI    | Carbon Recycling International                               |
| DNV    | Det Norske Veritas   |
| DWT    | Deadweight Tonnage   |
| ECL    | External Cooling Loop  |
| EEDI   | Energy Efficiency Design Index                               |
| EEOI   | Energy Efficiency Operational Indicator                      |
| e-fuel | Electro Fuel   |
| EGR    | Exhaust Gas Recycling  |
| EU     | European Union   |
| EU MRV | European Union Monitoring, Reporting and Verification scheme |
| GHG    | Greenhouse Gas   |
| GM     | Metacentric Height   |
| HFO    | Heavy Fuel Oil   |
| ICE    | Internal Combustion Engine                                   |
| ICRC   | Internal Combustion Rankine Cycle                            |
| IGCC   | Integrated coal Gasification Combined Cycle                  |
| IMO    | International Maritime Organization                          |
| IPCC   | Intergovernmental Panel on Climate Change                    |
| LCCC   | Levelized Costs of Carbon Captured                           |
| LCOE   | Levelized Costs Of Electricity                               |
| LNG    | Liquid Natural Gas   |
| MC     | Membrane Contactor   |
| MCDA   | Multiple-Criteria Decision Analysis                          |
| MGO    | Marine Gas Oil   |
| MGS    | Membrane Gas Separation                                      |
| MOF    | Metal Organic Framework                                      |
| OPEX   | Operational Expenses   |
| PM     | Particulate Matter   |
| PSA    | Pressure-Swing-Adsorption                                    |
| SDG    | Sustainable Development Goal                                 |
| SEEMP  | Ship Energy Efficiency Management Plan                       |
| TEA    | Techno-Economic Assessment                                   |
| TRL    | Technology Readiness Level                                   |
| TSA    | Temperature-Swing-Adsorption                                 |

| UN     | United Nations  |
|--------|---|
| UNCTAD | United Nations Conference on Trade and Development    |
| UNFCCC | United Nations Framework Convention on Climate Change |
| US     | United States   |
| VSA    | Vacuum-Swing-Adsorption                               |
| WGS    | Water Gas Shift reactor                               |

## Chemical formulae

| CaCO <sub>3</sub> | Calcium Carbonate   |
|-------------------|---------------------|
| CaO               | Calcium Oxide       |
| $CH_4$            | Methane             |
| $\mathrm{CO}_2$   | Carbon Dioxide      |
| F-Gases           | Fluorinated Gases   |
| $H_2$             | Hydrogen            |
| HCl               | Muriatic Acid       |
| Hg                | Mercury             |
| $K_2CO_3$         | Potassium Carbonate |
| MDEA              | Monodiethanolamine  |
| MEA               | Monoethanolamine    |
| $N_2$             | Nitrogen            |
| $N_2O$            | Nitrous Oxide       |
| NaOH              | Sodium Hydroxide    |
| $\mathrm{NH}_3$   | Ammonia             |
| $NO_2$            | Nitrogen Dioxide    |
| NO <sub>x</sub>   | Nitrous Oxides      |
| $O_2$             | Oxygen              |
| ΡZ                | Piperazine          |
| $SO_2$            | Sulphur Dioxide     |
| $SO_x$            | Sulphurous Oxides   |
|                   |                     |

## 1 Introduction

In 2018, the International Maritime Organisation (IMO) adopted the strategy on the reduction of greenhouse gas (GHG) emissions from international shipping by 50 % in 2050 in comparison to the 2008 emissions (IMO, 2019b). By this, the IMO is contributing to the goals of the Paris Agreement as well as the United Nations Sustainable Development Goal 13 "Climate Action". To reduce the total GHG emissions of the growing shipping sector, a wide range of actions is required.

The operation of vessels has the potential to reduce the GHG emissions by measures such as voyage optimisation, reduced operational speed or an improved energy management (Bouman et al., 2017). Operational measures can generally be applied immediately to the existing fleet without retrofitting or extensive technical changes. The financial risk for operational measures is limited, since the necessary investments are small in comparison to technical measures (Bullock et al., 2020). However, the potential impact of operational measures is varying among different ship types and is not capable to achieve the 2050 target set out by the IMO (Bullock et al., 2020). To meet this target, technical solutions for existing ships and planned newbuildings are required. The Energy Efficiency Design Index (EEDI) is regulating the requirements on energy efficiency of newbuildings. Since vessels are long-time assets, having an expected lifetime of about 28 years, upgrading the existing fleet with retrofit applications is essential to reduce their emissions, to be able to reach the goal of the Paris Agreement (Bullock et al., 2020). Besides, an improved hull and propulsion design, the biggest potential for reducing the carbon intensity of shipping is connected to the use of alternative energy sources.

Bouman et al. (2017) see a reduction potential of 25 to 84 % of carbon dioxide (CO<sub>2</sub>) emissions throughout the lifecycle, when conventional fuels are replaced with biofuels. The IMO (2019) is evaluating hydrogen (H<sub>2</sub>) and other synthetic fuels as so-called zero-carbon fuels, i.e., the full lifecycle emissions are close to zero. The environmental performance of alternative fuels is highly dependent on the emissions during the production, also considering other emissions apart from CO<sub>2</sub> (Bullock et al., 2020). Nevertheless, immediate action is required and alternative fuels and propulsion technologies, e.g. the production of H<sub>2</sub> and its use in fuel cells, are not yet introduced in large-scale (Hansson et al., 2019). Although, biofuels are already commercially available, they are not cost-competitive compared to fossil fuels (Hansson et al., 2019). Another problem emerging when considering biofuels as fuel for the global fleet, lies within the origin of the fuel (Rodionova et al., 2017). To grow energy crops, agricultural areas are used, potentially impacting the production of groceries. Furthermore, even if shipping would be forced by regulations to convert to renewable fuels immediately, the production capacity of such fuels cannot supply the demanded amounts thus far (Hansson et al., 2019).

These problems emphasise the current dependence of the marine shipping sector on fossil fuels as main energy carrier. Therefore, it is interesting to also assess other solutions for the reduction of the carbon intensity of shipping. Instead of neutralising the emitted carbon emissions e.g., by the use of biofuels and other potentially zero-carbon fuels, the exhaust gases can be filtered and carbon components captured. Such aftertreatment technology is called *carbon capture (CC)*.

CC technologies are already applied in production processes for clean gases such as oxygen (Wilcox, 2012). Within these processes,  $CO_2$  is absorbed and afterwards released to the atmosphere or stored for further use. The potential of carbon capture to filter exhaust gases from industrial applications is currently explored in trials e.g., at the Preem refinery in Lysekil, Sweden (Chalmers University of Technology, 2020). The trial in Lysekil is including the long-term storage of the captured  $CO_2$  in underground reservoirs in Norway and thereby also explores ways of

transporting  $CO_2$ . Besides the storage in underground, research is also addressing the possibility to store captured  $CO_2$  in deep sea areas (House et al., 2006). When such technology is applied to capture  $CO_2$  resulting from the combustion of biofuels, negative lifecycle emissions can be achieved, i.e., a reduction of atmospheric  $CO_2$  is reached.

An alternative to carbon capture and storage (CCS) is carbon capture and utilisation (CCU). The captured  $CO_2$  can be utilised as a commodity within industrial processes, e.g., to produce synthetic fuel. By combining H<sub>2</sub> with  $CO_2$ , so-called electro-fuels (e-fuels) can be synthesised. Using renewable energy sources for the hydrolysis of H<sub>2</sub> allows the produced fuel to be climate neutral (Cuéllar-Franca & Azapagic, 2015). Capture and reuse of  $CO_2$  resulting from the combustion of e-fuels allows to develop a circular economy for carbon. This is intended by the HyMethShip project as well, which is utilising methanol as e-fuel (Malmgren et al., 2020). Methanol is physically stable and can be stored and transported easily. It is already used as fuel in shipping. The infrastructure and technology for distribution and combustion of methanol is already relatively mature, although the biggest part is still synthesised from fossil sources, such as coal (Hansson et al., 2019).

Whereas the application of CCS technology in industrial processes ashore is already in trial, the feasibility of such technology for onboard applications is just discussed in theory. The shipping company K-Line has just formed an alliance with Mitsubishi Shipbuilding for the installation of a small-scale demonstration plant for  $CO_2$  capture onboard, in order to test the operation and performance of the plant under marine conditions (Ovcina, 2020).

While space and weight are less important in shoreside applications, these factors are of high interest onboard (Mac Dowell & Shah, 2012). The ships value is mainly defined by its ability to transport a certain amount of cargo. Especially the space needed for storage of the captured  $CO_2$  onboard, might reduce the ships transport capabilities and thereby its economic value. Due to the non-existence of CC technology onboard vessels, there is no infrastructure in ports being able to receive captured  $CO_2$  from vessels (Gibbins & Chalmers, 2008).

As mentioned before, research until today mainly focused on the application of CC in shoreside applications. However, the interest in economically and technically feasible solutions for reducing the  $CO_2$  emissions from shipping, is drawing the interest of research towards the application of CC technology onboard. CC could be a less costly option for the decarbonisation of shipping in comparison to alternative fuels and drive technologies, e.g., hydrogen converted in fuel cells. Moreover, it might be easier to integrate certain CC technologies into existing onboard installations in comparison to alternative drive technologies, i.e., CC may be a feasible solution to retrofit for the reduction of carbon intensity of existing vessels.

Whereas current research mainly focusses on specific technologies, this thesis is applying a topdown approach. A wide spectrum of currently researched CC technologies is identified and their feasibility for the application onboard vessels is assessed.

### 1.1 Aim and research questions

The aim of this thesis is to collect knowledge on CC technologies and evaluate their potential for the application onboard vessels. Linked to the objectives, the following **research questions** are formulated:

- Which technologies are most promising for CC onboard vessels in combination with internal combustion engines?
- Which limitations, constraints and criteria are important for the applicability of CC technology onboard vessels?

Since this thesis is taking a top-down approach, data is collected to identify general technology pathways for CC. This is including technologies that are already in commercial use, as well as technologies which are still under development. Furthermore, initiatives for the development of onboard CC applications are mapped out. Besides the technological setup and general operating principle of each CC method, the thesis aims to present data on costs, space and energy requirements, maturity level as well as specific advantages and disadvantages of each CC technology.

Based on the gathered data, a comparative assessment of the identified CC technologies is performed, with specific focus on their use onboard merchant ships. In the first stage the analysis is assessing, which of the identified technologies are feasible for onboard operation in general. The second stage is discussing, which of the feasible technologies is most promising for the application onboard. The technology evaluated as most promising, is the best alternative in regards of the identified constraints of the onboard appliance. Since retrofitting of such technology outlines additional criteria, the assessment evaluates newbuilding and retrofit applications separately. Thereby, the scope is limited to technologies being able to run in combination with internal combustion engines (ICEs), since it is probable that the majority of ships will be built with such propulsion technology, for at least one more decade (Bullock et al., 2020).

The outcome of the assessment is discussed critically, considering the feasibility of CC for different ship types and the maturity level of the identified CC technologies. Moreover, it is discussed whether the technology deemed best in the assessment, is also the one being most probable to be applied in merchant shipping.

## 1.2 Limitations

Apart from the allowed time frame for the thesis work, the authors have been limited by the data available in the literature and the data provided by interviewed stakeholders, to ensure a sufficient basis for the comparison of potential CC techniques. The objectives of the thesis and the included assessment have been limited as well. The thesis is focussing on CC technologies itself, alternatives for storage and utilisation of  $CO_2$  are excluded from the scope. The impact of CC technology on the environment and climate is addressed in the background section but is not considered as criterion in the assessment, since it is strongly dependent on how the captured  $CO_2$  is utilised or stored afterwards. Further, social factors (e.g., acceptance of CCS in society) are not taken into account.

#### 1.3 Structure of this thesis

To allow for an easy access of relevant information for the reader, the following paragraphs give a short overview of the thesis' structure and the comprised content of each chapter in terms of the approach and the work carried out.

In the background chapter, the shipping industries' contribution to the global  $CO_2$  emissions and the related climate impact are addressed. Further included in this chapter are information on the storage of the captured carbon and possibilities to make use of the same. Policies addressing the effect of carbon emissions on the climate and thereby urging for the need to reduce current and future emissions are described in the background as well. At last, a reasoning for the need to reduce the emissions from existing vessels rather than to purely concentrate on newbuild ships is presented.

The third chapter is describing the methodology on how the research is conducted and the procedure of gathering relevant data in order to answer the research questions of this thesis. Main sources in the knowledge-acquisition are the literature review and the expert interviews carried out by the authors. Search terms and prepared questions of interest are stated within the subchapters. Moreover, the structure of the comparative assessment of the CC technologies is explained.

Chapter 4 is presenting the capture technologies identified by the authors. The chapter is divided into post-, pre- and oxyfuel combustion, each including the identified CC technologies. All technologies are reviewed for a variety of aspects, including the state-of-the-art and maturity level. As a basis for comparison the post-combustion absorption technology with monoethanolamine (MEA) is used as benchmark process. The data presented in this chapter are the base for the comparative assessment in chapter 5.

The assessment in the fifth chapter is executed stagewise. The first stage is assessing the feasibility of the shipboard application of the different technologies, of which the TOP 3 candidates are further examined in the second stage of the assessment. A closer evaluation is done in stage 2.a and 2.b, where the most promising technology for newbuildings or retrofitting applications, respectively, is assessed.

Chapter 6 is critically discussing the outcome of the assessment and addresses aspects which need to be considered for the shipboard application of the capture technology deemed most promising. Alternatives and potential improvements for the developed assessment method are critically discussed. Furthermore, the feasibility of CC onboard vessels is debated and an outlook towards upcoming technologies and identified knowledge gaps is given.

The results of the research conducted in this thesis are presented in chapter 7, briefly answering the research questions and drawing conclusions from the findings. Based on the results of the conducted research, a sustainable way for decarbonising shipping is proposed.

## 2 Background

To understand the need of carbon abatement technologies for the marine transport sector, one needs to understand the contribution of this industry to the global  $CO_2$  emissions. This chapter is providing background knowledge on the global  $CO_2$  emissions and the share contributed by international shipping. CC is one of the possible pathways to reduce the carbon emissions from shipping, but CC itself is not reducing the climate impact of shipping. It depends on how the captured  $CO_2$  is further stored or utilised. Different approaches of the handling of captured emissions are presented, including ongoing incentives and prospects. Further, current regulatory measures for the reduction of present and future GHG emissions, in order to reduce the impact of the climate change are introduced, specifically focussing on internationally trading vessels. As previously mentioned, vessels are long time assets and thereby the retrofitting of abatement technologies to vessels becomes necessary to meet the goals of the Paris Agreement.

#### 2.1 CO<sub>2</sub> emissions from shipping

Since the 18th century, the beginning of industrialisation, humanity is utilising fossil fuels, to produce energy carriers in large-scale. Driven by the technical evolution and the inexpensive energy generated from fossil fuels, the worldwide economies and population grew, causing an even higher demand for energy (Ciais et al., 2013). The reliance on fossil fuels such as coal, petroleum products and natural gas, caused a dependence of the world's economy on these (Wilcox, 2012). Nowadays, the awareness for the negative effects of fossil fuel combustion is growing more and more, creating the need for abatement technologies to reduce the carbon intensity of the economy (T. M. Lee et al., 2015).

The main reason for the increase of the global mean temperature, also known as global warming, is the growing concentration of GHGs within the atmosphere (WMO, 2019). The major impact is generated by CO<sub>2</sub>, methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O) and fluorinated gases (F-gases) (WMO, 2019). Compared to the preindustrial era, the concentration of CO<sub>2</sub> within the atmosphere has increased by 40 % in 2011. Within the same interval, the concentration of CH<sub>4</sub> has increased by 150 % and the level of N<sub>2</sub>O respectively by 20 % (Ciais et al., 2013). Out of these GHGs, CO<sub>2</sub> is having by far the largest impact on climate, even though the other gases have a higher global warming potential (US EPA, 2020). It is the pure amount of CO<sub>2</sub> emitted (37,5 Gt CO<sub>2</sub> in relation to 14,3 Gt CH<sub>4</sub>, N<sub>2</sub>O and F-gases in 2018 (UNCTAD, 2020)) in combination with the persistence of CO<sub>2</sub> in the atmosphere (Solomon et al., 2009).

While other GHGs are depleted by chemical processes,  $CO_2$  persists over time within the atmosphere (Solomon et al., 2009). Considering the terrestrial carbon uptake, the average surface temperature on Earth is estimated to increase by 1,1 ± 0,5 °C for every 1.000 Pg (1 Pg = 10<sup>15</sup> g) carbon emitted to the atmosphere (Goodwin et al., 2015). The study of Solomon et al. (2009) indicates, that the increased concentration of  $CO_2$  has led to changes in climate, being mostly irreversible for thousand years, even after a total elimination of carbon emissions. After peaking the concentration of  $CO_2$  within the atmosphere, the level will not drop constantly, rather it will stabilise at about "40 % of the peak concentration enhancement over preindustrial values" (Solomon et al., 2009). This phenomenon results from the equilibrium of  $CO_2$  is increasing within the atmosphere, the locean is taking up gas and thereby acts as a buffer. Conversely, the ocean is releasing  $CO_2$  when the concentration within the atmosphere is sinking (Solomon et al., 2009).

The buffering function of the ocean in connection with the long-lasting biochemical processes to store emitted carbon (further described in appendix A 1), are leading to a relatively stable CO<sub>2</sub> level within the atmosphere (Solomon et al., 2009). This also implies that the global mean temperature is not going to sink significantly and remains approximately constant at  $\pm 0.5$  °C of the peak temperature. Since the ocean is not only acting as a buffer for CO<sub>2</sub> but also as a buffer for heat, the increased surface temperature will lead to a further heating-up of the ocean and thereby to an expansion of the water. Besides a rising sea level and the atmospheric warming, the climate change will also impact precipitation amounts and locations (Solomon et al., 2009).

Including the emissions caused by change of land-use, which are hard to calculate, the total anthropogenic  $CO_2$  emissions for 2018 are estimated to be 37,5 Gt (UNCTAD, 2020). Out of these, 36,3 Gt are resulting from the combustion of fossil fuels: 15,82 Gt from coal and coke, 7,61 Gt from combustion of natural gas and 12,87 Gt from consumption of petroleum and other liquid fuels (US EIA, 2020).

The latest IMO GHG study, published in 2020, finds that the GHG emissions of total shipping, expressed in CO<sub>2</sub> equivalents, have increased from 977 Mt in 2012 to 1.076 Mt in 2018, which is an increase of 9,6 % (Faber et al., 2020). The CO<sub>2</sub> emissions of total shipping have increased by 9,3 % from 962 Mt to 1.056 Mt within the same period. Taking 36.573 Mt of total anthropogenic CO<sub>2</sub> emissions in 2018 as a basis, the study concludes that the share of shipping in global anthropogenic emissions did rise from 2,76 % in 2012 to 2,89 % in 2018.

To separate the emissions from international and national transport by sea, the *Fourth IMO GHG Study 2020* is applying a different method than the third GHG study (Faber et al., 2020). The preceding study did distinguish between international and domestic transport by assuming that certain ship types are trading only domestic and others merely international (vessel-based approach). The advances in AIS data utilisation enabled the latest study to allocate the emissions of each voyage of a vessel to be either domestic or international (voyage-based approach) (Faber et al., 2020).

According to this *voyage-based approach*, the CO<sub>2</sub> emissions from international shipping did only increase slightly from 701 Mt (2012) to 740 Mt (2018), which is resulting in a constant share of about 2 % in global CO<sub>2</sub> emissions. These emissions are accounting for 98 % of the climate impact of international shipping and are mainly caused by bulk carriers, container vessels and oil tankers (Faber et al., 2020).

Furthermore, the study is evaluating the carbon intensity of international shipping. The EEOI, which expresses the CO<sub>2</sub> emitted per ton-mile of transport work in grams of CO<sub>2</sub> emitted per ton of cargo and nautical mile transported ( $g_{CO2}/t/nm$ ), has decreased by 29,7 % since 2008 from 17,10 to 11,67 ( $g_{CO2}/t/nm$ ) (Faber et al., 2020). This development is mainly driven by the increasing ship sizes and the reduction of operational speeds, so called slow steaming. The study highlights that most of the achievements have been gained before 2015 and that since then only minor improvements have been seen.

It has to be seen critically, that the reduction in operational speed was driven by the need to reduce productivity of the world's merchant fleet, due to an overtonnaged market, rather than by the aim to reduce emissions (Faber et al., 2020). The economic pressure forced shipowners to lower the transport work per unit of capacity, to fit the demand on the market and to save fuel costs. The savings in emissions and improvements in carbon intensity could be reversed, when the market is demanding for a higher productivity, i.e., shipowners decide to raise the operational speed again.

Herein lies an increased risk for a rapid growth of emissions, should these latent emissions materialise (Faber et al., 2020).

The demand for shipping is a derived demand, i.e., it is closely coupled to the global economic development. The *Fourth IMO GHG study 2020* does predict the emissions from international shipping to be within the range from 90 up to 130 % of 2008 emissions by 2050. Depending on the market development and dynamics of the future industry, the emissions might be higher or lower (Faber et al., 2020). Even though, the ongoing COVID-19 crisis has caused emissions to decrease significantly in 2020 (also expected for 2021), the impact of this decrease is projected to be between 1 - 2 % in the future. This lies within the uncertainty range of the study and thereby does not cause a significant impact (Faber et al., 2020).

#### 2.2 Storage versus utilisation of captured carbon

Since the dependence of our civilisation on energy generation from fossil fuel makes it illusionistic to end carbon emissions in short term, technical solutions are developed to reduce the emission of  $CO_2$ . One of these solutions is CC. The different techniques available for CC are a central part of this thesis and are therefore presented separately in chapter 4. This section is going to give a brief introduction into different concepts for the storage and the usage of captured  $CO_2$ .

The impact of CC on the global carbon cycle is depending on the option chosen for further processing of the captured carbon. Capturing carbon emissions from large point sources and transporting them to safe geological storage, rather than releasing the emissions into the atmosphere, is known as **carbon capture and storage (CCS)** (Gibbins & Chalmers, 2008). Doing so, the "slow" biochemical processes of removing carbon from the fast domain and returning it for permanent storage into the slow domain, are skipped by the employment of technology (see Appendix *A 1 The global carbon cycle* for description of the global carbon cycle). In theory, this allows the usage of fossil fuels without the emissions cannot be avoided completely due to the leakage of CO<sub>2</sub> through the capturing process as well as leakages from the reservoirs used for storage (Gibbins & Chalmers, 2008).

The captured  $CO_2$  can be stored within the ground, the ocean or as a mineral carbonate (Cuéllar-Franca & Azapagic, 2015). The storage within the ground, known as geological storage, is relying on the injection of  $CO_2$  into reservoirs in more than 1 km depth (Gibbins & Chalmers, 2008). Depleted oil and gas reservoirs as well as deep saline aquifers are geological formations that allow the injection of  $CO_2$  for permanent storage (Cuéllar-Franca & Azapagic, 2015). Either the injected carbon is trapped inside the reservoir by an impermeable layer on top of the reservoir, dissolved by fluids or absorbed by organic matter (IPCC, 2005). Depending on the temperature and pressure of the reservoir,  $CO_2$  can be stored as compressed gas or in liquid phase. The high pressure within the reservoirs allows densities of 500 kg/m<sup>3</sup> CO<sub>2</sub> (Gibbins & Chalmers, 2008).

The storage within geological formations appears to be the most promising approach, due to the experience gained by the oil and gas industry (Gibbins & Chalmers, 2008). Existing drilling and injection techniques can be adapted. The industry has gained a good understanding of the characteristics and behaviour of depleted gas and oil reservoirs. The storage within deep saline aquifers is another promising approach, having an estimated capacity of 700-900 Gt of  $CO_2$ . Both reservoir types are already used within commercial applications: The Sleipner and the Snøhvit project in Norway are operating in deep saline aquifers (Cuéllar-Franca & Azapagic, 2015). The

Weyburn-Midale in Canada, the In Salah in Algeria and the Salt Creek project in the USA are utilising depleted oil and gas reservoirs for the storage of CO<sub>2</sub>.

Besides these commercial-scale applications, there are several other CCS projects in the pilot phase around the world. This also applies for the storage of  $CO_2$  within deep-sea sediments, which is expected to have immense capacity but has never been tested in large-scale (Cuéllar-Franca & Azapagic, 2015). In their study, House et al. (2006) examine the potential and requirements for the injection of  $CO_2$  into deep-sea sediments. They see the biggest advantage within the high pressure and low temperature of the storage. When injected into deep-sea sediments at a water depth of more than 3.000 m and a few hundred meters into sediments, the  $CO_2$  stays liquid and is denser than the overlying layer of water. Besides the overlying layer of less dense liquid, the formation of  $CO_2$  hydrates is expected to serve as a second cap (House et al., 2006).

The main concern connected to CCS are the consequences for the local environment, in case a leakage is releasing a concentrated  $CO_2$  stream (Cuéllar-Franca & Azapagic, 2015). For a better evaluation of connected risks and the development of strategies for monitoring of storage sites, knowledge from real-life applications is needed (Gibbins & Chalmers, 2008). The risk for leakage of  $CO_2$  does not exist when mineral carbonation is applied for the storage of  $CO_2$ . Going beyond the pure storage of carbon, the carbonates formed by the reaction of metal and calcium oxides with  $CO_2$ , can be utilised within the construction industry.

Technologies that combine CC with processes for further usage of the  $CO_2$  in industry applications are known as **carbon capture and utilisation (CCU)** (Philbin, 2020). CCU technologies have the potential to develop a sustainable circular economy solution for carbon, by reusing carbon and thereby reducing the amount of fossil carbon extracted. In relation to the impact on the global carbon cycle, this would mean a reduction of the transfer of carbon from the slow to the fast domain (Ciais et al., 2013).

Within some industries,  $CO_2$  is utilised directly. It is commonly used as carbonating agent in the beverage industry, as packing gas and as intermediate in chemical processes (Cuéllar-Franca & Azapagic, 2015; Wilcox, 2012). However, these processes demand a high purity of the gas, which is limiting the sources to waste streams with a high purity, such as  $CO_2$  from the production of ammonia (Cuéllar-Franca & Azapagic, 2015; IPCC, 2005). Furthermore, the  $CO_2$  utilised in such a way is often released into the atmosphere at a later point, which makes them irrelevant as a mitigation measure for climate change.

Direct utilisation of  $CO_2$  is also applied within the oil industry. For enhanced oil recovery from an oil field, a mixture of different agents, including  $CO_2$ , is injected into the oil reservoir to remove the oil trapped in the rocks (Cuéllar-Franca & Azapagic, 2015). This technology is already applied for 40 years in several oil-producing countries but for economic and availability reasons mainly  $CO_2$  from natural sources, such as below-surface  $CO_2$  reservoirs, is used. Moreover, the biggest part of the injected  $CO_2$  is returning to the surface again, well mixed with the extracted crude oil. Even though effort is made to recycle the  $CO_2$  for injection, some of it is released to the atmosphere. Taking the climate change into account,  $CO_2$  from natural sources could be replaced by  $CO_2$  captured from anthropogenic sources. It is further possible, to increase the amount of injected  $CO_2$  remaining within the reservoir, similar to geological storage as described before (Cuéllar-Franca & Azapagic, 2015).

The conversion of  $CO_2$  into chemicals and fuels is another field for the utilisation of  $CO_2$ . As an example, together with their industry partners, the German company Covestro AG developed a

precursor for plastic production, reducing the need for fossil resources by up to 20 %, by utilising  $CO_2$  instead (Covesto AG, 2020). The precursor cardyon® is used to produce foam material within the automotive industry, for mattresses as well as for clothing and shoes. Currently, research is conducted to develop further applications for the use of the precursor generated from  $CO_2$  as a resource (Covesto AG, 2020).

Generating fuel from captured  $CO_2$  is often evaluated as unsustainable, since the lifetime of fuels is generally quite short (about 6 months), i.e., the carbon is locked-in merely for a short period, before it is released into the atmosphere (Cuéllar-Franca & Azapagic, 2015). Nevertheless, if renewable energy is used for the energy intensive conversion of  $CO_2$  into fuel, the production and combustion of this fuel can still lead to reduced emissions, since it can be considered to replace the use of fossil fuels.

Utilising  $CO_2$  as feedstock within the Fischer-Tropsch process, a wide variety of renewable fuels can be generated by controlling the process parameters (Wilcox, 2012). So-called power-to-liquid processes are converting electricity from renewable sources into liquid fuel, indirectly allowing the use of renewable electricity in aviation, marine and road transport (Sunfire GmbH, 2020). The renewable liquid fuels can be stored, transported and utilised by existing infrastructure. Another advantage of such e-fuels is seen within their purity. Fuels refined from fossil sources contain impurities like sulphur and aromatic components, which are avoided in the Fischer-Tropsch process, by using pure feedstocks (Sunfire GmbH, 2020). In 2017, Sunfire successfully tested their pilot plant within an industrial-scale endurance test (Sunfire GmbH, 2017) and is currently contributing with their technology to the world's first industrial-size demonstration plant of the power-to-liquid process in the Norsk e-Fuel project (Sunfire GmbH, 2020). The Norsk e-Fuel plant is built in Herøya and is planned to deliver 10 million litres of renewable fuel annually from 2023 on. It will utilise renewable energy from Norway's hydropower plants and  $CO_2$  from directair-capture (Norsk e-Fuel AS, 2020).

Another pathway of the power-to-liquid process is the production of methanol from captured  $CO_2$ . The Icelandic company Carbon Recycling International (CRI) is claiming to be the world leader in power to methanol technology and the only company being able to provide such technology for industrial-scale applications (CRI, 2021a). The renewable methanol is produced from  $CO_2$  captured from industrial exhausts,  $H_2$  generated by electrolysis and renewable electricity. The generated methanol can be used as a fuel or as a chemical component in production processes. Currently, three plants are in operation (Iceland, Germany & Sweden) and one more is planned to be commissioned in 2021 in China. The current plants capture  $CO_2$  from the exhaust of power plants (Iceland & Germany), steel production (Sweden) and coke oven gas production (China) (CRI, 2021b).

Besides these examples of production processes for renewable fuels from captured carbon, there are a few studies focussing on the development of a circular economy for carbon. The carbon contained within the fuel synthetised from  $CO_2$  is captured again and recycled to produce new fuel. The HyMethShip concept is an example for such a concept. Within this concept, methanol is used as a safe way to store and transport H<sub>2</sub> (Malmgren et al., 2020). Furthermore, the energy density of methanol is much higher than the one of pure H<sub>2</sub>. For energy generation the methanol is split, the carbon is captured and the H<sub>2</sub> is combusted (Malmgren et al., 2020).

Since the concentration of CO<sub>2</sub> within the atmosphere is significantly lower (about 0,04 vol % in 2019 (Lindsey, 2020)) than within the exhaust of industrial processes (range from 3 - 100 vol % (Wilcox, 2012)), current methods are focussing on the removal of CO<sub>2</sub> from industrial emissions.

However, research is conducted within the capture of carbon from biomass, such as algae and energy crops like maize (Chum et al., 2011; Cuéllar-Franca & Azapagic, 2015; Hansson et al., 2019). The combination of bio-energy with carbon capture and storage (BECCS) is able to remove  $CO_2$  from the atmosphere and thereby makes it a negative emission technology (Global CCS Institute, 2019). Besides several demonstration and pilot plants, the Illinois Industrial Carbon Capture and Storage facility is the only large-scale application producing ethanol from biomass and storing  $CO_2$  captured during the process (Global CCS Institute, 2019).

#### 2.3 Policy background of carbon capture

The global economy is, to a fair extent, dependent on the maritime transport sector, since about 80 % of the global trade volume is shipped by sea (IMO, 2019b). A review by the United Nations Conference on Trade and Development (UNCTAD) in 2018 found, that the international trade on seaways increased continuously in the last decades (UNCTAD, 2018). As a part of the United Nations (UN), the IMO has the obligation to ensure clean and sustainable shipping. This chapter is showing that it is inevitable for the shipping industry to adjust to governing and stricter regulations. Nevertheless, a reduction below today's emission level may not be enough, i.e., an interaction of emission reduction and capturing is required, to minimise the GHG emissions in the long-term. As aforementioned, technologies to capture the carbon emissions from the industry do already exist in land-based applications. However, in comparison to the non-abatement alternative, the investment into an abatement technology and the operational expenses of such make CC uneconomic for the owner/investor. Without legal requirements and incentives to promote the appliance of CC, the wide use of this technology is improbable (Gibbins & Chalmers, 2008).

About ten years ago, in 2011, the IMO introduced a new, legally binding, resolution to MARPOL Annex VI, the MEPC.203(62). Within this resolution, "Regulations on energy efficiency for ships" are addressed (IMO, 2018a). The regulations comprise technical as well as operational measures regarding the ships' energy efficiency and design. One of these regulating amendments is referred to as the Energy Efficiency Design Index (EEDI), which is valid for new-build vessels of 400 GT and above. The EEDI is not legislating the kind of technologies to be used in order to meet the requirements. This enables shipowners to use preferred technologies within their fleets, as long as the requirements of the EEDI are met (IMO, 2018a). The second amendment is known as the Ship Energy Efficiency Management Plan (SEEMP) and is, contrary to the EEDI, applicable to all vessels of 400 GT and above. Both regulations went into force in January 2013. The SEEMP does not implicitly require physical alterations on the ship, rather its purpose is to "improve the energy efficiency of existing ships against business-as-usual operations, in a cost-effective manner and also provides an approach for monitoring ship and fleet efficiency performance over time" (IMO, 2018a). While the SEEMP is implying immediate enhancements towards a reduction of GHG emissions of ships, the visible improvements of the EEDI will take longer, since the adoption of new technologies to the shipowners' fleets will require time. A study by Lloyds Register and DNV predicted, that a successful implementation of the EEDI and SEEMP would lead to a carbon emission reduction of approximately 3,6 % by 2050, in comparison to the emissions of 2012 (IMO, 2018a).

To combat the emissions of GHGs and the related climate impacts, the UN as well as the European Union (EU) have formulated their own goals and targets. The overall long-term goal of both federations is to achieve a total decarbonisation of the shipping sector. In the "2030 climate and energy framework" of the EU, waypoints to be achieved on this pathway are defined. A reduction

of the GHG emissions of 40 % by 2030 and 60 % by 2040, in comparison to the 1990's level, is intended (Joung et al., 2020).

The UN, however, included their perspective of encountering the GHG emissions when they introduced their "17 Sustainable Development Goals (SDGs)" back in 2015, as a part of their "Agenda 2030". At least three of the SDGs are stating a clear point towards emission-related issues:

- SDG7 (namely "Affordable & Clean Energy") in target 7.a: amongst others, by 2030, to enhance energy efficiency and to promote investment in energy infrastructure and clean energy technology (UN, 2021c);
- SDG11 (namely "Sustainable Cities and Communities") in target 11.6: amongst others, to reduce the environmental impact of cities and to improve air quality (UN, 2021a); and
- SDG13 (namely "*Climate Action*") in general, as the goals' missions statement defines it: "*Take urgent action to combat climate change and its impacts by regulating emissions and promoting developments in renewable energy* (UN, 2021b)".

Ideally, the SDGs are applicable and valid for all kinds of organisations and can be implemented into any company. They shall be seen as a framework when improvements towards sustainability are desired. The more parties are integrating the emission-related SDGs into their actions, the better the contribution towards the set climate targets will be.

The awareness and interest by national and international regulatory organisations regarding the ongoing GHG emissions from shipping and their respective climate impact, was continuously rising in the last decades. Based on this, various policies were introduced over time, in order to limit the GHG footprint, but also other hazardous emissions of the shipping sector. In the following captions of this chapter, the relevant paragraphs of the policies being in place today are presented. As this thesis is focussed on carbon emissions, the paragraphs addressing the reduction of carbon and GHG emissions were primarily considered.

#### 2.3.1 The Paris Agreement

Adopted in 2015 as a part of the Annexes of the United Nations Framework Convention on Climate Change (UNFCCC), the Paris Agreement, a legally binding international treaty, is intending to support the global response on the effects of the ongoing climate change. The agreements' targets are based on the goal of the framework convention, which is "to stabilize greenhouse gas emissions in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system" (Horowitz, 2016). However, the UN convention is not determining this level, nor at which point it may be reached. The same applies for countermeasures to be undertaken to avoid reaching the critical level. This is where the Paris Agreement ties on. In a wider perspective, the agreements' main objectives lie in peaking global GHG emissions and further, to achieve emission neutrality by the end of this century. Article 2 of the Paris Agreement is comprising the key paragraphs in respect to the climate related goals, which are:

1. Holding the increase in the global average temperature to well below 2 °C above preindustrial levels and pursuing efforts to limit the temperature increase to 1.5 °C above preindustrial levels, recognising that this would significantly reduce the risks and impacts of climate change;

- 2. Increasing the ability to adapt to the adverse impacts of climate change and foster climate resilience and low GHG emissions development, in a manner that does not threaten food production; and
- 3. Making finance flows consistent with a pathway towards low GHG emissions and climate resilient development (UN, 2015)

The paragraphs above are setting out clear targets of what is intended to be achieved by the agreement in the future. Innovations and solutions need to be found to make progress, requiring efforts from every party involved. Since Article 2 is not setting out a time frame for achieving the targets, the fourth article of the Agreement is acting supportive here. According to Article 4, the peaking of the GHG emissions is to be accomplished "as soon as possible", as it is understood that the earlier the emissions are reduced or phased out completely, the more likely it will be to stay within the critical two-degree-limit (UN, 2015).

#### 2.3.2 The IMO GHG Strategy 2018

To counteract the growing emission rates, the IMO adopted an initial GHG strategy in 2018, in which they are stating three main objectives as well as a *Vision* they are aiming for. The latter reads as follows:

"IMO remains committed to reducing GHG emissions from international shipping and, as a matter of urgency, aims to phase them out as soon as possible in this century."

The objectives of the initial strategy to face off GHGs are (in short):

- 1. to enhance the IMO's contribution in addressing GHG emissions from international shipping, including the *Paris Agreement* and the *United Nations 2030 Agenda for Sustainable Development* as well as the *Sustainable Development Goal 13 "Climate Action";*
- 2. to identify actions to be implemented by the international shipping sector, as appropriate, [...]; and
- 3. identifying actions and measures, as appropriate, to help achieve the above objectives, including incentives for research and development and monitoring of GHG emissions from international shipping (IMO, 2018b).

Associated to the objectives and the *Vision* of the strategy, the IMO states three *Levels of Ambition* within the resolution paper of the strategy. These levels are directing the initial strategy and are giving clear targets to achieve a reduction of GHG emissions from ships. In the following, an overview of the central statements of the three Levels of Ambition is shown:

Level 1: to decline the carbon intensity of the ship through the implementation of further phases of the energy efficiency design index (EEDI) for new ships;

Level 2: to decline the carbon intensity of international shipping; and

Level 3: to peak and decline GHG emissions from international shipping (IMO, 2018b).

The progress of the shipping sector in each level is under continuous review by the IMO. The reviews are including, but are not limited to, updated emission estimates as well as reports by the *Intergovernmental Panel on Climate Change* (IPCC). Particularly the last two levels are of interest, as

they are stating percentages of carbon and GHG reductions, attached to a fixed timeline. According to the second level, the carbon intensity which is expressed by the carbon emissions per transport work, is to be reduced by a minimum of 40 % by 2030, striving for up to 70 % reduction by 2050, in comparison to the respective emissions in 2008. Continued in the third level, the total GHG emissions from international shipping are to be peaked as soon as possible, with an intended reduction of at least 50 % in the annual GHG emissions in 2050, again, in comparison to the emissions of 2008. There is a visible link between the first objective of the IMO's GHG strategy and the Paris Agreement. Moreover, in connection to their vision, commitment and efforts are made by the IMO to phase out the GHG emissions from international shipping completely, before the end of this century (IMO, 2018b). In 2023, the initial GHG strategy from 2018 will be taken under revision and predictively yield even more ambitious targets.

## 2.4 Retrofitting versus Newbuilding

To achieve the goals of the Paris Agreement,  $CO_2$  emissions need to be reduced by all emitters, i.e., the shipping sector has a limited carbon budget as a proportion of the global carbon budget. To express the proportion each industry sector is potentially taking up from the global carbon budget, the concept of "committed emissions" has been introduced (Bullock et al., 2020). Committed emissions are the cumulated  $CO_2$  emissions expected by an industry sector until 2050.

In order to not exceed the constrained carbon budget, different strategies for a reduction of  $CO_2$  emissions from shipping exist. The EEDI and the SEEMP are regulations to increase the efficiency and reduce the fuel consumption of vessels. They are described in 2.3 Policy background of carbon capture. Due to the long lifespan of vessels, the IMO's focus on newbuildings will not be sufficient in order to stay within the carbon budget, as indicated by the study by Bullock et al. (2020). In comparison to the land-based transportation, the average lifetime of marine assets is much longer (in 2018 the average age of a ship was 28,3 years when scrapped) and therefore a turnover will several more years (Bullock et al., 2020). Furthermore, many measures for reducing the emissions of the shipping sector can be applied to the existing fleet as well (Bows-Larkin, 2015), bearing the potential to reduce the emissions of the existing fleet.

Using the data on  $CO_2$  emissions reported to the EU Monitoring, Reporting and Verification Scheme (EU MRV) by about 11.000 vessels in 2018, Bullock et al. (2020) calculated the carbon budget for the vessels covered from the EU MRV. The carbon budget for a 50 % probability to stay below 1,5 °C global warming is 1670 Mt CO<sub>2</sub>, whereby the committed emissions are estimated to 2260 Mt CO<sub>2</sub>, 135 % of the allowed budget (Bullock et al., 2020). Ships replacing scrapped units and additional ships which are built within the decade from 2020 - 2030 are expected to contribute to these emissions, since they will certainly run with fossil fuel.

Therefore, to reduce the committed emissions of the shipping sector, a balance of  $CO_2$  mitigation measures addressing the existing fleet and newbuildings is needed (Bullock et al., 2020). Policy interventions should thereby take the ship type and the expected lifetime of the ship into account. An owner is going to be less willing to invest in retrofitting a vessel with a short remaining lifetime, i.e., policies are needed to force the owner to uptake emission reduction measures. To prevent that the old vessel is sold to a market where emission requirements are lower, policy makers should consider a premium for early scrappage of such vessels. The need to address the existing fleet rather than to focus on newbuildings with measures like the EEDI is urged by the following example: Assuming that zero-carbon ships are available from 2030, about 80 % of the committed emissions will still result from the currently existing fleet, not from the vessels built between 2020 and 2030 (Bullock et al., 2020).

Bullock et al. (2020) summarise, that the remaining time to implement the necessary changes to meet the goals of the Paris Agreement is too short in order to rely on the replacement of less efficient vessels by newbuildings. Policies promoting the replacement of old vessels by new low-carbon ships and mitigation measures for the existing fleet need to be in force soon.

## 3 Methodology

This chapter is describing the methods applied by the authors to retrieve, evaluate and assess the information required to answer the research questions. Information has been collected by literature review as well as interviewing experts in various CC technologies. To assess which of the identified CC technologies is most promising for the application onboard, a method for a comparative assessment has been developed and is presented.

#### 3.1 Literature review

As a base for this thesis, knowledge on CC technologies was gathered by a review of existing literature. The literature review has been divided into two parts: First, a review to assess which technologies for CC are currently researched in general and second, a review of ongoing research for the application of CC technology onboard seagoing vessels.

To ensure that both literature reviews are based on peer-reviewed scientific articles, Scopus by Elsevier was utilised. This database covers a wide range of scientific publications within science and engineering areas (Elsevier B.V, 2021). To narrow down the results of each search and to ensure that the publications are still relevant, each search has been limited to publications between 2011 and 2021 (a 10-year period).

For the bibliography study on currently available CC technologies the search term "carbon capture" AND "technology" AND "assessment" has been used within the category *keywords* in Scopus. This search was conducted on 05.03.2021 and resulted in 317 document results for a period of the last ten years. The term "assessment" has been added to the search terms to find comparative assessments for CC technologies, which are summing up several technologies in one paper. For comparison, without the additional "assessment" term, the same search resulted in 1.715 related documents. The large number of articles proves that the field of CC technology is intensively researched.

To decide, which of the 317 articles are providing a proper overview on currently available CC technologies, the authors read the titles and, when a title appeared relevant, the abstract as well. One of the articles identified by this method, is the article by Cuéllar-Franca & Azapagic (2015), which is analysing and comparing the life cycle environmental impacts of several options for CC, storage and utilisation technologies. Cuéllar-Franca and Azapagic classify a wide spectrum of CC technologies, providing the best and most comprehensible overview.

To identify additional sources and gather knowledge on each technology, the snowballing method was applied. Snowballing uses the bibliography of relevant articles, to build up a network of literature in order to gain further knowledge and a deeper understanding on the technologies. Besides snowballing, further knowledge on the identified technologies is gained by detailed searches for each technology.

Since the literature search on currently available CC technologies is limited to scientific articles, which are focussing on one or few specific technologies, the authors conducted an additional search with the Chalmers Library search engine on the search term "carbon capture", limiting the results to the foregone 10-year period and to books as form of publication. This search resulted in 3.935 books, of which only Carbon Capture by Wilcox (2012) does purely focus on technologies for CC. The other search results merely mention CC in a wider context and are not describing the

technology in detail. The identified CC technologies and the knowledge gathered on those is found in chapter 4.

For the second literature review, focussed on research in the field of CC in marine onboard applications, the search term "carbon capture" AND "technology" AND "ship" was applied. This search in Scopus was conducted on the 08.03.2021 and resulted in 61 related articles, when searching within title, abstract and keywords. Out of these, seven were found to be relevant for the literature review after reading the title and abstract. The remaining articles are mainly considering shipping as a way to transport the captured carbon, but do not regard CC onboard the vessels. During snowballing within the articles identified as relevant, it was found that some relevant articles where not captured by the search previously carried out. To ensure that no relevant scientific article is missed, another search using the search term "on-board" OR "onboard" AND "carbon capture" was carried out on 23.03.21, which resulted in five hits out of which two were identified as relevant for this thesis. On the 22.04.21 the literature search on the search term "carbon capture" AND "technology" AND "ship" was conducted again to ensure no relevant research published during the thesis project time has been omitted. By this repetition one more relevant article, published in the beginning of April was identified. In addition, the basics of the HyMethShip project, which has been named as a possible pathway towards a circular economy in section 2.2, are presented, mainly focussing on the development of the CC technology included within the project.

Since the field of CC in marine applications is relatively new, there are some projects that just have been started and for which no scientific articles are published yet. Nevertheless, these are still worth mentioning. The search terms "carbon capture" AND "technology" AND "ship" were also applied in the Google search engine on the 16.03.21. Thereby, two incentives where identified: The CC-Ocean and the decarbonICE project.

Further literature on CC onboard vessels, that has not been identified by the foregoing searches, has been provided by interviewed experts. The literature provided by each expert is listed in Appendix A 2.

Depending on the technology researched for the application onboard, the review of the article is allocated to the related technology in chapter 4. In the final subsection of each technology section the mains of the conducted research for the application of this technology onboard vessels are presented. Associated to each of these review sections, a table is summarising the outline and main findings of each paper.

## 3.2 Expert interviews

To retrieve further information and to validate assumptions, this thesis project reached out to experts in CC technology. Besides the authors of papers on CC technology for the application onboard, also companies developing CC technology for the application onboard have been contacted. Most experts are researchers at Chalmers University and were recommended by the supervisors of this thesis. Further, contacts have been provided by Karl Jivén from IVL Swedish Environmental Research Institute.

The identified interviewees have been contacted via email, briefly introducing to the topic of the thesis and the required kind of data. Since the thesis is carrying out a comparative assessment, it was highlighted that no specific figures are required and relative information (e.g., technology X has 2 times higher CAPEX than technology Y) are sufficient. To emphasise this, the experts were asked for a qualified guess, also to increase the number of responses. To fit the expertise of the expert, the emails have been personalised in terms of the CC technology. The questions sent out to experts for CC technologies in common can be seen in the following:

- 1. Will the technology be feasible to be used in combination with <u>large</u> internal combustion engines on ships?
  - a. On which technology readiness level (TRL) do you rank the carbon capture technologies?
- 2. How high is the **initial investment** for each plant in comparison to other carbon capture technologies (e.g., X times higher/lower than absorption by MEA solvents)?
- 3. How high are the **operational costs** in comparison to other carbon capture technologies (e.g., costs per tonne of captured CO<sub>2</sub>, X times higher/lower than absorption by MEA solvents)?
- 4. Which other costs are connected to each technology?
  - a. Which factors are cost-drivers of each technology?
- 5. The available space on vessels is one of the main constraints for the application of carbon capture onboard. How much **space/volume** does each carbon capture plant occupy, excluding the intermediate storage of CO<sub>2</sub> (e.g., X times higher/lower than absorption by MEA solvents)?
- 6. Where do you see the **main advantages** of each technology towards other carbon capture technologies?

It was left to the addressed experts, whether to reply by email or discuss the questions during a semi-structured interview, scheduled by the authors of this thesis.

*Table 3.1* is summarising the contacted experts and the kind of data that have been retrieved from the responders. To summarise the data retrieved from the experts, whether by email or during interviews, transcripts are produced. The transcripts can be requested from the authors as supplementary information to this thesis. The literature sources received from the experts can be found in the appendix. Some experts replied that they cannot provide the kind of data requested. In such cases, no transcript was produced.

The conducted interviews have been semi-structured, based on the questions sent out to the experts. All experts granted the permission to record the interview, which were conducted in form of an online meeting. The summary of each interview has been sent out to the expert for approval.

When referring to information retrieved from the experts, it is marked as *personal communication* in the text.

| Expert                         | Technology | Contacted  | Replied    | Interview  | Data | Literature |
|--------------------------------|------------|------------|------------|------------|------|------------|
| Filip Johnsson <sup>1</sup>    | -          | 27.04.2021 | 29.04.2021 | 03.05.2021 | YES  | YES        |
| Magnus Ryden <sup>1</sup>      |            | 27.04.2021 | 27.04.2021 | N/A        | YES  | NO         |
| Anders Lyngfelt <sup>1</sup>   |            | 27.04.2021 | 27.04.2021 | N/A        | NO   | YES        |
| Mikael Odenberger <sup>1</sup> |            | 27.04.2021 | 27.04.2021 | N/A        | NO   | NO         |
| Lisa Göransson <sup>1</sup>    | CC         | 27.04.2021 | N/A        | N/A        | NO   | NO         |
| Tobias Mattisson <sup>1</sup>  | common     | 27.04.2021 | N/A        | N/A        | NO   | NO         |
| Christophe Duwig <sup>2</sup>  | common     | 27.04.2021 | 27.04.2021 | N/A        | YES  | YES        |
| Max Biermann <sup>1</sup>      |            | 28.04.2021 | 07.05.2021 | N/A        | YES  | YES        |
| Anna Emanuelsson <sup>1</sup>  |            | 28.04.2021 | 29.04.2021 | N/A        | NO   | NO         |
| Christian Azar <sup>1</sup>    |            | 29.04.2021 | 29.04.2021 | N/A        | NO   | NO         |
| Shareq Mohd Nazir <sup>2</sup> | Absorption | 27.04.2021 | 28.04.2021 | 06.05.2021 | YES  | YES        |
| Francois Marechal <sup>3</sup> | Adsorption | 27.04.2021 | N/A        | N/A        | NO   | NO         |
| Thomas Gehring <sup>4</sup>    | Membrane   | 27.04.2021 | N/A        | N/A        | NO   | NO         |
| Jan Boyesen <sup>5</sup>       | <u> </u>   | 27.04.2021 | 28.04.2021 | N/A        | YES  | YES        |
| Elin Malmgren <sup>1</sup>     | Cryogenic  | 27.04.2021 | 29.04.2021 | 12.05.2021 | YES  | NO         |
| Fredrik Normann <sup>1</sup>   | Oxyfuel    | 27.04.2021 | 02.05.2021 | 04.05.2021 | YES  | YES        |
| Zhijun Peng <sup>6</sup>       | Oxyfuel in | 27.04.2021 | N/A        | N/A        | NO   | NO         |
| Zhijun Wu <sup>7</sup>         | ICEs       | 27.04.2021 | N/A        | N/A        | NO   | NO         |

<sup>1</sup>Chalmers University of Technology, Gothenburg; <sup>2</sup> KTH Royal Institute of Technology, Stockholm; <sup>3</sup>EPFL Swiss Federal Institute of Technology, Lausanne; <sup>4</sup>Ionada Corporation; <sup>5</sup>decarbonICE<sup>TM</sup>; <sup>6</sup> University of Lincoln; <sup>7</sup>Tongji University

#### 3.3 Comparative assessment of technologies

To evaluate which of the CC technologies presented in chapter 4 is the most promising for the onboard application, a two-stage approach has been developed for the assessment. The environmental impact of each technology, also including up- and downstream impact, is not taken into concern. Especially the downstream impact of each technology is dependent on how the captured  $CO_2$  is utilised or stored. *Figure 3.1* is showing a schematic overview of the assessment method, which is described in further detail in the following.

As already stated within the limitations, the conducted assessment is focussing on the technical feasibility and specifications of CC technologies for the application in combination with ICEs. Since it is probable that newbuildings are still going to be equipped with ICEs in the foreseeable future (Bullock et al., 2020), the need for technologies being able to decarbonise this drive technology is urging. Therefore, the assessment is starting with a preselection of technologies, being able to run in combination with ICEs. Requiring a different type of engine (e.g., fuel cells) is evaluated as an excluding criterion, i.e., these technologies are excluded from the further assessment.

Since actions to mitigate the climate change are needed urgently to meet the goals of the Paris Agreement, a second "no-go" criterion is excluding all CC technologies that have not been developed to a certain stage yet. Only technologies that have achieved TRL 4 or higher are included

for further assessment. Having achieved TRL 4 indicates that these technologies have left the pure research phase. The system setup has been validated under laboratory conditions, i.e., the function of the whole system as such has been proven. A higher TRL would make the soon implementation of the technologies even more probable, contributing to the targets of the Paris Agreement but would limit the scope of the assessment to very few technologies.

The CC technologies that are not excluded by the "no-go" criteria, are taken into account for further assessment. The feasibility of each technology for the onboard application is going to be evaluated in the first stage. Therefore, the following criteria will be considered:

1.1 **Safety and stability**: Are the ship's safety and/or stability negatively impacted when installing the CC technology onboard? Are there additional hazards or an increased risk for the operating crew? How would a failure of the CC plant impact the vessel? How do the additional installations affect the metacentric height (GM) and thereby impacting the stability?

The technology bearing the lowest risk for the ship's safety and having the lowest impact on its stability are rated best.

1.2 **Ship's movement and vibration**: Is the CC technology negatively impacted by the movement of the ship at sea? Could vibrations onboard reduce the efficiency of the CC plant?

The technology impacted the least by movement and vibrations is rated best.

1.3 Fluctuations in energy demand: Is the technology capable to operate reliably when the energy demand is fluctuating? Due to the different operation modes of a vessel the energy demand is changing, i.e., the use of fuel is variable and thereby the generated mass flow of CO<sub>2</sub> is fluctuating. Especially during manoeuvring, the energy demand may change rapidly. The CC plant must be able to follow these fluctuations, i.e., it has to provide sufficient fuel to deliver the required energy (pre-combustion) or capture CO<sub>2</sub> reliably from a fluctuating exhaust gas flow (post-combustion).

The technology being most capable to meet the fluctuating energy demand and still reliably capture  $CO_2$  under these conditions, is rated best.

1.4 **Impurities in fuel/exhaust**: How is the technology affected by impurities in the fuel/exhaust stream? Is the technique feasible to capture CO<sub>2</sub> from all kinds of engines and fuels or is it limited to a certain engine or fuel type? The technology being the least affected by and tolerant towards impurities in the fuel/exhaust stream is rated the best.

For each criterion, a ranking of the CC technologies in regard of their performance is established. The best technology is ranked on the first, and the worst performing technology on the last place. To summarise the results of all criteria included in stage one of the assessment, each technology is assigned "scores" according to their position in the ranking (1<sup>st</sup> place = 1 score, 2<sup>nd</sup> place = 2 scores, and so forth). The CC technology earning the least scores, is therefore rated the highest in the overall ranking of stage one in the assessment. In cases where no reasoning for a differentiation between certain technologies can be found, equal scores are assigned to these technologies. In such cases the range of scores is reduced (e.g., even if three technologies are ranked on the 3<sup>rd</sup> place (3 scores), the 4<sup>th</sup> place is assigned 4 and not 6 scores). This is done to avoid that the technology ranked last, gains a higher score in relation to the other technologies. For example, when three technologies are ranked on the 3<sup>rd</sup> place (3 scores) and the 4<sup>th</sup> place would be assigned 6 scores, i.e., 200 % of the score achieved by the technologies ranked third. This large gap might lead to an overall bad performance of the affected technology, although it is performing better in other criteria.
To evaluate which CC method is the most promising for the application onboard vessels, the three best-ranked technologies in the first stage will be evaluated in relation to the typical constraints, set out by the specifics of the onboard application as well as demands from shipowners. Thereby, the same ranking system as in the first stage will be applied in the second stage. The following criteria are evaluated:

- 2.1 **Space requirements**: The vessels purpose lies in the transport of goods and therefore the value of a ship is strongly dependent on the space that can be utilised for cargo. The less space is consumed for the installation of the CC plant and the related tanks for intermediate storage of CO<sub>2</sub>, the more cargo can be carried and a higher revenue can be achieved. The less space is required, the higher the CC technique is ranked.
- 2.2 Additional weight: Ships are designed to carry a defined weight of cargo, the so-called deadweight tonnage (DWT). Weight added by the installation of a CC plant and the intermediate storage of captured CO<sub>2</sub>, as well as required chemicals, is reducing the DWT. Therefore, the technology adding the least weight, i.e., reducing the ships transport capacity the least, is evaluated best.
- 2.3 **Energy requirements**: All energy required to run the plants onboard a ship needs to be generated onboard, i.e., the energy required to run the CC plant needs to be produced by generators onboard. A higher energy demand is increasing the operational costs (fuel, maintenance). Therefore, the assessment is ranking the technique with the least energy requirements best.
- 2.4 **Capture-rate**: Which CO<sub>2</sub> capture-rate can be achieved? Considering the additional energy consumption: what carbon reduction rate can be achieved? The more CO<sub>2</sub> is captured, the better the technology is evaluated in the assessment.
- 2.5 **Investment costs**: The initial investment costs are of high importance for the shipowner. High investment costs may make it uneconomical to invest in such technology and will increase the payback period of an investment. The lower the investment costs, the higher the technology is ranked.
- 2.6 **Operational costs**: How expensive is it to capture one ton of CO<sub>2</sub>? The operational costs mainly originate from consumed energy and consumables. The lower the operational costs, the more economical the operation of the CC plant, the better the technology is ranked in the assessment.
- 2.7 **Maturity level**: How far is the technology developed? When is the technology ready to be applied in commercial onboard operation? Since actions for the mitigation of climate change need to be conducted as soon as possible, the technology with the highest maturity level is preferred i.e., ranked best in the assessment.

The technology which earned the lowest score overall is rated best in the seven criteria above and is therefore considered the **most promising technology for newbuildings**. However, ships have a long lifespan and retrofitting of new technology for emission reduction of existing vessels is essential in order to meet the goals of the Paris Agreement (Bullock et al., 2020). Therefore, additional criteria are included in stage 2.b of the assessment, to evaluate the feasibility of the three best technologies as retrofit solution. The technologies will be ranked according to the intensity of required changes in the technical installation onboard. The less changes are needed, the higher the technology is ranked. The score gained in stage 2.b will be added to the ones earned in stage 2.a.

Following aspects are considered:

- 2.8 **Engine**: Is it possible to modify the installed engine(s) or does the engine need to be replaced to run with the CC technology?
- 2.9 **Fuel**: Does the fuel and/or fuel system need to be changed to meet the requirements of the CC technology?
- 2.10 **Repowering required**: As already described in criteria 2.1, all power required to run the CC plant needs to be generated onboard. If the installed equipment onboard is not able to provide sufficient power, additional generators need to be installed, increasing the investment as well as the operational costs.

The technology rated the best in the criteria of stage 2.a and 2.b overall, is the one requiring the least changes to the existing design and technical systems of the ship and at same time performing satisfactory in the general criteria for CC technologies. Therefore, it is the **most promising technology for retrofitting** of existing vessels with CC technology.

Most of the criteria for the evaluation of the CC methods are depending on each other. For example, the capture-rate of each technology could be increased by scaling up the complete installation, but this would increase the space and energy requirements. Furthermore, the data retrieved from literature review and expert interviews is lacking comparable figures. Consequently, the assessment is discussing the properties of the included technologies for each criterion, providing a reasoning for the performed ranking.

For a better overview of the outcome of the assessment, the intermediate and final results are presented in form of tables. Each table is summarising the reasoning behind the score achieved by the technology.



Figure 3.1: Schematic overview of the assessment method

## 3.4 Technology readiness levels (TRLs)

Having its origin at the NASA and US Department of Defence, TRLs have been adopted by the EU Horizon 2020 program in 2014 for civil use (Héder, 2017). Within the EU project TRLs are used to set goals and boundaries for founding. This thesis applies TRLs as a more precise way to describe the maturity level of identified CC technologies. The definitions applied in the EU Horizon 2020 program, which will also be used in this report, are given in *Table 3.2*.

| Phase         | TRL | Definition   |
|---------------|-----|--|
|               | 1   | basic principles observed  |
| Research      | 2   | technology concept formulated  |
|               | 3   | experimental proof of concept  |
|               | 4   | technology validated in lab  |
|               | ц   | technology validated in relevant environment (industrially relevant    |
| Development   | 5   | environment in the case of key enabling technologies)                  |
|               | 6   | technology demonstrated in relevant environment (industrially relevant |
|               |     | environment in the case of key enabling technologies)                  |
|               | 7   | system prototype demonstration in operational environment              |
| Domonstration | 8   | system complete and qualified  |
| Demonstration | 0   | actual system proven in operational environment (competitive           |
|               | 9   | manufacturing in the case of key enabling technologies; or in space)   |

Table 3.2: TRLs adapted from the EU Horizon 2020 program

Thereby TRLs can be grouped into three phases. In the early stage (TRL 1 - 3) the achievements required to elevate the TRL are related to pure research, starting from the basic idea and the formulation of a concept, up to an experimental proof of the proposed concept. The development phase describes the scaling up of the technology and the related experiments to validate and demonstrate the functionality of the technology concept, beginning with the validation of the system in a laboratory environment (TRL 4) up to a fully integrated pilot plant tested in a relevant environment (TRL 6). The last phase, the demonstration, comprises the development from the pilot plant until the normal commercial service (TRL 9).

Chapter 4 is including the current TRL for each of the identified CC technologies in the corresponding subsection *Field of current application and TRL*. The TRL given here refers to the current maturity of the CC technology in general, i.e., it does not relate to the appliance of the technology onboard a vessel. Therefore, the authors referred to recent literature sources, which are evaluating the TRL. In cases where such literature sources could not be identified, the authors base their TRL evaluation on sources providing evidence of the latest development of the corresponding technology.

Besides the general appliance of CC technologies, chapter 4 is also including the results of the literature review on research for the onboard application of CC. The TRL for the research presented in each article/report is evaluated by the authors as well. Most articles are deemed to have achieved TRL 2 since simulations of the proposed concept have been conducted and results of these are presented in the report. When results from existing pilot or demonstration plants are been used within the research as a basis for the simulation or to verify simulation results, the article is deemed to have achieved TRL 3. A higher TRL rating is given, when specific evidence, regarding a further progress in development of the system, is provided within the article.

# 4 Carbon capture technologies

This chapter is presenting the results of the literature review on the identified CC technologies, also including data retrieved from the interviewed experts. Thereby, the focus lies on the CC process itself, i.e., up- and downstream processes like required pre-treatment of flue gases and the compression and liquefaction of the captured CO<sub>2</sub>, respectively, are not considered in detail.

In general, three methods for CC can be distinguished: post-combustion capture, pre-combustion capture and oxyfuel combustion.

Post-combustion CC is applied in flue gas environments and refers to the capture of  $CO_2$  from a carbonaceous fuel, after the fuel has been combusted. The  $CO_2$  concentration in the exhaust gases is typically low, due to the high dilution with combustion air (X. Wang & Song, 2020). When fuel cells are applied to convert the fuel, the more applicable term "post-conversion capture" is used. In pre-combustion capture, as the name implies, the  $CO_2$  is removed from the fuel before an energy conversion occurs. This is generally done by converting the fuel into a syngas with a high  $CO_2$  concentration and the subsequent capture of  $CO_2$  from the syngas (X. Wang & Song, 2020). Oxyfuel combustion is using another approach to capture  $CO_2$  from flue gases. This technology combusts fuels in an  $O_2$ -enriched environment, to create a flue gas mixture which is ideally only consisting of  $CO_2$  and water vapour. After the condensation of the vapour, the  $CO_2$  is ready for sequestration (X. Wang & Song, 2020).

Post-combustion capture by absorption, using a 30 wt% solution of MEA, is the most mature technology for CC (TRL 9). Therefore, in the consulted literature it is widely used as a benchmark for the comparison of different CC technologies. This approach is adopted by the authors of this thesis. The details of the MEA benchmark process are described in section 4.1.1.

At the beginning of each subsection, which presents a CC technology, key data on the technology in relation to the benchmark process will be summarised in form of a table. No absolute numbers can be given here, since the comparability of the literature is limited due to varying parameters and boundary conditions in each study. A summary of these key data is provided in *Table 4.1*.

The key data provided in the tables is including the TRL, the estimated capital expenses (CAPEX) and operational expenses (OPEX) as well as the required space in comparison to the MEA benchmark technology. The TRL is evaluated applying the scale published by the EU in 2014 and is described in section *3.4*. Furthermore, the feasibility of the technology to run in combination with a marine ICE is included. In the last column, the number of articles, reports and projects on the application of the CC technology onboard vessels, which have been identified by the authors, is given.

Besides the technology setup and operating principle, the following is covered for each CC method:

- Field of current application and TRL
- Costs
- Space requirements
- Advantages and drawbacks
- Research for the application onboard

Each section is describing how the data retrieved from the consulted literature are used to determine the key data presented in the included table. The data presented in this chapter are forming the basis for the comparative assessment, to determine which CC technology is the most promising.

| Туре                  | CC technology                         | Described in section | TRL   | CAPEX               | OPEX               | Space              | ICE<br>compatibility | # of articles |
|-----------------------|---------------------------------------|----------------------|-------|---------------------|--------------------|--------------------|----------------------|---------------|
| Post-<br>combustion   | Absorption by<br>chemical<br>solvents | 4.1.1                | 9     | Same as<br>MEA      | 0,27 – 1 x<br>MEA  | Same as<br>MEA     | Yes                  | 15            |
|                       | Adsorption by<br>physical<br>sorbents | 4.1.2                | 6     | -                   | Lower<br>than MEA  | -                  | No                   | 2             |
|                       | Membrane<br>technology                | 4.1.3                | 5     | Higher<br>than MEA  | Higher<br>than MEA | Less than<br>MEA   | Yes                  | 1             |
|                       | Cryogenic<br>carbon capture           | 4.1.4                | 6     | 0.7 x<br>MEA        | 0.5 x<br>MEA       | Less than<br>MEA   | Yes                  | 2             |
| Pre-<br>combustion    | Absorption/<br>Adsorption             | 4.2                  | 9 (5) | Higher<br>than MEA  | Higher<br>than MEA | Higher<br>than MEA | Yes                  | 1             |
| Oxyfuel<br>combustion | Oxyfuel<br>combustion                 | 4.3                  | 7 (4) | ~1,7 - 3,8 x<br>MEA | ~0,76 x<br>MEA     | Same as<br>MEA     | Yes                  | 2             |

## 4.1 Post-combustion capture

As introduced above, post-combustion CC is describing the removal of  $CO_2$  from flue gases with typically low  $CO_2$  concentrations, which arise from the combustion of hydrocarbons. There are different technologies available to capture  $CO_2$  from exhaust fumes. The most common technologies are presented in the following subsections. Some of these technologies are already in commercial operation, while others are still under research and need further development, before implementation in industrial applications becomes feasible.

#### 4.1.1 Absorption by chemical solvents

CC by chemical absorption is the most mature technology of all post-combustion technologies (Sreedhar et al., 2017). It is used in large-scale applications, e.g., coal-fired power plants, for the removal of  $CO_2$  from their exhaust (NRG Energy Inc., 2021). Although this technology is well developed, continuous research is ongoing to improve the processes (Vega et al., 2020). *Table 4.2* is summarising key data on absorption by chemical solvents. Since the table includes data of several solvents, a range is given for some of the parameters.

#### Table 4.2: Key data on absorption by chemical solvents

| TRL | CAPEX       | OPEX                    | Space       | ICE<br>compatible | # of<br>articles |
|-----|-------------|-------------------------|-------------|-------------------|------------------|
| 9   | Same as MEA | 0 <b>,</b> 27 – 1 x MEA | Same as MEA | Yes               | 15               |

The benchmark process, in the comparative assessment of this thesis, is based on chemical absorption as well. An amine-based solvent, namely MEA, is used in a 30 wt% solution for the selective absorption of  $CO_2$  from a flue gas. The high reactivity of this solvent in connection to its low purchase price are main arguments for the wide usage of MEA in different flue gas conditions (Sreedhar et al., 2017). Below the following caption, MEA and other chemical solvents are described regarding their properties and their application in chemical absorption processes for CC.

#### 4.1.1.1 Technology setup and operating principle

The general setup in the conventional absorption technology is rather simple. Two main units are primarily required to establish a working  $CO_2$  capturing cycle. Firstly, the absorber unit, comprising a lean absorbing solvent and secondly, the stripper unit for regeneration of the solvent (Sreedhar et al., 2017). Both processes, absorption and regeneration of the solvent, are based on the mass transfer of  $CO_2$  from gas to liquid or vice versa, respectively. The  $CO_2$  absorber is installed in the exhaust stream. As a result of this the flow resistance in the exhaust will be higher. Additional exhaust fans or blowers may therefore be required to overcome the pressure drop (Sreedhar et al., 2017).

Before the flue gases reach the absorber unit in which the CC process occurs, they are usually led through a complex flue gas aftertreatment system, to remove other undesired flue gas contaminants such as  $NO_x$  and  $SO_x$  (especially valid for exhaust gases from marine diesel engines). Depending on the available space, the absorber might consist of several columns, which contain the absorbent. These columns are perfused by the flue gas from below. To improve the efficiency of the absorber, the columns are packed in specific structures. The structured packing of the columns is increasing the contact surface between the absorbent and the flue gas (Wilcox, 2012). Especially in post-combustion CC, the flue gas pre-treatment system is also comprising a direct contact cooler, to lower the temperature of the gas mixture before entering the absorber.

Contaminants in the flue gas, as well as excessive heat, can lead to solvent degradation (Rieder et al., 2017).

The feeding-point for the lean absorbent is located on the top of the absorber unit, creating a counter-current between the exhaust gas and the solvent stream. This counter-current is supporting a better diffusion between the two streams.  $CO_2$  contained in the flue gas is reacting with the lean solvent from the feed and is thereby removed from the gas. This occurrence is the actual absorption process, where a mass transfer from the solute  $CO_2$  to the liquid solvent takes place. The chemical bond between  $CO_2$  and solvent is reversible. The  $CO_2$  concentration in the gas phase is increasing, the lower the solvent sinks in the absorber column, allowing the solvent to bind more  $CO_2$  (Kothandaraman, 2010; Wilcox, 2012). At the bottom of the absorber, the  $CO_2$ -rich solvent is discharged and pumped into the coupled stripper unit. On the gas outlet of the absorber, the treated flue gas with low- $CO_2$  content is passed on to the funnel of the plant.

For a better understanding of the technology setup, a simplified schematic, including the process flow, is presented in *Figure 4.1*. As mentioned above, absorber and stripper are connected to each other.  $CO_2$ -rich solvent is forwarded from the absorber to the stripper and regenerated  $CO_2$ -lean solvent is returned from the stripper to the absorber. In this way, a circulation of lean and rich absorbent between these two units is established. To pre-heat the solvent before the stripper and to prevent heat losses from the stripper, a cross heat exchanger is installed in the circulation of lean/rich solvent. Subsequently, after the heat exchanger, before the lean solutions is injected in the absorber, it is cooled by a cooler unit.



Figure 4.1: Simplified schematic of the chemical absorption process

Equivalent to the absorber, the inside of the stripper is filled with packed columns. However, the operating principle in the stripper is opposite to the absorber. When the CO<sub>2</sub>-rich solvent enters the upper section of the stripper, it is led through the packed columns. From below, a regeneration steam by a reboiler is created, acting as the counter-current to the rich solvent. When both streams converge, the CO<sub>2</sub>-rich solvent is absorbing energy from the so-called stripping stream and CO<sub>2</sub> is released from the solvent feed stream (P. C. Chen & Lai, 2019). The mass transfer of CO<sub>2</sub> from the liquid to the gas phase is declared as the desorption process (Wilcox, 2012). The released gaseous CO<sub>2</sub> is fuming to the top of the stripper, where it exits the unit on the gas outlet. After the CO<sub>2</sub> got separated, the regenerated solvent is lean again. It is collected at the lower part of the stripper and returned into the feed cycle to the absorber (P. C. Chen & Lai, 2019). The pure stream of CO<sub>2</sub> on the gas outlet of the stripper is further pressurised in a compressor to a desired level and finally forwarded to the dedicated CO<sub>2</sub> storage.

Besides MEA, which is already commercially available, a variety of alternative chemical absorbents has been researched in the past decade (X. Wang & Song, 2020). A fair amount of them were amine-based, but also ammonia solvents, aqueous liquids and ionic liquids have been under consideration. All these chemicals come with individual benefits and drawbacks in different applications, but also demand distinct boundary conditions, which is limiting their area of application. Furthermore, the usage of blended chemicals to increase the advantages and, at the same time, diminish the disadvantages of the individual chemicals, was tested (Kothandaraman, 2010; Sreedhar et al., 2017). *Table 4.3* is comprising some of the researched chemical solvents and provides an overview of their specifics.

|   |  |  | Energy  |   |   |
|---|--|--|---|---|---|
| Absorbent   | Advantages   | Disadvantages  | demand for  | Remarks   | Literature Source   |
|   |  |  | regeneration  |   |   |
| Monoethanol-<br>amine<br>(MEA)                              | Low costs;<br>high reactivity  | Degrades in contact<br>with air, SO <sub>x</sub> or<br>NO <sub>x</sub> ;<br>corrosive;<br>volatile   | Intense<br>(2,2 – 6<br>MJ/kg <sub>CO2</sub> )                             | 8,2 - 14 %<br>efficiency<br>penalty for a<br>power plant  | Kothandaraman, 2010;<br>Sreedhar et al., 2017;<br>M. Wang et al., 2015                                  |
| Piperazine<br>(PZ)  | Resistant to<br>thermal<br>degradation and<br>corrosion  | Can form<br>precipitation and<br>nitrosamine (toxic)<br>during CO <sub>2</sub> capture<br>→ concerns<br>regarding<br>environmental<br>friendliness | About 85 %<br>of MEA  | Can be used<br>as a blend to<br>MEA to<br>increase<br>efficiency<br>(activated<br>MEA)                    | Cousins et al., 2014;<br>Feenstra et al., 2019;<br>Sreedhar et al., 2017;<br>X. Wang & Song, 2020       |
| Ammonia<br>(NH3)  | Good availability;<br>lower chemical<br>costs than MEA;<br>resistant to<br>thermal<br>degradation and<br>corrosion | High volatility  | Very low,<br>requires only<br>27 % reboiler<br>duty<br>compared to<br>MEA | Tested in<br>pilot-scale<br>only  | Awoyomi et al., 2019,<br>2020;<br>Sreedhar et al., 2017   |
| Ionic Liquids   | Less costs than<br>MEA;<br>resistant to<br>degradation<br>(thermally &<br>chemically stable);<br>non-volatile      | Particularly toxic to<br>aquatic organisms   | Lower than<br>MEA   | Some liquids<br>show high<br>regeneration<br>efficiency (up<br>to 95%);<br>tested in pilot-<br>scale only | Krishnan et al., 2020;<br>Mac Dowell & Shah,<br>2012;<br>Sreedhar et al., 2017;<br>Y. Zhou et al., 2020 |
| Potassium<br>carbonate<br>(K <sub>2</sub> CO <sub>3</sub> ) | High thermal &<br>chemical stability;<br>non-volatile;<br>no degradation;<br>more efficient than<br>MEA            | Low mass transfer<br>rate;<br>higher space demand<br>than MEA  | Lower than<br>MEA   |   | Kothandaraman, 2010;<br>Sreedhar et al., 2017;<br>M. Wang et al., 2015                                  |

| Table 4.3: | <b>Overview</b> | of different | chemical | solvents |
|------------|-----------------|--------------|----------|----------|
|------------|-----------------|--------------|----------|----------|

The use of different solvents is affecting the technology setup of the absorption process. As a result of this, differences in the setup, space requirements, costs (OPEX & CAPEX) and TRL of the absorption technology can be found. The aspects of the most commonly used processes are discussed in the following subsections.

#### 4.1.1.2 Field of current application and TRL

CC plants in post-combustion applications that utilise chemical absorption by amines are already commercially available for several years now. Industrial applications are even scaled up to the usage of absorption technologies for  $CO_2$  removal from power plants. Post-combustion capture

technologies are a kind of exhaust gas aftertreatment system and hence provide the possibility to integrate this CC technology into an existing flue gas stream. Amine-based solvents, such as 30 wt% MEA, are the most common and successfully used solvents for the chemical absorption from flue gases (Sreedhar et al., 2017).

In 2016, the world's biggest CO<sub>2</sub> capture plant so far went into commercial operation. The NRG Petra Nova coal-fired power plant in Texas, United States, was retrofitted with an amine-based absorption technology. Within a three-year demonstration period, more than 92 % of CO<sub>2</sub> from the processed flue gas were captured. However, in May 2020 the plant was shut down due to low oil prices, making its operation uneconomical. Nevertheless, the commercial demonstration of the amine-based absorption technology was successful (NRG Energy Inc., 2021). Oko, Wang, & Joel (2017) evaluate the post-combustion absorption technology, in general, to be at TRL 6-8. Based on all stated facts and the proven use in an operational environment, the authors of this thesis assess the amine-based chemical absorption technology to be at TRL 9.

Different applications for the usage of  $NH_3$  in absorption CC are reviewed by Augustsson et al. (2017). In the WE Energy pilot plant,  $CO_2$  capture-rates of 89 % were proven under real flue gas conditions, with  $NH_3$  as the absorbing solvent. In another pilot-scale plant by EONCAP in Karlshamn, Sweden, the absorption capabilities of  $NH_3$  from flue gases from the combustion of heavy fuel oil (with high  $SO_x$  and  $NO_x$  contaminants in the flue gas) were tested (Augustsson et al., 2017). Based on the successful testing of  $NH_3$  in relevant flue gas conditions, the absorption process by  $NH_3$  is evaluated to be at TRL 6.

Concentrated piperazine (PZ) as an absorbent was tested in different test plants under flue gas conditions. A report by E. Chen et al. summarised the results of the tests at the SRP pilot plant with synthetic flue gas and the DOE NCCC coal-fired flue gas. The  $CO_2$  concentration in the flue gas varied between 10,6 – 12,3 %.  $CO_2$  capture-rates of 83,1 – 99,1 % were achieved in the test plants, using concentrated PZ. Therefore, PZ absorption is evaluated to be at TRL 6 as well.

According to the report by Kearns, Liu, & Consoli, the application of ionic liquids for CC is still under early research (2021). So far, only laboratory tests with these solvents have been carried out. The TRL is considered to be at 2-3 (Kearns et al., 2021).

#### 4.1.1.3 Costs

The lower the  $CO_2$  concentration in the flue gas and the lower the quantity of flue gas from the source, the higher are the costs per captured tonne  $CO_2$  of the respective CC technology (economies-of-scale effect) (F. Johnsson, personal communication, 03.05.21). Vice versa, the more  $CO_2$  can be captured from the flue gas, the lower are the costs per captured tonne  $CO_2$ , which means that an increasing capture-rate (e.g. from 60 to 90 %) significantly lowers the costs per captured tonne  $CO_2$  (Feenstra et al., 2019).

The installation of large-scale chemical absorption equipment to power plants is causing immense CAPEX for the owner (Oko et al., 2017; M. Wang et al., 2015). The costs of the investment originate to a large extent from the costs for the absorber and stripper unit, where especially the packed columns are main contributors to the price (M. Wang et al., 2015). When considering the investment costs, it must be noted that it is possible to reduce the CAPEX when higher OPEX are acceptable. Since this trade-off between CAPEX and OPEX is also affecting the space requirements, it is described in detail in the next subsections. As mentioned under 4.1.1.1, the CAPEX and OPEX are further influenced by the choice of solvent. However, the general technology setup including the main cost contributing units is similar in all chemical absorption

processes. Therefore, the authors estimate that the CAPEX in chemical absorption by alternative solvents are about the same as in the MEA benchmark process.

The OPEX of the absorption technology mainly composes of the purchase price for the utilised solvent and the energy costs for absorption and stripping. Breaking down the additional energy, the biggest share in energy demand is associated to the regeneration of the solvent, if conventional absorption with packed columns is used (Kothandaraman et al., 2009). A study by Rubin, Davison, & Herzog (2015) estimates, that the levelized costs of electricity (LCOE) are increasing by about 25-40 %, due to the extra energy requirements from the CC plant, in case packed-bed columns are utilised in the capture plant. It has to be noted that the LCOE comprises both, CAPEX and OPEX, since it represents all energy expenses related to the electricity generation (e.g., the investment cost for the generator).

As mentioned, the choice of absorbing solvent is influencing the OPEX. MEA has a relatively low-cost price in the purchase, but demands immense energy for regeneration (Sreedhar et al., 2017). Several sources refer to a required regeneration energy for MEA between 3.2-4.2 GJ per tonne of captured  $CO_2$ . In some cases more than a third of the power output of the power plant is required for solvent regeneration (Oko et al., 2017; M. Wang et al., 2015).

Compared to MEA, K<sub>2</sub>CO<sub>3</sub> has an even lower purchasing price, at the same time less solvent is needed and the energy demand for regeneration is lower (M. Wang et al., 2015). The absorption process with NH<sub>3</sub> requires up to 73 % less energy than the MEA process (Awoyomi et al., 2020; Mac Dowell & Shah, 2012). The same fact of lower energy demand also applies for PZ, which directly relates to lower OPEX for the operator, when PZ, K2CO3 or NH3 are used instead of MEA (Sreedhar et al., 2017). Additionally, favourable for PZ and K<sub>2</sub>CO<sub>3</sub> is their high resistance to solvent degradation, i.e., less replenishment of the solvent is required. Contrary to that, MEA is affected by such degradation and requires solvent replenishment when the capture-rate is decreasing. This is contributing to higher OPEX of MEA in comparison to the other solvents (Raksajati et al., 2013). Concluding, in case alternative solvents to MEA are applied in chemical absorption, the OPEX can be lowered significantly in comparison to the MEA process, due to the lower purchase price, lesser energy demand and longer service lifetime of specific solvents. Out of the solvents considered in this comparison, NH<sub>3</sub> has the least OPEX and is therefore marking the lower end of the range. A study by Cousins et al. (2014) found, that the energy demand for solvent regeneration of PZ is about 15 % lower than for MEA, i.e., the translated OPEX in the PZ process are at a level of 85 %, compared to the benchmark process.

#### 4.1.1.4 Space requirements

Depending on the intended rate of captured carbon from the flue gases, the physical dimensions of the absorber and stripper unit may vary. The higher the desired fraction of captured  $CO_2$ , the higher the columns of the absorber need to be, to allow for a longer mass transfer zone. The diameter of the columns is defining the maximum allowed flow rate of the different streams. Additional factors, influencing the rate of mass transfer, are the solubility and the diffusivity of  $CO_2$  in the absorbing solvent, as well as the chemical reactivity of the solvent with  $CO_2$  (Wilcox, 2012).

An underestimated space consumer is the cross-heat exchanger in the lean/rich solvent circulation between absorber and stripper (F. Normann, personal communication, 04.05.21). In the research study by Feenstra et al., (see *4.1.1.3 Costs*) dimensions of the heat exchanger unit from 6 m x 1.15 m (L x D) are stated. In comparison, the associated absorber (packed columns) dimensions to this

capture plant are 10 m x 1.5 m (H x D) and the stripper (packed columns) is 14 m x 0.76 m (L x D). Further, the direct contact cooler (seawater/exhaust gas) as a part of the flue gas treatment system, upstream to the absorber unit, is dimensioned 13.9 m x 2.29 m (H x D) (Feenstra et al., 2019). The respective dimensions of the study by Luo & Wang, (2017) are as follows: the absorber (packed columns) 12.5 m x 4.2 m (H x D) and the stripper (packed columns) 6.5 m x 1.6 m (H x D). Both studies are examining MEA processes. As it can be seen from the dimensions, the whole absorption process with its required components is taking up much space. Further, the weight of the components needs to be considered as well, since the individual parts are fairly heavy. For example the lean/rich heat exchanger unit is accounting for about 17 tons and the absorber for almost 5 tons (Feenstra et al., 2019). Especially for onboard applications, these issues need to be faced and overcome.

The immense packaging height of absorber and stripper units (packed columns), particularly in large-scale applications, is contributing to the enormous space demand of this technology. Rotating packed-beds could be a key alternative to conventional systems, since they show similar capture performances at reduced unit sizes. However, the technology of rotating packed-beds is still in lab-scale and therefore currently not available for commercial use (Zhao et al., 2014).

Another possibility to reduce the equipment size, is to increase the flowrate of the solvent in the reboiler and the connected electrical auxiliaries (circulating pumps for the solvent). Thereby, the size of the absorber and stripper can be reduced but electric consumers, such as pumps, are requiring more energy. Further, the reboiler duty needs to be increased, to allow for a faster regeneration of the solvent in the stripper. A lower height of stripper and absorber equals to lower CAPEX and less space demand but at the same time the OPEX of the process are increasing (Einbu et al., 2021).

It can be concluded that the space requirements of the components in absorption technologies are dependent on the CC application and are subject to numerous degrees of freedom. Higher mass flows and/or velocities of the flue gas are accounting for bigger sizes of the components. However, the general setup in absorption is not differing much between the alternative solvents and the benchmark MEA process. For this reason, the authors estimate that the space demand of the compared absorption processes is about the same.

#### 4.1.1.5 Advantages and drawbacks

One of the biggest merits of the post-combustion CC technology by chemical absorption is the general possibility of retrofitting it to an existing plant, without major changes to the actual power-generating process (Sreedhar et al., 2017). Since this technology has reached high maturity, it can immediately be used in arbitrary flue gas applications. The components involved in the processes have been tested in real flue gas conditions over extended time periods, which contributes to the technology's reliability.

However, the intense energy demand for solvent regeneration is a major drawback of the chemical absorption technology. Additional energy penalties are accounted to the power requirements of the solvent pumps and blower/fans in the exhaust stream, to overcome the pressure drop of the absorber (Wilcox, 2012). Another disadvantage is the toxicity and corrosivity of some solvents and the fact of their gradual degradation over time. As aforementioned under 4.1.1.4, the CC related equipment is both, space and weight intensive, which can be limiting for confined-space applications (Feenstra et al., 2019; Sreedhar et al., 2017).

#### 4.1.1.6 Research for the application onboard

Due to its application in land-based industrial processes, absorption by chemical solvents is the most advanced process for CC. This is also represented by the number of articles on research for the application in the naval sector. This thesis identified 15 articles and reports proposing processes and evaluating the feasibility of CC for reducing carbon emissions from shipping. The main findings of each paper are summarised in *Table 4.4*.

In their 2012 published review on options to reduce the carbon emissions from international shipping, Mac Dowell and Shah introduced post-combustion CC by absorption with chemical solvents as an option to reduce the carbon footprint of the maritime transport sector. Based on the absorption process using MEA solvents and its drawbacks, the authors define four criteria for sorbent materials:

- 1. High CO<sub>2</sub> absorption capacity to reduce the equipment size,
- 2. High thermal and chemical stability to reduce the degradation,
- 3. Low volatility to reduce solvent losses,
- 4. A weak bonding of CO<sub>2</sub> to reduce the costs of solvent regeneration (Mac Dowell & Shah, 2012).

Mac Dowell and Shah (2012) propose two alternative solvents, which are showing a better performance than MEA in regards of these criteria. Firstly,  $NH_3$  allowing a reduction of at least 7,5 % of the energy required for regeneration in comparison to MEA and secondly, ionic liquids offering a saving potential of up to 16 %, in comparison to MEA. The volatile nature of  $NH_3$  and the low density of ionic liquids are highlighted as critical, increasing the footprint of CC (Mac Dowell & Shah, 2012).

In 2014, Zhou and Wang published their proposal for a new technology for post-combustion capture applications onboard vessels. Rather than other CC technologies applied ashore, this technology consists of chemical processes for carbon solidification. Therefore, a solution out of the reactants sodium hydroxide (NaOH) and calcium oxide (CaO) is used to bind CO2. The product of this process is calcium carbonate (CaCO<sub>3</sub>), which can be filtered from the solution and stored as solid powder onboard, until its discharge. Apart from the advantages in reduction of power and space requirements as well as the avoidance of stability issues due to storage of liquified CO2 onboard, the authors see a financial advantage. Based on a 16-days voyage of a 157.500 DWT bulk carrier, from port of Qinhuangdao to San Francisco, a cost estimation has been carried out. The CC system for this example ship is designed to reach the IMO 2020 target of 20 % reduction of carbon emissions from shipping. The conducted laboratory experiments show, that for a 20 %reduction of CO2 emissions, about 30 % of the exhaust gases need to be lead through the absorption tower. Including the costs for required energy, chemicals and freight reduction, the authors cost analysis still comes to the result, that the profits from a sale of the produced CaCO3 will exceed the running costs of the capturing plant. It is concluded that this new technology has, at least for the example of the case study, major advantages in comparison with a capture plant that stores CO<sub>2</sub> in a liquid phase onboard (P. Zhou & Wang, 2014).

The literature review on EEDI, EEOI and CCS by Wang et al., published in 2017, is studying current policies for carbon emission reduction from shipping and is giving an overview of the different CC techniques. The paper is briefly analysing the feasibility of the described technologies and is discussing impediments and constraints for the application of CC onboard. The authors do

not see pre-combustion capture and oxyfuel combustion as a currently feasible solution for CC from ships exhaust due to their low TRL (H. Wang et al., 2017).

Post-combustion capture is seen as the most applicable method for onboard CC since it is a "relatively mature method" (H. Wang et al., 2017) in shoreside applications. The investment costs for such a plant are lower than for the other two options described in the previous paragraph. Hindrances for this technology are seen in the required space and risks connected to the storage of liquified  $CO_2$  onboard. As an example, for a feasible CC solution, the paper is presenting the method described by Zhou and Wang (2014). Finally, Wang et al. conclude, that more research is required in order to develop a practical CCS application for onboard installation.

Based on the technology developed by Zhou and Wang (2014), Fang et al. (2019) presented their model for the optimal sizing of a CCS system for onboard application. The model for a so-called *all-electric ship* is determining the optimal size of an energy storage system first and in the second step evaluates the feasible size of the CCS system based on the identified constraints. The case study is based on actual operating data from a vessel's voyage and discloses, that the vessels energy system in combination with an energy storage system, is able to power a CCS system capturing up to 60 % of the CO<sub>2</sub> emissions. For a higher capturing rate, an additional gas turbine for power generation would be required (Fang et al., 2019).

Another review on options for decarbonising shipping has been conducted by Balcombe et al. (2019). CCS is named as one potential course of action to reduce the carbon intensity of shipping and the concept of Calix RECAST is presented as an example for a CCS technology. Calix RECAST is also using CaO for binding CO<sub>2</sub> but other than the concept of Zhou and Wang (2014), the CaO is added as powder into the exhaust stream, rather than being contained within a solution. The resulting CaCO<sub>3</sub> can be dumped into the sea, where remaining non-reacted CaO is going to bind further CO<sub>2</sub> from the ocean. Balcombe et al. highlight, that the shoreside production of CaO would emit significant amounts of CO<sub>2</sub> and if these emissions are not captured, the technology would just lead to a shift of emissions from one sector to another. Furthermore, additional research is needed to address the impact of an increased pH-value on the ocean when disposing unreacted CaO (Balcombe et al., 2019).

The first study for the application of solvent-based CC onboard ships has been carried out by Luo and Wang and was published in 2017. The proposed post-combustion capture technology is designed to run with a 30 wt% aqueous solution of MEA for the absorption of CO<sub>2</sub>. Based on a middle-sized general cargo ship as an example, the researchers developed a model of the ships energy system to simulate the efficiency and conduct a techno-economic assessment. Without the installation of additional power generation equipment, a CC rate of 73 % can be achieved at costs of 77,50  $\notin$ /t<sub>CO2</sub>. To obtain a capture-rate of 90 %, additional power is required, which is generated by a gas turbine within the model and is raising the costs to 163,07  $\notin$ /t<sub>CO2</sub>, mainly due to an increased fuel consumption. Limitations of CC onboard technology were identified by the researchers as tank storage of the solvent and captured CO<sub>2</sub>, limited space for the equipment, limited supply of heat, electric power and cooling utilities as well as in the construction due to the constant movement of the ship. In conclusion, this CC technology is feasible for the onboard application but requires additional energy production onboard (Luo & Wang, 2017).

Feenstra et al. (2019) evaluate CC to be a transition solution on the way to zero emission shipping and therefore researched the application of post-combustion CC technology for diesel and LNG-fuelled ships. For two dual-fuel reference ships, a 1.280 kW inland ship and a 3.000 kW general cargo vessel, the process for chemical absorption is simulated with 30 wt% aqueous MEA and

30 wt% aqueous PZ as solvents. The process simulation for the inland ship revealed that the cooling capacity from the evaporation of LNG is sufficient to cover the liquefaction of the compressed  $CO_2$  for onboard storage. When the ship is running on diesel, i.e., no evaporation of LNG takes place, an additional refrigeration unit is needed to liquify the  $CO_2$  for intermediate storage and thereby is raising the costs for equipment and operation. Besides the different fuel options, different options for solvents have been compared. Since PZ has a higher desorption pressure, the required compression work for the captured  $CO_2$  is lowered, reducing operational and equipment costs. Another option examined is the difference resulting from a capture-rate of 60% or 90%, showing that the costs per tonne of captured CO<sub>2</sub> are lower, the more CO<sub>2</sub> is captured. In almost all cases, the heat derived from the exhaust gases was sufficient to cover the energy demand needed for desorption. By 98 €/t<sub>CO2</sub>, the lowest costs were achieved for the 3.000 kW reference ship, when using PZ as solvent and running on LNG. Nevertheless, due to concerns on the environmental friendliness of PZ, the feasibility study for modifying the reference vessel to fit the CC plant was carried out for the use of MEA as solvent instead and LNG as fuel at a capture-rate of 90 %. It is shown how the additional equipment and storage tanks can be fitted onboard without impacting the ships stability. Feenstra et al. (2019) conclude, that CC might be a more cost-effective option for larger and LNG-fuelled ships, also due to the purer exhaust gas stream reducing the degrading of the used solvent. More research is needed to reduce the initial investment costs and examine the impact of the ships movement on the ab- and desorption processes (Feenstra et al., 2019).

Chemical absorption with MEA as solvent is applied in the concept for a H<sub>2</sub>-powered vessel by Lee et al. (2020) as well. Since the volumetric energy density of H<sub>2</sub> is low and there is no infrastructure for supplying vessels with H<sub>2</sub> as of now, the authors propose a system for onboard production of H<sub>2</sub> from two fuel alternatives: LNG (CH<sub>4</sub>) and methanol. An energetic and exergetic analyses is carried out to compare the two options, including the integrated CC plant. *Figure 4.2* shows a block diagram of the LNG-based option.



Figure 4.2: Block diagram of the steam methane reforming-based system as proposed by H. Lee et al. (2020)

The LNG from the onboard storage tank is evaporated by the heat of the captured and compressed  $CO_2$ . Afterwards, the gas stream is divided into two streams: one is utilised as feedstock for the reformer, the other one as fuel for the combustor. The feedstock  $CH_4$  stream is mixed with high temperature steam and is further preheated by reformate gas leaving the reformer before the feedstock is transferred into the reformer. Within the reformer, the  $CH_4$ -steam mixture is converted into  $H_2$ , CO and  $CO_2$ . Since these reactions are highly endothermic, additional heat

needs to be transferred from the combustor by burning  $CH_4$  added as fuel and burning-off gas from the fuel cell (unreacted  $CH_4$  and unused  $H_2$ ). The generated reformate gas is led to the water gas shift reactor, where CO and  $H_2O$  react exothermic to form further  $H_2$  and  $CO_2$ . Within the fuel cell, the chemical energy of the  $H_2$  is converted into electricity and heat, which is used for steam production. The anode off gas of the fuel cell is fed to the combustor, to convert unused  $H_2$  and unreacted  $CH_4$  for further heat generation. The exhaust of the combustor is supplied to the CC unit. The high amount of heat required for the desorption reaction is supplied from the excessive heat generated within the process. The captured  $CO_2$  is compressed and liquified using the cold energy from evaporating the LNG. The liquified  $CO_2$  is stored within onboard storage tanks.

The system using methanol as feedstock instead of LNG is similar, but, since the process is operating at lower temperatures, it is simpler. This means the heat generated by combusting the anode off gases is sufficient to cover the energy required for reforming the methanol. On the other hand, the methanol does not have to be vaporised before entering the process, which conversely means, that an additional refrigeration unit is required to liquify the captured  $CO_2$ .

Even though the simulations for the example vessel (3.000 DWT general cargo vessel), carried out for a fixed load of 475 kW, have shown that the methanol-based system gains a higher electrical efficiency, the authors highlight the advantages of the CH<sub>4</sub>-based system. The methanol-based system requires 1.1 times more space, and the fuel costs are 2.2 times higher than the CH<sub>4</sub>-fuelled alternative. It is concluded, that this technology is a feasible alternative on the transition to H<sub>2</sub>-fuelled ships, but further development is required (H. Lee et al., 2020).

Exploring the potential of a post-combustion CC process using aqueous ammonia onboard a  $CO_2$ carrier for simultaneous removal of  $CO_2$  and  $SO_x$  emissions from the exhaust, was the motivation of the research of Awoyomi et al. (2019). The advantages of using ammonia (NH<sub>3</sub>) instead of conventional amine solvents, are the lower heat required for regeneration, the low chemical costs, the thermal stability and tolerance towards pollutants and  $O_2$ . Additionally, its ability to release  $CO_2$  at higher pressure is reducing the required power for compression. Further, the integration of  $SO_x$  capture allows the production of saleable by-products. Challenges of the NH<sub>3</sub> absorption process have been revealed during the trials at the Munmorah pilot plant. The slow kinetics of  $CO_2$  absorption and the high volatility of NH<sub>3</sub> require larger equipment in regards to capacity and abatement technologies to reduce the ammonia-slip (Awoyomi et al., 2019).

The process simulated for a Wärtsilä 9L46F four-stroke engine running on HFO consists of a pretreatment for the removal of sulphur emissions and cooling of the exhaust gases, an NH<sub>3</sub> wash column to remove volatile NH<sub>3</sub> from the flue gas and an absorption tower to capture  $CO_2$ (Awoyomi et al., 2019). Thereby, the NH<sub>3</sub> contained within the flue gas leaving the  $CO_2$  absorber is scrubbed in the wash column by water. The NH<sub>3</sub>-rich wash water is pumped to the pre-treatment where the NH<sub>3</sub> reacts with the SO<sub>x</sub> contained in the exhaust, forming ammonia sulphate. The ammonia sulphate is filtered out of the NH<sub>3</sub> lean wash water and can be sold as fertiliser. The lean wash water is pumped back in to the NH<sub>3</sub> washing column. The results of the simulation show that at 85 % engine load, this process is able to capture 70 % of the  $CO_2$  and 98 % of the SO<sub>x</sub> emissions contained in the flue gas, merely using the waste heat of the engine (Awoyomi et al., 2019).

The required absorber packing height is 10 m at a diameter of 5 m (Awoyomi et al., 2019). The pre-treatment column has a packing height of 3 m and a diameter of 0,5 m. The stripper for regeneration of the  $NH_3$  solvent is determined to have a packing height of 6 m at a diameter of 2

m. These dimensions are similar to the measurements required for an MEA absorption plant. The two wash columns required for the absorber and the stripper need to have a packing height of 3 m, at a diameter of 0,5 m. Since the stripper is operating at an elevated pressure of 6 bar, the required energy for compression of the captured  $CO_2$  is reduced. The simulation includes a two-stage compression and liquefaction process, combining the liquefaction of the captured  $CO_2$  and the reliquefication of the boil-off gases from the  $CO_2$  in the cargo tanks. The liquified  $CO_2$  is pumped into the cargo tanks, thus eliminating the need for extra storage tanks (Awoyomi et al., 2019).

An economical evaluation of the proposed process for post-combustion CC using aqueous ammonia as solvent was conducted by Awoyomi et al. (2020) and published as a separate paper. Contradictory to the foregoing study, it was assumed that the engine is running on LNG. This makes the pre-treatment column redundant since LNG contains almost no sulphur. To achieve the required temperature of the exhaust gases prior entering the absorber, a direct contact cooler is replacing the pre-treatment column. Besides the utilisation of cold energy from vaporising the LNG before combustion, the economic effect of exhaust gas recycling (EGR) and the optimum concentration of the NH<sub>3</sub> solvent are investigated (Awoyomi et al., 2020).

The optimum solvent concentration is determined as 10 wt% ammonia, minimising the required energy for solvent regeneration (Awoyomi et al., 2020). Due to the reduced volume flow of exhaust gases and increased CO<sub>2</sub> concentration when applying EGR, the costs per ton of captured CO<sub>2</sub> could be lowered from 130  $f_{CO2}$  to 117  $f_{CO2}$  at a capture-rate of 90 %. Further, it is concluded that the costs per tonne of captured CO<sub>2</sub> are rising when the capture-rate is lowered, even if capital expenses are reduced (Awoyomi et al., 2020).

In connection to the Northern Lights project, Einbu et al. (2021) researched the potential of absorption-based CC using a 30 wt% MEA solvent onboard a CO<sub>2</sub>-carrier, thus also eliminating the need for additional storage tanks for the captured CO<sub>2</sub>. The results of their simulation demonstrate that the waste heat of the engine is not capable to achieve capture-rates above 50 %. The additional demand of thermal energy can be met by using a fuel afterburner, which would increase the fuel consumption by 6 - 9 % when running on LNG and by 8 - 12 % when running on MGO, respectively. The afterburning of fuel in the engine's exhaust gases increases the available heat for regeneration of the solvent and simultaneously increases the CO<sub>2</sub> concentration of the flue gas stream (Einbu et al., 2021).

To reduce the exhaust temperature to the required temperature prior entering the absorption column, the proposed design includes a direct contact cooler, which could potentially function as  $SO_x$  scrubber (Einbu et al., 2021). The conducted simulation achieved the lowest energy penalty with an absorption bed height of about 20 meters, which results in a total absorber tower height of approximately 30 meters. The authors propose that the absorption column could be split in several absorbers in series, to reduce the height, if required by the ships design. Further, the height could be reduced when the solvent flow through the absorber is increased, which would lower the initial investment but raise the operational expenses due to a higher energy demand for solvent regeneration. Reducing the absorption bed height from 20 to 5 m would result in an increase in fuel consumption from 6,5 % to 8 % (LNG), at a capture-rate of 90 %. This trade-off between CAPEX and OPEX is seen as an important degree of freedom in determining the required absorption bed height (Einbu et al., 2021).

In 2020, the Roadmap to Zero Emission from International Shipping, funded by the Japanese government, was released. The paper presents a strategy for the transition towards climate neutral shipping.

Besides concepts for alternative fuel and drive technologies, the Shipping Zero Emission Project developed a concept for a 20.000 TEU container vessel, equipped with onboard CC (Japan Ship Technology Research Association et al., 2020). The vessel is designed to operate on routes between the Far East and Europe, using a slow-running reciprocating engine to burn methanol fuels and is equipped with a liquid amine absorption plant for CO<sub>2</sub> capture. Furthermore, other CC techniques have been evaluated for the concept, but according to the report's authors these are not feasible, due to the low partial pressure of CO<sub>2</sub> in the exhaust. Considering the membrane technology for CC, a vacuum pump would be required to lower the pressure within the membranes for an efficient CO<sub>2</sub> capturing process, which would significantly increase equipment and operational costs. Therefore, the authors propose liquid amine absorption with KS-1<sup>TM</sup> as absorption liquid. The technical arrangement is expected to be able to achieve a capture-rate of 85,7 %, which might be increased by further development. The captured CO<sub>2</sub> is liquified for temporary storage onboard. Figure 4.3 shows the general arrangement drawing of the 20.000 TEU concept vessel. The vessel was extended by one additional container bay in comparison to a common 20.000 TEU vessel, to allow for the placement of the CC system in front of the stern funnel and the placement of the CO<sub>2</sub> and methanol tanks below the accommodation. The equipment connected to CC is occupying a space equivalent to 1.820 TEU for a single voyage and 2.550 TEU in case the CC system is designed for a round voyage. Since the study is just presenting a concept, it is addressing issues for the practical use of such technology onboard from a general point of view. The problems identified are similar to the ones named by Luo and Wang (2017) and are related to the ships motion during navigation, safety concerns, size and costs of the equipment and its operation. In order to achieve the goals of the proposed plan, it is concluded that further funding of research and technical development is required (JSTRA et al., 2020).



Figure 4.3: General arrangement of 20.000 TEU Container ship equipped with CC developed by JSTRA et al. (2020)

Utilising a medium range tanker with a capacity of 47.000 DWT and a 9.960 kW two-stroke main engine, Stec et al. (2021) conducted simulations to assess to which degree it is possible to capture  $CO_2$  with waste heat as only energy source for the post-combustion CC process. The authors thereby decided to use a 30 wt% MEA-based post-combustion CC for their model, since it can be installed without major changes to the ship's existing propulsion system. To enable the vessel to run on HFO and to protect the amine-solvent from degrading, the model is including a desulphurisation unit, which is installed upstream of the CC plant. The proposed closed-loop system for sulphur removal from the exhaust gases is also in charge of cooling the exhaust gases before entering the absorption tower (Stec et al., 2021). An exhaust gas fan is providing the necessary pressure to overcome the pressure drop through the absorber (Stee et al., 2021). The absorbent-fluid is continuously cycled between the absorber and the stripper, thereby heat is transferred from the lean solvent leaving the stripper to the rich solvent entering the stripper. To separate the  $CO_2$  bound by the amine-solvent, the liquid is heated up in the stripper by utilising waste heat from the engines exhaust gases and the  $CO_2$  compression unit. Since the study aims to merely use waste heat to regenerate the amine-solvent in the stripper, the capacity of the CC process is limited by the available waste heat. Depending on the available waste heat, a certain percentage of the exhaust gases is processed by the CC unit. The remaining exhaust is bypassed, i.e., only treated by the desulphurisation unit (Stee et al., 2021).

The available waste heat is dependent on the area of operation of the vessel, the study of Stec et al. (2021) therefore researched three scenarios: arctic, ISO reference and tropical conditions. The least waste heat is available under artic conditions, whereas under tropical conditions the most waste heat is available. Based on the results of Feenstra et al. (2019), the simulation is designed to capture 90 % of the CO<sub>2</sub> lead through the absorber, as this achieves the lowest costs per captured ton of CO<sub>2</sub>. Under arctic conditions, 35 % of the exhaust are passing the CC unit, achieving an overall capture-rate of 31,4 % of CO<sub>2</sub> emissions in the simulation. In the best case, under tropical conditions, 62 % of the exhaust are passing the absorber, achieving a simulation result of 56,5 % capture-rate. Further, the simulation is showing that the additional auxiliary power, needed to run the electrical pumps of the exhaust treatment plant, does not affect the overall CO<sub>2</sub> emission reduction. Excluding the occupied space and weight of the system the authors estimate, that the EEDI of the reference ship could be reduced by approximately 40 %, when installing the simulated CC process. Thereby, it would exceed the 30 % EEDI reduction factor required from 2025 onwards (Stec et al., 2021).

To include the impact of CC in the formula for the calculation of the EEDI, Sanghyuk Lee et al. (2021) introduce a factor representing the captured percentage of CO<sub>2</sub>. To validate the proposed method, the authors carry out a case study for a 53.000 DWT container feeder with a capacity of 3.840 TEU, fuelled by LNG. The case study is examining three cases: 45 %, 55 % and 70 % reduction of emitted CO<sub>2</sub>. In all cases, only a part of the exhaust stream is passing the CC unit, which is sized to achieve a capture-rate of 92 %. Due to the low partial pressure of CO<sub>2</sub> in the exhaust stream of the case study vessel, an amine solution is chosen for CC. The simulated process consists of a post-combustion chemical absorption process with activated MDEA as solvent. The solvent consists of MDEA as base component and PZ as activator. The activator is added to increase the absorption rate of CO<sub>2</sub>, to be able to reduce the necessary height of the absorption column. The downside is, that the energy required for sorbent regeneration is increasing. This disadvantage is accepted, in order to reduce cargo loss and the impact on the ships stability (Sanghyuk Lee et al., 2021).

The simulation is carried out to investigate the sizing of the required equipment to estimate the cargo loss, which is negatively impacting the EEDI (Sanghyuk Lee et al., 2021). The waste heat of the engine is utilised to regenerate the solvent in the stripper and was sufficient in all cases. The compression and liquefaction process is consuming more power than the actual capturing process, where the most energy is consumed by the blower required to overcome the pressure drop through the absorber. Irrespective of the differing volume flow of exhaust passing the absorber in the three examined cases, the packing height in the absorber is unchanged since it is more affected by the concentration of  $CO_2$  in the exhaust stream. The solvent flowrate as well as the diameter of the absorption columns are varied, to achieve the targeted capture-rate of 92 % (Sanghyuk Lee et al., 2021).

Based on the results of the simulation, the cargo loss is calculated by the equipment sizes and the respective arrangement in the vessel (Sanghyuk Lee et al., 2021). Thereby, the equipment is positioned centric in the ship's hull to reduce the impact on the stability. Overall, the case study reveals, that the CC ratio needs to be higher than the EEDI reduction intended, to take account of the cargo loss and increased energy demand (Sanghyuk Lee et al., 2021).

The CC-Ocean project is in line with the conclusion of the Japanese study (JSTRA et al., 2020) presented above. Supported by the Japanese government, K-Line, Mitsubishi Shipbuilding and ClassNK have formed an alliance in 2020 to develop and install a small-scale CC demonstration plant onboard a vessel (Ovcina, 2020). The test operation of the plant is planned to start in the middle of 2021 ashore, before it is installed onboard of the Corona Utility, an 88.715 DWT bulk carrier, by the end of 2021. The project aims to develop more compact equipment for the application onboard and to explore the requirements for a stable continuous operation at sea (Ovcina, 2020). Unfortunately, no further information can be found on which solvent is applied for the demonstration plant.

### Table 4.4: Literature on post-combustion chemical absorption for the application onboard ships

| Authors<br>(Year)         | Title  | Solvent                                       | TRL <sup>1</sup> | Ship type   | Main conclusion  | Additional information  |
|---------------------------|--|---|------------------|---|--|---|
| Dowell &<br>Shah (2012)   | Shipping and CCS: A system perspective   | MEA,<br>NH <sub>3</sub> ,<br>ionic<br>liquids | N/A              | Not specified   | MEA has major<br>drawbacks, NH3 and ionic<br>liquids are having energetic<br>advantages  | Literature review on alternatives for carbon<br>emission reduction of international shipping,<br>disadvantages of MEA, criteria for solvents in<br>shipping, advantages of NH <sub>3</sub> and ionic liquids        |
| Zhou &<br>Wang (2014)     | Carbon capture and storage -<br>Solidification and storage of carbon<br>dioxide captured on ships                | NaOH<br>+ CaO                                 | 3                | Not specified   | Major advantages in<br>comparison to liquefaction<br>of CO <sub>2</sub> , more research<br>needed to increase<br>efficiency          | Case ship study for capture of 20 % of CO <sub>2</sub> to meet<br>IMO 2020 goal, profit from selling product of CC<br>is able to exceed running costs   |
| Luo & Wang<br>(2017)      | Study of solvent-based carbon<br>capture for cargo ships through<br>process modelling and simulation             | MEA   | 2                | General cargo<br>vessel,<br>12.500 DWT,<br>17 MW                              | Ship design bears<br>constraints for CC,<br>additional power needed<br>to gain 90 % capture-rate                                     | Without additional power generation on board a capture-rate of 73 % is possible at a cost of 77,50 $\notin/t_{CO2}$ ; with additional power installation 90 % capture-rate is achievable at 163,07 $\notin/t_{CO2}$ |
| Wang et al.<br>(2017)     | Reviews on Current Carbon<br>Emission Reduction Technologies<br>and Projects and their Feasibilities on<br>Ships | N/A   | N/A              | Container<br>vessel,<br>6.300 TEU,<br>57.059 kW                               | High energy, material and<br>space requirements as<br>constraints; further<br>development necessary                                  | Review on current situation for emissions, policies<br>and technologies; prediction for future<br>development; comparison of different CC<br>technologies; examples for current incentives for<br>CCS included      |
| Fang et al.<br>(2019)     | Optimal Sizing of Shipboard Carbon<br>Capture System for Maritime<br>Greenhouse Emission Control                 | NaOH<br>+ CaO                                 | 2                | All-electric<br>ship concept  | CC needed to meet future<br>IMO GHG emission goals   | Including model based on real-life case study for an existing ship; cost/profit calculation   |
| Balcombe et<br>al. (2019) | How to decarbonise international<br>shipping: Options for fuels,<br>technologies and policies                    | CaO<br>powder                                 | N/A              | Not specified   | Combination of policies,<br>fuels and technology is<br>needed  | Overview of existing/researched technologies and policies to reduce the emissions by shipping   |
| Feenstra et<br>al. (2019) | Ship-based carbon capture onboard<br>of diesel or LNG-fuelled ships  | MEA +<br>PZ                                   | 2                | Inland ship<br>1.280 kW;<br>general cargo<br>vessel<br>8.000 DWT,<br>3.000 kW | CC is technically feasible<br>for onboard application;<br>costs per ton of captured<br>carbon are lower the<br>bigger the ship/plant | Both reference ships are equipped with dual fuel<br>engines (Diesel/LNG); diesel options are more<br>expensive due to additional refrigeration unit for<br>liquifying CO <sub>2</sub>                               |

| Authors<br>(Year)        | Title  | Solvent         | TRL <sup>1</sup> | Ship type  | Main conclusion   | Additional information  |
|--------------------------|--|-----------------|------------------|--|---|---|
| Awoyomi et<br>al. (2019) | CO <sub>2</sub> /SO <sub>2</sub> emission reduction in CO <sub>2</sub><br>shipping infrastructure  | NH <sub>3</sub> | 3                | CO <sub>2</sub> carrier,<br>10.800 kW                          | Maximum available waste<br>heat is sufficient to achieve<br>a capture-rate of 70 %  | NH <sub>3</sub> as solvent allows simultaneous removal of SO <sub>x</sub> and CO <sub>2</sub> ; by-products can be sold; simulation for different operation modes of the vessel; simulation of CC process based on Munmorah pilot plant |
| Lee et al.<br>(2020)     | Comparative Analysis of On-Board<br>Methane and Methanol Reforming<br>Systems Combined with HT-PEM<br>Fuel Cell and CO <sub>2</sub><br>Capture/Liquefaction System for<br>Hydrogen Fueled Ship Application | MEA             | 2                | General cargo<br>vessel,<br>3.000 DWT,<br>3.800 kW             | Alternative for hydrogen<br>fuelled ships is feasible,<br>but more extensive<br>research is needed                                    | Energetical analysis of methane/methanol-based<br>systems for comparison; general cargo ship with<br>shaft power of 3800 kW as reference for simulation   |
| JSTRA et al.<br>(2020)   | Roadmap to Zero Emission from<br>International Shipping  | KS-1™           | 2                | Container<br>vessel,<br>20.000 TEU,<br>55.000 kW               | Further funding and<br>research are needed to<br>achieve outlined goals   | Conceptual design for a 20.000 TEU container<br>vessel trading between Far East and Europe;<br>specific technical issues for onboard installation are<br>identified   |
| Awoyomi et<br>al. (2020) | Process and Economic Evaluation of<br>an Onboard Capture System for<br>LNG-Fueled CO <sub>2</sub> Carriers   | NH3             | 3                | CO <sub>2</sub> carrier,<br>10.305 kW                          | Operational profile of the<br>specific ship must be<br>studied to designing the<br>CC system  | Economic evaluation of NH <sub>3</sub> process developed by<br>Awoyomi et al. (2019); EGR reduces plant size and<br>increases capture efficiency; lowest cost achieved<br>were 117 $/t_{CO2}$ at a capture-rate of 90 %                 |
| Stec et al.<br>(2021)    | Reducing the energy efficiency design<br>index for ships through a post-<br>combustion carbon capture process  | MEA             | 2                | Medium range<br>tanker,<br>47.000 DWT,<br>9.960 kW             | Post-combustion CC is<br>feasible to fulfil EEDI<br>requirements just by<br>utilising waste heat                                      | Simulation investigating CC process under various<br>ambient conditions (arctic, ISO, tropical); capture-<br>rate is adjusted to the available waste heat; exhaust<br>gas desulphurisation to protect amine solvent from<br>degrading   |
| Lee et al.<br>(2021)     | Novel methodology for EEDI<br>calculation considering onboard<br>carbon capture and storage system   | MDEA<br>+ PZ    | 2                | Container<br>feeder,<br>3.840 TEU,<br>53.000 DWT,<br>18.200 kW | CO <sub>2</sub> capture-rate needs to<br>be higher than intended<br>EEDI reduction to<br>compensate additional<br>power demand for CC | Waste heat of the engine is sufficient to supply<br>energy required for regeneration of the solvent in<br>all cases simulated; compression and liquefaction<br>consumes more power than CC process itself                               |

| Authors<br>(Year)     | Title   | Solvent          | TRL <sup>1</sup> | Ship type                                | Main conclusion   | Additional information  |
|-----------------------|---|------------------|------------------|--|---|---|
| Einbu et al<br>(2021) | Onboard CO <sub>2</sub> capture from ship<br>engines                          | MEA              | 2                | CO <sub>2</sub> carrier,<br>5675 kW      | Available waste heat is not<br>sufficient to supply energy<br>required for capture-rate<br>higher than 50 % | Part of the Northern Lights project; fuel<br>afterburner required to increase available heat for<br>regeneration of solvent; reduction of absorber<br>height and increase of solvent flow rate offer trade-<br>off opportunity CAPEX/OPEX |
| Ovcina<br>(2020)      | K Line to test world's 1st CO <sub>2</sub><br>capture plant on board its ship | Not<br>specified | 7                | Bulk carrier,<br>88.715 DWT,<br>9.960 kW | N/A   | CC-Ocean project is funded by the Japanese<br>government; world's first carbon capture<br>application onboard a vessel; no scientific papers<br>published   |

<sup>1</sup> The TRL in this table is reflecting the state of the research described in the respective article/report. It is not indicating the TRL of the corresponding technology and is not used as basis for the assessment in chapter 5.

#### 4.1.2 Adsorption by solid sorbents

Adsorption describes the adherence of atoms, molecules or ions from a gas or liquid to an adsorbent surface, on which a film of adsorbate is formed. When the adsorption is occurring through van der Waals forces at the adsorbents surface, the process is defined as physisorption. Contrary to that, when adsorption proceeds through a covalent bonding of the substances to the surface, it is referred to as chemisorption (Ben-Mansour et al., 2016; Wilcox, 2012). *Table 4.5* is summarising key data on adsorption by solid sorbents obtained from the consulted literature.

Chemisorption is proceeding much slower than physisorption, caused by the electron transfer which is required to establish a proper bonding to the adsorbent. Based on the comparably slow pace of adherence, chemisorption is an inappropriate method when large volumes of  $CO_2$  are to be captured from the flue gases. The principle of physisorption is providing a more suitable solution in terms of faster capturing process and lower energy requirements for sorbent regeneration (Ben-Mansour et al., 2016; Wilcox, 2012).

Another difference between these two processes is the temperature, at which the process is occurring. A relatively low heat of adsorption is typically connected to physisorption, whereas high adsorption heat usually refers to chemisorption (Ben-Mansour et al., 2016; Wilcox, 2012).

Table 4.5: Key data on adsorption by solid sorbents

| TRL | CAPEX | OPEX           | Space | ICE<br>compatible | # of<br>articles |
|-----|-------|----------------|-------|-------------------|------------------|
| 6   | -     | Lower than MEA | -     | No                | 2                |

#### 4.1.2.1 Technology setup and operating principle

The adsorption of  $CO_2$  takes place in an adsorber unit, which is containing solid sorbent materials, arranged in columns. Flue gas is perfusing the adsorber where it is contacting with the surface of the adsorbent. The adsorbent itself is specifically designed for a selective adsorption of  $CO_2$  from the gas mixture. Especially  $CO_2$  contained in dilute mixtures, can effectively be separated by adsorption (Wilcox, 2012).

There are two general technology setups of CC identified in the consulted literature, namely fixedbed adsorbers and moving-bed adsorbers. In a fixed-bed adsorber system, one adsorber unit (one bed) is in charge for adsorbing  $CO_2$  from a feed stream at a time. Another bed is kept off the gas stream as long as there is an ongoing adsorption in the first unit. When saturation of the adsorbent in the first bed is reached, a switch-over to the second unit is conducted. To allow for the time of regeneration of the beds, a cyclic alternation in each unit between capturing and desorption is required (Wilcox, 2012). A simplified schematic of the general setup of a fixed-bed adsorber is displayed in *Figure 4.4*.



Figure 4.4: Simplified schematic of a fixed bed adsorber using TSA

Moving-bed adsorbers use a different component setup. Contrary to the fixed-bed system, the adsorption and regeneration processes are not performed in the same unit. As soon as it reaches saturation the solid adsorbent is transferred from the adsorber to a regeneration unit. In return, regenerated adsorbent from the regeneration unit is added to the adsorber in a cyclic process. The  $CO_2$  feed stream is perfusing the adsorber unit in a counter-current to the adsorbent, which enters the adsorber from the contrary end of the unit (Wilcox, 2012). Favourable for this system is the continuous exhaust gas stream in the adsorber, without required interruptions for regeneration of the adsorbert. Additionally, the undesirable pressure drop of the flue stream within the adsorber unit is lower than in the fixed-bed system (K. Kim et al., 2013). A drawback of this system is the occurring wear and tear, due to the movement of the adsorbent within the system. This is reducing the lifetime of both, the solid adsorbent and the contacting components, which ultimately leads to additional costs for the operator (Wilcox, 2012)

Same as the absorption system, the adsorption setup involves a variety of auxiliary equipment, such as blowers/fans to overcome the pressure drop of the adsorber and to elevate the flue gas pressure before it reaches the adsorber (see *PSA*). In addition, heat exchangers are used to cool down the inlet flue gas of the adsorber.

The  $CO_2$  adsorption and sorbent regeneration within the adsorption beds can be executed through different adsorption cycles. Three of the most common cycles in fixed-bed systems are presented in the following paragraphs. The volume of gas to be treated and the concentration of  $CO_2$  within the gas mixture are main factors which have to be considered when selecting the appropriate adsorption cycle for the application (Wilcox, 2012).

In a pressure-swing adsorption (PSA) cycle, the  $CO_2$ -containing gas mixture is led into the adsorber unit at an elevated pressure, typically between 6-10 bar (Ben-Mansour et al., 2016). While the gas mixture perfuses the adsorber, the adsorption of  $CO_2$  is proceeding.  $CO_2$ -lean gas is leaving the adsorber unit while the captured  $CO_2$  is retained in the solid adsorbent. When saturation of the sorbent bed is reached, the feed-value to this bed is closed and a switch-over to another sorbent bed is conducted. The regeneration of the saturated sorbent bed is done by lowering the pressure into the unit, which releases the captured  $CO_2$  from the adsorbent. The displaced  $CO_2$  is then

discharged from the unit for storage. After successful desorption of the  $CO_2$  from the adsorbent, the regenerated sorbent bed is ready for the takeover of the next adsorption cycle (Ben-Mansour et al., 2016; Wilcox, 2012).

Similar to the technology of PSA, vacuum-swing adsorption (VSA) can be applied. Instead of pressurising the flue gas when entering the adsorber, the pressure is lowered to a level below the atmospheric pressure for the adsorption process, and contrary, elevated again for the desorption process (Ben-Mansour et al., 2016).

Temperature differences can be used for adsorption and desorption cycles as well. *Figure 4.4* is showing a fixed-bed adsorber, utilising temperature-swing adsorption (TSA). In TSA, the gas feed is cooled down by utilising a cooling gas stream before it reaches the adsorber. After the adsorption occurred, the adsorber bed is changed over to another unit in the same manner as in the other adsorption cycles, when  $CO_2$  saturation is attained. Desorption in TSA is done by heating up the sorbent bed in the regeneration process with a hot gas stream, generated by an additional heater unit, which is setting free the  $CO_2$  from the sorbent bed (Creamer & Gao, 2016). The regeneration process in PSA and VSA is working similar to TSA but instead of a steam regeneration, compressor units or vacuum pumps are used to elevate or lower the pressure in the adsorber bed.

Different technologies of adsorption and desorption demand different properties of the sorbent (Creamer & Gao, 2016). According to Ben-Mansour et al. (2016), crucial properties for a sorbent, that decide the suitable adsorption concept, are: "adsorbent selectivity, adsorbent capacity, ease of and energy required in desorption". Liu, Shi, Wang, Gao, & Xu (2021) further added, that a good mechanical strength, which equals to a longer lifetime of the sorbent. Related costs (purchasing price) need to be considered, to find an appropriate adsorbent for the individual application. Samanta, Zhao, Shimizu, Sarkar, & Gupta (2012) also highlighted the chemical stability, which is describing the tolerance to impurities and oxidising (flue gas) environments of the sorbent.

Extensive research has been carried out on different adsorbent materials for CC. Zeolites, metalorganic frameworks (MOF), porous silica and carbon-based materials (such as activated carbon) are common physical adsorbents, but also solid amine-based materials which are based on chemical reactions with the CO<sub>2</sub>, have been examined (X. Wang & Song, 2020).

#### 4.1.2.2 Field of current application and TRL

All of the aforementioned sorbent materials are lacking maturity and are currently not applied in commercial CC from flue gas applications. According to Ben-Mansour et al. (2016), further research of the adsorbents regarding their stability and performance is required. Synthetic zeolite materials have been tested in simulations as well as on experimental base and are considered the most promising adsorbent for CC from flue gases (TRL 3). Currently, zeolites are used for direct air capture gas separation and  $H_2$  purification (Ben-Mansour et al., 2016).

Simulations and experimental modelling of moving-bed adsorption systems for CC in flue gas environments were carried out in various researches (Jung et al., 2018; K. Kim et al., 2013; Mondino et al., 2017). In simulated flue gas environments of coal-fired power plants, high purities of  $CO_2$  were achieved. Further, the total energy demand of the simulated processes was much lower than in conventional adsorption systems, therefore the potential for costs savings of this setup has been demonstrated. In an outlook for commercial CC applications, TSA and PSA cycles are considered to be the most practically feasible technologies (Ben-Mansour et al., 2016). Wilcox (2012) is indicating the same conclusion, based on a  $CO_2$  concentration in the flue gas between 3 - 10 %.

X. Wang & Song (2020) reported the development of a structured solid adsorbent, used in a large adsorption pilot plant in flue gas environments. The pilot plant by Svante is a novel rotary singleunit, operated by TSA cycles and designed for large flue gas volumes at low pressures of diluted flue gases from industrial plants, e.g., from the cement and steel industry (Svante Inc., 2021). According to Kearns et al. (2021), the CC plant by Svante is marking the latest development in the post-combustion adsorption technology (TRL 6). However, the simulated flue gas conditions which were used in the pilot plant by Svante had a CO<sub>2</sub> concentration of 17 % in the flue gas stream (Hovington et al., 2021). This concentration is a lot higher than the one arising from fuel combustion in ICEs. The lower the CO<sub>2</sub> concentration is, the less effective the capture process will be, i.e., less economically favourable and therefore less feasible for the operator. Moreover, adsorbent materials which are currently available are affected by efficiency losses due to thermal degradation, caused by the high temperatures prevalent in flue gases from ICEs (X. Wang & Song, 2020). The authors of this thesis evaluate the post-combustion CC adsorption technology from flue gases to not be feasible for the use in connection with flue gases from ICEs, at current state.

#### 4.1.2.3 Costs

The CAPEX of the adsorption technology comprises of the costs for the equipment involved in the capture process. Main contributors to the CAPEX are the adsorber unit, particularly the packing with the adsorbent being in correlation to the required height of the bed. Further involved are the costs for the auxiliaries, such as the blowers in the flue gas, compressors or vacuum pumps (depending on the chosen adsorption cycle) and coolers (Wilcox, 2012). The equipment needs to be dimensioned for the application, which means that large-scale applications naturally require larger equipment for the CC process. Consequently, the CAPEX for the adsorber are increasing with larger sorbent beds and decreasing with smaller beds. The connection between the adsorber size and the cycle time is described under 4.1.2.4 Space requirements. Another influencing factor to the adsorber size is the adsorbent. The better the adsorbent is, e.g., the higher its porosity, the better the mass-transfer rate of  $CO_2$  to the sorbent, which directly relates to smaller bed sizes and therefore to lower CAPEX and further, to lower OPEX for bed regeneration and blower electricity (Wilcox, 2012).

Operating and maintenance costs, including the energy requirements for the process and its auxiliaries, compose the OPEX of this technology. Two major sources of the overall energy demand are the electricity costs for the blowers, to overcome the pressure drop in the adsorber and the regeneration costs for the adsorbent. In PSA and VSA, the energy costs are related to the required elevated pressures in the adsorption/desorption process or the vacuum conditions, respectively. The higher the flowrates of flue gas and the larger the volumes, the more energy is required for the compression. In TSA, the energy demand originates from the heat required for regeneration (Wilcox, 2012). The costs for the solid sorbent are further contributing to the OPEX. Zeolites and silica are advantageous in comparison to other adsorbents, because of their low production costs and their lower purchase price. In the contrary, MOFs are considered to be uneconomical, due to their high production costs, which make them less competitive to other sorbents (Seul-yi Lee & Park, 2015). An optimal adsorbent is cheap in the purchase and shows low OPEX for sorbent regeneration.

No specific price-linked statements are provided in the available literature. Nevertheless, a range of the additional load which arises by the CC technology, is stated in a study by M. Wang et al. (2015). Between 5.4 to 9 % energy penalty is added, by installing an adsorption technology. As aforementioned, the main energy demand is dedicated to the sorbent regeneration, which in this case is between  $0.5 - 3.12 \text{ MJ/kg}_{CO2}$  (M. Wang et al., 2015). The same study also comprises data of the energy penalty for the comparison with a MEA absorption technology (8.2 – 14 % additional load), and an energy demand of up to 6 MJ/kg<sub>CO2</sub> (M. Wang et al., 2015). It is apparent, that the adsorption technology is less energy demanding than the benchmark process, which directly relates to lower OPEX for the operator.

Concluding, without stated figures in the consulted literature for the CAPEX of an adsorption plant, providing qualified estimates for the CAPEX in comparison to the benchmark process is problematic. Therefore, the CAPEX of the post-combustion adsorption technology cannot be compared against the MEA absorption within this thesis.

#### 4.1.2.4 Space requirements

When adsorption CC with fixed-bed adsorbers is applied in continuous flue gas flows, multiple beds are needed, to allow for adsorption and regeneration cycles without having to reduce the flue gas volumes. Depending on the duration and type of adsorption cycle, the adsorption or regeneration of the bed may take longer than the opposing cycle. Meaning, in case of a slower regeneration, two (or even more) adsorbent beds will have to be in the regeneration cycle, while one bed is in the adsorption cycle, to ensure that at least one bed is available for the takeover of the adsorption cycle at any time. Inevitably, more space is required by the adsorption system (Wilcox, 2012).

As stated above, the adsorption/desorption cycle time may vary. Together with the volume of flue gas, which is sent through the adsorber, the cycle time is an influencing factor to the length of the adsorber bed. A higher bed is elongating the cycle time but at the same time, the unfavourable pressure drop through the adsorber unit increases. Vice versa, the faster the cycle-frequency, the lower the required bed size and therefore less space demand of the adsorber unit. A potential drawback of reduced cycle times due to higher cycle frequency, is the lower efficiency of the beds since saturation of the adsorbent may not be achieved in a short-time period (Wilcox, 2012). Generally, an estimation of the required bed size can be done by utilising the flowrate and the intended cycle time for the process. According to Wilcox (2012), the superficial velocity of the gas mixture through the adsorbent bed should not exceed 0.45 m/s, to ensure enough time for the adsorption process. Consequently, in high gas flows, immense bed sizes are required to handle the streams.

The total space demand of this technology is determined by the components and the connected auxiliaries required for the CC process. However, the available literature is lacking specific data on the dimensions of a post-combustion CC adsorption plant. Therefore, no assumption in regards of the space demand of this technology, nor in relation to the MEA absorption can be made.

#### 4.1.2.5 Advantages and drawbacks

Drawbacks of this technology in connection with the potential use in flue gases are mostly connected to the properties of the adsorbents. Most of the physical adsorbents are operated at low-temperature conditions, which are unlikely to be prevalent in flue gases (Sayari et al., 2011). Especially at higher temperatures, the capacity of the physical adsorbents is decreasing (X. Wang & Song, 2020). Amine adsorbents are affected by oxidation and further by thermal degradation.

Another major drawback of these kinds of adsorbents is their incompatibility to  $SO_x$  and  $NO_x$  contaminants in the flue gas since it causes them to degrade (X. Wang & Song, 2020). The efficiency of zeolites and MOFs is affected by the presence of water vapour in the flue gas, since these adsorbents preferentially adsorb water before  $CO_2$  (Sayari et al., 2011).

Favourable for physical adsorbents, such as zeolites and MOFs, is their good  $CO_2$  capture capacity at high pressures and low temperatures. Solid amine-based sorbents, however, are able to capture high capacities at low partial pressures of  $CO_2$ . Further, they also show better  $CO_2$  selectivity than physical adsorbents (X. Wang & Song, 2020). Adsorption technologies in general have a high potential in capturing  $CO_2$  directly from air, rather than from (high-temperature) flue gases (X. Wang & Song, 2020). Nonetheless, advances in the technology as well as in new adsorbents have been made, which is demonstrated by the Svante pilot plant and its capability of  $CO_2$  capture from flue gas (Svante Inc., 2021).

#### 4.1.2.6 Research for the application onboard

Only a single study could be identified, which is exclusively focussing on the application of adsorption by physical solvents in marine applications. The second research presented in this section developed a model for the application in road transport but is claiming that the technology could be sized up to be feasible for the capture of  $CO_2$  from ships exhaust. It is worth noting, that both identified articles are applying TSA. The main information on both articles is summarised in *Table 4.6*.

In 2018, Erto et al. published the results of their research, investigating the potential of aluminasupported  $K_2CO_3$  for the capture of  $CO_2$  from the exhaust of marine diesel engines. In comparison to absorption with solvents, the authors name several advantages of the fixed-bed adsorption process: use of non-hazardous and non-corrosive materials as well as a high operating flexibility (able to manage variable inlet gas flow and  $CO_2$  concentrations). Further, the chosen sorbent ( $K_2CO_3$ ) can capture  $CO_2$  at temperatures below 100 °C and in humid conditions. The regeneration temperature is generally lower than 200 °C. Since sulphur dioxide ( $SO_2$ ) is competing with  $CO_2$  for the adsorption, a sulphur scrubber is needed when the ship is operating on high sulphur fuels (Erto et al., 2018).

Following lab-scale experiments to determine the best operating temperatures and  $K_2CO_3$  concentration, a case study is conducted for a RoPax ferry (Erto et al., 2018). The ferry is propelled by a 4.350 kW engine running on MGO and is operating on a one-hour route. Based on the lab-scale results, a conventional TSA unit is designed. The adsorption takes place at 60 °C and the regeneration at 120 – 200 °C using steam. The proposed system consists of two columns: one being in service, one being generated. To handle the exhaust flow of the case study vessel, the sorbent beds are calculated to be 3,89 m in diameter and 0,56 m in height. Unfortunately, the regeneration time is almost double the time required to saturate the adsorbent with  $CO_2$ , i.e., the adsorber is operating effectively only for half of the cycle time. Nevertheless, a  $CO_2$  reduction rate of 27,8 to 28,4 % (including the additional power required to operate the plant) can be achieved (Erto et al., 2018).

Erto et al. (2018) conclude, that the plant design has large margins for improvement, especially in regard of the optimisation of the  $CO_2$  loading capacity of the  $K_2CO_3$  sorbent. Since the proposed process is operating at similar temperatures as the absorption process using MEA, but without the typical drawbacks of such, the proposed method is seen as promising for the marine application (Erto et al., 2018).

Sharma and Maréchal (2019) have developed a concept for an energy self-sufficient CC and liquefaction system. In the centre of the proposed technology is a TSA-cycle using PPN-6-CH2-TETA as adsorption material for  $CO_2$ . Besides the adsorption cycle, the system consists of a Rankine cycle, a heat pump and  $CO_2$  compression and liquefaction unit. Thereby, the Rankine cycle utilises the waste heat available in the exhaust stream to provide the mechanical power required to drive the heat pump compressor and the  $CO_2$  compressor. In the simulation, the system reached a 90 % capture-rate. Even though the model and simulations have been designed for a truck engine, the researchers claim that this technology can be scaled up to any internal combustion engine within the transportation sector, also including marine diesel engines (Sharma & Maréchal, 2019).

| Authors<br>(Year)              | Title  | Sorbent  | TRL <sup>1</sup>   | Ship type   |
|--------------------------------|--|--|--|---|
| Erto et al.<br>(2018)          | Utilization of alumina-supported<br>K <sub>2</sub> CO <sub>3</sub> as CO <sub>2</sub> -selective sorbent:<br>A promising strategy to mitigate the<br>carbon footprint of the maritime sector | Alumina<br>supported<br>K <sub>2</sub> CO <sub>3</sub>   | 3  | RoPax ferry<br>4.350 kW   |
| Sharma &<br>Maréchal<br>(2019) | Carbon Dioxide Capture From Internal<br>Combustion Engine Exhaust Using<br>Temperature Swing Adsorption  | PPN-6-<br>CH-TETA  | 2  | Not specified   |
| Authors<br>(Year)              | Main conclusion  | Additional in  | nformat  | ion   |
| Erto et al.<br>(2018)          | Potential for marine application, but<br>improvements regarding the loading<br>capacity of the sorbent need to be<br>achieved  | TSA process is operating on same temperature level<br>as MEA process but without drawbacks of MEA;<br>regeneration of the adsorption column takes double<br>time than adsorption |  |   |
| Sharma &<br>Maréchal<br>(2019) | Proposed system is energy self-<br>sufficient, development of prototype<br>required to gain experimental data  | System utilise<br>additional en-<br>analysis; com<br>the example o<br>combination  | es waste l<br>ergy cons<br>parison v<br>of a truck<br>with any | heat from exhaust for<br>sumed by CC; energetical<br>with installation of fuel cells for<br>x; technology can be used in<br>ICE |

| Table 4.6: Literature on | post-combustion | adsorption for | r the application | onboard |
|--------------------------|-----------------|----------------|-------------------|---------|
|--------------------------|-----------------|----------------|-------------------|---------|

<sup>1</sup> The TRL in this table is reflecting the state of the research described in the respective article/report. It is not indicating the TRL of the corresponding technology and is not used as basis for the assessment in chapter 5.

#### 4.1.3 Membrane technology

Post-combustion CC through membrane separation is a widely researched topic with continuous growing interest in the past two decades (Siagian et al., 2019). In the industry, membranes are used in various different fields due to their ease of separation, which is one of the biggest merits of this technology (Wilcox, 2012). In marine applications, membrane technologies are currently utilised in reverse osmosis plants for desalination of seawater, for the purpose of freshwater generation onboard (Greenlee et al., 2009). *Table 4.7* is summarising key data on membrane separation of  $CO_2$ , which are further described in this section.

Table 4.7: Key data on membrane technology

| TRL | CAPEX           | OPEX            | Space         | ICE<br>compatible | # of<br>articles |
|-----|-----------------|-----------------|---------------|-------------------|------------------|
| 5   | Higher than MEA | Higher than MEA | Less than MEA | Yes               | 1                |

#### 4.1.3.1 Technology setup and operating principle

The configuration of the membranes as well as the membrane design can vary in the different applications. Common membrane configurations in commercial use are plate & frame membranes, spiral wound membranes or hollow fibre membranes (Wilcox, 2012). However, for the purpose of  $CO_2$  removal from a feed gas, two main technologies can be identified: membrane gas separation (MGS) and membrane contactors (MC), which are further described in the following paragraphs (Siagian et al., 2019; Wilcox, 2012).

MC technologies are operated with microporous membranes, acting as a separating wall between a  $CO_2$ -rich gas stream and a liquid phase of absorbing solvent. The solvent, which is often aminebased, is meant to selectively absorb  $CO_2$  once it diffused through the membrane. The selectivity for the explicit removal of  $CO_2$  from the feed gas is, for the greater part, achieved by the properties of the solvent and lesser by the membrane itself. (Siagian et al., 2019).

The operating principle of the MC technology is rather simple. Flue gases containing  $CO_2$  are entering the gas side of the membrane and are treated and separated by contacting the membranes surface. On the gas outlet, the retentate, a gas stream with lean  $CO_2$  concentration is leaving the unit. Whereas on the sorbent side of the membrane the absorbing solvent is circulating, which is referred to as the permeate, after the  $CO_2$  has been absorbed (Khalilpour et al., 2015). The liquid sorbent in the MC process is regenerated in a regeneration unit in the same way as described in chapter 4.1.1 Absorption by chemical solvents.

The pores of the membrane are ideally only filled with feed gas but no absorbing solvent. Hydrophobic membrane materials are used in MC, to prevent the so-called wetting phenomenon of the membrane where liquid solvent is soaked into the membrane and therefore lowering the mass transfer rate by raising the resistance (Siagian et al., 2019). Generally, the higher the porosity the lower the resistance in mass transfer but at the same time the higher the risk of wetting of the membrane. Furthermore, the utilised membrane material needs to withstand the characteristics of the chemical solvent and the feed gas as well as thermal and chemical influences. All of those in sum could lead to the degradation or fouling of the membrane (Khalilpour et al., 2015; Siagian et al., 2019).

In the MGS system, the general technology setup is similar to the MC technologies. The main difference in the setup is, that the permeate side of the membrane is a gaseous phase too. To

enhance the effectivity of  $CO_2$  removal from the flue gas, a compressor unit is elevating the pressure of the feed gas before entering the membrane unit. Some systems use vacuum pumps on the permeate side of the membrane, to achieve similar effects of increased efficiencies (Xu et al., 2018).

It is possible to recirculate the  $CO_2$ -enriched permeate stream into a second or third membrane unit and thereby increase the  $CO_2$  capture-rate, as it is shown in *Figure 4.5* (Khalilpour et al., 2015). On the other hand, this will result in to additional costs for compressors or vacuum pumps and membranes, higher space requirements and extra energy consumption (Siagian et al., 2019; Xu et al., 2018). The principle of serial or parallel use of multiple membranes can be applied for the MC system as well.



Figure 4.5: Schematic of a multi-stage membrane CO<sub>2</sub> separation process

In MGS, the membrane design is slightly different than in MC, as the membrane is denser and non-porous (Siagian et al., 2019; Wilcox, 2012). Contrary to MC technologies, the  $CO_2$  selectivity in MGS is only attained by the membrane, which means that the appropriate choice of membrane design, configuration and material is crucial for a high selectivity and efficiency of the process (Siagian et al., 2019). The separation of  $CO_2$  can occur through different mechanisms, e.g. via *molecular sieving*, where larger molecules are excluded by the membranes' dense design and the virtue of their size (Siagian et al., 2019; Wilcox, 2012). Another mechanism is the *solution diffusion* through polymeric membranes, where  $CO_2$  molecules are absorbed by the membrane, subsequently diffuse through the same and are desorbed on the permeate gas side. Solution diffusion is the most commonly used mechanism at the present day (Siagian et al., 2019).

#### 4.1.3.2 Field of current application and TRL

MGS technologies for  $CO_2$  removal from natural gas are used in industrial-scale applications since several decades. Numerous natural gas on- and offshore applications have successfully been upgraded by a membrane-based  $CO_2$  capture plant (Siagian et al., 2019).

However, several challenging factors are retaining membrane technologies from the use in flue gas separation. The large volume of feed gas with typically low  $CO_2$  concentration of less than 20 % in flue gases from power plants is making the use of MGS membranes uneconomically. The flue gas compression, required to achieve the driving force of separation, causes high operational costs. MC technologies are capable of capturing  $CO_2$  in lower concentrations (< 20 %) but are affected to membrane degradation caused by the flue gas (Siagian et al., 2019).

Even though research has shown that membrane technologies in general have high potential to be applied in commercial CO<sub>2</sub> separation from flue gases, they are not used in large-scale applications

yet. However, both membrane processes have been used in research and development stages e.g. pilot plants, but are retained by the reasons given above (Han et al., 2020; Khalilpour et al., 2015; Siagian et al., 2019). Therefore, the authors assess the membrane separation to be at TRL 5.

### 4.1.3.3 Costs

The CC efficiency of membrane technologies is depending on various factors, some of them have been mentioned in 4.1.3.1 Technology setup and operating principle. Of course, the operating efficiency is directly related to OPEX and CAPEX. In flue gas applications one particularly important factor influencing the capturing efficiency of the membrane, is the typically low concentration of  $CO_2$  in the flue gas (3 - 14 vol%). Different researches validated, that "at such conditions, a single-stage membrane cannot produce high quality permeate or retentate even at very high inlet pressures and/or over large membrane areas" (Khalilpour et al., 2015; Siagian et al., 2019).

To make up for the low efficiency of a single membrane, multiple membrane units have to be used. This means, that the CAPEX are significantly rising, since more membrane separation units are required and therefore extra membrane surfaces. The OPEX are higher as well, based on the additional energy requirements for the compression (Khalilpour et al., 2015). Siagian et al. (2019) show in their review article, that the MGS technology at a concentration of 13 % CO<sub>2</sub> in the flue gas and a flue gas flow of about 1600 m<sup>3</sup>/h has CO<sub>2</sub> capturing costs of 82 \$/t<sub>CO2</sub>. Compared to that, a MC technology used in almost the same CO<sub>2</sub> concentration (13.31 vol% in flue gas) with a flowrate of 894 kg/s, has CO<sub>2</sub> capture costs of about 39.3 \$/t<sub>CO2</sub> (Siagian et al., 2019).

#### 4.1.3.4 Space requirements

As stated in the cost section above, low  $CO_2$  concentrations in the flue gas require multiple membrane units and/or larger membrane contact surfaces. Consequently, more space is required by the CC plant (Xu et al., 2018). The space occupied by the membranes further depends on the flowrate of the flue gas, i.e., higher flowrates demand larger CC plants. Additional space is occupied by the compressor units, which are required by the working principle of the MGS technology.

Probably the largest issue contributing to the space requirements of this technology, is the need of intense pre-treatment of the flue gases before  $CO_2$  can be captured (Siagian et al., 2019). However, since space considerations have not been an issue for land-based applications of CC from flue gases by membrane technologies yet, there is no literature published which is addressing the occupied space of such a plant.

Nevertheless, membrane technologies are a promising solution for small-space environments, and further, e.g., for onboard applications (S. M. Nazir, personal communication, 06.05.2021). The authors evaluate the CC process by membranes to be less space consuming than MEA absorption technologies.

#### 4.1.3.5 Advantages and drawbacks

For commercial applications of  $CO_2$  removal from natural gases, polymeric membranes are preferably used, due to their high selectivity, ease of fabrication into different configurations and low manufacturing costs. The downside of the polymers is the physical aging and plasticisation, which occurs when  $CO_2$  is solubilising in the membrane and therefore lowering the permeability of the membrane. This is negatively affecting the efficiency of the separation process (Siagian et al., 2019). Both membrane technologies (MC and MGS) require intense pre-treatment of the flue gas. This is due to the fact, that impurities in the flue gas are negatively influencing the performance of the membrane. Membrane fouling, membrane degradation and the wetting phenomenon are possible results, if harmful contaminants (including water) are not removed from the flue gas, upstream of the  $CO_2$  capture process (Siagian et al., 2019).

Favourable for MGS systems is the unnecessity of the liquid absorbent in comparison to MC, which means that there is no need of additional equipment for chemical regeneration in this process. Nevertheless, due to the higher energy penalty for flue gas compression, MGS results in higher operational costs than MC. In favour for both technologies is the general possibility of retrofitting into existing systems (Siagian et al., 2019).

#### 4.1.3.6 Research for the application onboard

As stated above, the membrane technology is not yet readily developed for CC from flue gases, since major problems still need to be solved to increase the lifetime of the membranes. This is also reflected by the consulted literature, where only one article could be identified, that is considering the application of membrane technology for CC from marine exhaust gases. *Table 4.8* is summarising the key statements of the literature for membrane separation onboard vessels.

Thereby, Su et al. (2020) mainly focussed on options to utilise waste heat from marine ICEs and integrated the membrane technology for CC in their concept, as it is expected to significantly decrease the required energy for CC, once it is available for commercial use. The simulation is developed based on a marine ICE, fuelled by LNG. The captured  $CO_2$  is liquified by using the cold energy generated from evaporating the LNG, prior combustion. Furthermore,  $CO_2$  is used as working fluid within one of the waste heat recovery cycles (Su et al., 2020). Even though, CC technology is not the focus of this study, it shows that the combination of LNG-evaporation and  $CO_2$ -liquefaction has high potential for energy savings.

The HyMethShip project, a pre-combustion CC concept, is including a membrane reactor, which is combining the conversion of methanol into  $H_2$  and  $CO_2$  and the separation of  $H_2$  in one process step (Zelenka et al., 2019). Nevertheless, the HyMethShip concept is a pre-combustion application of membrane technology and is therefore addressed in section 4.2.6.

| Authors<br>(Year)  | Title  | TRL <sup>1</sup>   | Ship type     |  |
|--------------------|--|--|---------------|--|
|                    | Green and efficient configuration of integrated waste<br>heat and cold energy recovery for marine natural<br>gas/diesel dual-fuel engine | 2  | Not specified |  |
| Su et al. $(2020)$ | Main conclusion  | Additional information   |               |  |
| (2020)             | Proposed waste heat recovery system offers potential for<br>additional energy savings  | Cold energy recovered from<br>evaporating LNG is used to liquify<br>captured CO <sub>2</sub> |               |  |

Table 4.8: Literature on membrane separation for the application onboard

<sup>1</sup> The TRL in this table is reflecting the state of the research described in the respective article. It is not indicating the TRL of the corresponding technology and is not used as basis for the assessment in chapter 5.

#### 4.1.4 Cryogenic carbon capture

The technology of cryogenic separation is making use of transformational phase changes of  $CO_2$ , when the  $CO_2$  is cryogenically cooled in the flue gas stream from fuel combustion. More precisely, the  $CO_2$  is changing from its gaseous phase directly to the solid phase, so that the solid  $CO_2$  can efficiently be separated from the flue gas stream. Generally, all other flue gas contaminants can be separated in the same way as the  $CO_2$ , which is one of the advantages this technology offers. The application of this technology for the specific use in CC increased recently, due to overall good capture performance (Song et al., 2019). *Table 4.9* is summarising key data on cryogenic carbon capture.

Table 4.9: Key data on cryogenic carbon capture

| TRL | CAPEX         | OPEX      | Space         | ICE<br>compatible | # of<br>articles |
|-----|---------------|-----------|---------------|-------------------|------------------|
| 6   | $0.7 \ge MEA$ | 0.5 x MEA | Less than MEA | Yes               | 2                |

#### 4.1.4.1 Technology setup and operating principle

As introduced, cryogenic carbon capture (CCC) is making use of the phase change of gaseous CO<sub>2</sub> directly into a solid. This process is called "desublimation" and is achieved by cryogenic cooling of the flue gases. Depending on the preferred way of CCC, the system setups may differ slightly from another. Two potential technology setups of CCC from flue gases and their respective operating principle are described in the following paragraphs: Compressed Flue Gas (CFG) and External Cooling Loop (ECL) (Sustainable Energy Solutions, 2021a, 2021c).

In the CFG system, flue gases from a power plant are firstly sent through a dryer unit, to condense water contained in the exhaust gases. After this pre-separation, the flue gas stream pressure is elevated by a compressor to the operating pressure required for further processing (Sustainable Energy Solutions, 2021a). With the compression, the temperature of the flue gas is raising. Subsequently, the flue gases are cooled in a heat exchanger unit while attaining the operating pressure. Specific components of the flue gas such as SO<sub>2</sub>, NO<sub>2</sub>, Hg, HCl are then removed in a condensed phase by a separator unit (see Figure 4.6) with high efficiencies. After this separation, the remaining flue gas is mainly consisting of N2 and CO2. Via an expansion valve (in some systems also turbines are used for the expansion of the gas), the gaseous stream is expanded and cryogenically cooled to solidify the CO2. The solid CO2 and the left gaseous N2 stream are then separated in a solid-gas separator. The solid  $CO_2$  is pressurised to 70 - 80 bar. Both streams, solid  $CO_2$  and gaseous N<sub>2</sub>, are sent back and utilised at the low-temperature side of the heat exchanger, to cool the incoming flue gases and, at the same time, melting the solid CO<sub>2</sub>. At the output of the CFG system, CO<sub>2</sub> is present in a pressurised liquid phase and can be stored or further utilised. The remaining N<sub>2</sub> gas-stream can be released into the atmosphere at ambient air pressure (L. Baxter et al., 2011).


Figure 4.6: Simplified schematic of the CFG system developed by Baxter et al. (2011)

The general setup in the ECL system is similar to the CFG system. However, the biggest difference in the setup and working principle of the ECL system is, that it does not require flue gas compression. Generally, the system consists of a two-stage CO<sub>2</sub> cooling process, a multi-stream heat exchanger and a desublimating heat exchanger. A simplified schematic of the ECL system can be seen in *Figure 4.7*. Firstly, the flue gas stream, supported by a blower, is passed through a dryer unit to strip off moisture. The dry flue gas is further led into the multi-stream heat exchanger for precooling. The cooling energy for the multi-stream heat exchanger is drawn from an external cooling cycle, that is operated by refrigerant compression and expansion. Additional cold energy is provided from the recirculation of solid CO<sub>2</sub> and liquid nitrogen from the outlet of the desublimating heat exchanger into the multi-stream heat exchanger.



Figure 4.7: Simplified schematic of the ECL system developed by L. L. Baxter et al. (2019)

After the precooling in the first stage, the cold dry flue gas is forwarded to the second stage, the desublimating heat exchanger, in which  $CO_2$  is condensed and thereby cooled until the  $CO_2$  is precipitating in solid form. As aforementioned, the solid  $CO_2$  is recirculated into the multi-stage heat exchanger, where it liquefies during the heat transfer, and subsequently ejected from the heat exchanger unit. During the cooling process in the desublimating heat exchanger, other flue gas contaminants such as  $SO_2$ ,  $NO_2$ , Hg, HCL are condensed and separated from the flue gas stream

(Sustainable Energy Solutions, 2021c). The liquid  $CO_2$ , which is exiting the multi-stream heat exchanger, is pressurised and sent to storage. The flue gas treated by the ECL system is an N<sub>2</sub>-rich light gas at near ambient temperature, that can be released into the atmosphere directly.

# 4.1.4.2 Field of current application and TRL

CCC technologies, as described above, have successfully been tested in pilot plants at different scales (L. L. Baxter et al., 2019; Sustainable Energy Solutions, 2021c). CO<sub>2</sub> capture-rates of more than 90 % were achieved under real flue gas conditions. Further, the capability of the CCC process for successful separation from other flue gas components was proven (Sustainable Energy Solutions, 2021b). Small-scale CFG pilot plans have been running for several weeks at different locations, with capture-rates of up to 95 %. ECL systems have been demonstrated in different environments in pilot plants, also in relation to the usage of various fuels such as coal, natural gas and biomass mixtures. In a coal-fired power plant test of 600 running hours, an average capture-rate of the ECL system of 91 % was proven (L. L. Baxter et al., 2019; Sustainable Energy Solutions, 2021b). The performance tests of the described pilot plants have been carried out at fluctuating concentrations of 5 to 15 % CO<sub>2</sub> in the flue gas. When steady-state operation was attained, the average flue gas concentration was at 8 % CO<sub>2</sub>. Based on the stated facts, the CCC technology is evaluated to have a current TRL 6.

## 4.1.4.3 Costs

Compared to MEA absorption technologies for CC, the CCC technology has high potential for cost savings (Lang, 2016). When integrating the CCC process into the design of a newbuild power plant, the CAPEX of a CCC plant are only at 50 % of the costs of an amine-based absorption process. The same applies for the energy penalty, where CCC technology requires only half of the respective load of an MEA plant (L. Baxter et al., 2011; Lang, 2016).

Contrary to MEA absorption, CCC requires only the electricity to run the cryogenic processes, but no excessive heat energy for solvent regeneration. Resultingly, the load requirements of the technology are lower, which is decreasing the fuel costs (OPEX) to a lower level than MEA technologies. The CAPEX for a CCC system are lower than conventional MEA absorption technologies (L. Baxter et al., 2011).

Comparing various options for post-combustion CC, Roberts (2021) states, that the OPEX in CCC are 50 % lower than in MEA absorption and the CAPEX are 30 % lower, respectively. This statement of lower costs for CCC than for MEA absorption is supported by an interviewed expert (E. Malmgren, personal communication, 12.05.21).

## 4.1.4.4 Space requirements

Heat exchangers are accounting for a substantial amount of the space requirements of the CCC technology. Various types of heat exchangers are used in CCC, most commonly tubular types, coil or plate heat exchangers (Wilcox, 2012). Multiple heat exchanger units may become necessary, especially for large volumes or high velocities of flue gas, which then will require more space. In CFG systems, additional space for compressor units and turbines for the expansion of the compressed flue gases has to be considered. Higher velocities/ larger volumes of the flue gas also demand bigger units for compression and expansion.

The available literature is not covering space related issues of the CCC technology. Therefore, no profound statement in regards of the required space of this technology, especially in connection

with the use in flue gases from ICEs can be made. The authors assume, that CCC requires less space than the MEA absorption.

## 4.1.4.5 Advantages and drawbacks

Provided that an existing energy system is capable of supplying sufficient electric energy for the CCC process, the technology can be retrofitted to any combustion process. In such case, apart from the additional components of the CCC plant which need to be installed, no further changes in the power plant are required (if the existing power plant had flue gas treatment facilities already in place). Furthermore, CCC is less energy consuming than the commonly used CC technology of chemical absorption (see 4.1.4.3) (L. Baxter et al., 2011; Safdarnejad et al., 2015). High CC efficiencies of 90 % and more have been validated in pilot plants (Lang, 2016). This contributes to lower costs for the technology, which is favourable for the operator of the plant. As stated in the working principle above, the cryogenic process is also able to remove particles and pollutants such as SO<sub>x</sub>, NO<sub>x</sub>, Hg and HCl from the exhaust gases, even with high efficiencies, which is seen as a major advantage of this technology.

Nevertheless, high amounts of impurities in the flue gas still have to be pre-treated by adequate facilities (e.g.,  $SO_x$  scrubbers in the flue gases from fossil-fuelled ICEs) and cannot be replaced by a CCC plant (E. Malmgren, personal communication, 12.05.2021). Unfortunately, the reuse of waste heat energy from other processes for performance improvements of this technology is not possible, which means that all the required energy for the cryogenic processes needs to be provided by electrical generation. CCC technologies are producing waste heat, which can be integrated into the existing waste heat regeneration cycle of a power plant, but for onboard applications the additional waste heat is not desirable, since there is already an abundance of waste heat generated onboard.

## 4.1.4.6 Research for the application onboard

Cryogenic separation is a mature process in the industry and applied for gas separation but highly energy intense. Therefore, research on CCC is concentrating on ways to increase the energy efficiency of the related processes. This thesis identified one report evaluating the feasibility and impact of cryogenic separation for applications in the marine sector. Further, a project utilising CCC will be addressed in this section. The main insights of the identified articles are summarised in *Table 4.11*.

In 2020, Willson published a report evaluating the application of an advanced cryogenic carbon capture (A3C) process onboard vessels. The report takes a holistic approach, considering technical and economic impacts as well as the impact on the operation of the vessel and required shoreside infrastructure. Therefore, case studies for two example vessels are carried out.

The core of the report is the A3C technology which has been developed and patented by PMW Technology in 2016 (Willson, 2020). Currently, it is at TRL 3 to 4. In a foregoing study, the A3C process in connection with shoreside industrial and power plant applications, is estimated to reduce the costs of CC by up to 70 % compared to the absorption by MEA, for scales below  $10 t_{CO2}/h$  (Willson et al., 2019). This range is typical for marine applications, where a capture-rate of 90 - 95 % is expected to be achieved (Willson, 2020).

The A3C process (*Figure 4.8*) itself consists of two stages, each containing a moving-bed of metallic beads (Willson, 2020). In the first stage, the cooler-drier removes the water contained in the exhaust gases. The second stage is further cooling down the gases and contained  $CO_2$  is forming

a solid coating on the metallic beads. Due to the fineness of the moving-bed material, the surface for heat exchange is increased, allowing a very compact design of the process. For comparison, a metallic beads bed of 50 - 100 mm is able to achieve the same separation results as a 15 m high column in chemical absorption (Willson, 2020).



Figure 4.8: Schematic of the A3C separation process

The solid  $CO_2$  on the metal beads is vaporised using the waste heat of the refrigeration unit, enabling the refrigeration unit to recuperate the cold energy and thereby significantly lowering the energy required for the cryogenic system (Willson, 2020). The  $CO_2$  stream is transferred to the compression and liquefaction unit, whereas the metal beads are transported by a screw conveyor to the top of the separator, where they are cooled down again. The cold  $CO_2$ -lean flue gases leaving the separator are cooling down the moving-bed of the cooler dryer in the first stage (Willson, 2020).

As it can be seen in *Figure 4.8*, the A3C process requires a gas inlet temperature of 30 °C, which requires further cooling of the exhaust gases prior entering the CC process. Therefore, the concept of Willson (2020) includes a direct contact cooler upstream of the CC unit, which is also utilised to scrub contaminants such as  $SO_x$ ,  $NO_x$  and particulate matter (PM) from the exhaust stream. Willson (2020) states, that the resulting wash water is treated to remove contaminants before discharge into the sea but does not specify this process in further detail. The separated  $CO_2$  is liquified by compressing it to 30 bar and afterwards condensed by cooling. The pressure of the liquid is reduced to 10 bar, causing a small part to vaporise, and thereby further cooling the remaining liquid phase. The liquid  $CO_2$  is stored in tanks at about -40 °C, whereas the gaseous phase is recompressed.

To evaluate the impact and feasibility of this process, Willson (2020) carried out simulations based on two case studies. Even though the case studies refer to specific vessels, the implementation of A3C onboard was considered for the development of a newbuild ship design, not as a retrofit solution. The first case study is carried out for a car carrier with 10.200 DWT, propelled by a dualfuel two-stroke engine being able to run on LNG and MGO, rated at 12.614 kW. In addition, the ship design includes three dual-fuel four-stroke auxiliary engines (2 x 1.710 kW, 1 x 1.330 kW). The vessel is designed to trade between Europe and US.

For the first case-ship, three cases are assessed using LNG as fuel: no CC, CC only from the main engine and CC from all engines (Willson, 2020). The same cases are assessed using MGO as fuel, resulting in six cases overall. Depending on the case, the dimensions and weights of the A3C unit vary. Whereas the base dimensions of 5 x 9 m are similar for all cases and the height is varying slightly between 4,5 - 5,2 m, the weight is corresponding to the gas flow. Therefore, the weight is estimated to be around 100 t for CC only from the main engine and is ranging from 150 - 170 t for CC from all engines (Willson, 2020). Further results are summarised in *Table 4.10*.

|                                     |       | LNG     |                |       | MGO     |                |  |
|-------------------------------------|-------|---------|----------------|-------|---------|----------------|--|
| Case                                | No CC | ME only | All<br>engines | No CC | ME only | All<br>engines |  |
| Reduction rate (%)                  | 0     | 60      | 88             | 0     | 57      | 87             |  |
| Effect on cargo space (%)           | 0     | -5      | -6             | N/A   | 1       | -1             |  |
| Auxiliary power<br>consumption (kW) | 1854  | 3543    | 4278           | 1854  | 3918    | 4973           |  |
| CAPEX (£1000)                       | 0     | 11541   | 14801          | 0     | 10139   | 15117          |  |
| OPEX (£1000)                        | 0     | 1152    | 1632           | 0     | 1457    | 2205           |  |
| LCCC ( $f_{c}/t_{CO2}$ )            | 0     | 82,3    | 75,1           | 0     | 69      | 66,9           |  |

Table 4.10: Results of the car carrier case study for A3C application (Willson, 2020)

The highest  $CO_2$  reduction rate is achieved when the ship is operating on LNG and CC equipment is installed for all engines (Willson, 2020). In the MGO cases, the  $CO_2$  tanks are placed in the LNG tank space having only minor impact ( $\pm 1$  %) on the cargo space. Assessing the auxiliary power required to run the CC plant, the simulation results show that all three auxiliary engines are required to run continuously to operate the A3C process. Therefore, it is suggested to add an additional auxiliary engine to the ship's design, to achieve redundancy and allow the CC plant to run and carry out maintenance at one of the auxiliary engines simultaneously. For all cases, the impact on the ships stability has been assessed and the results show, that the stability criteria can be satisfied in all cases (Willson, 2020).

The CAPEX given in *Table 4.10* are calculated without the investment required for an additional auxiliary engine but those figures are included in the study as well (Willson, 2020). The OPEX are including additional fuel and maintenance costs, whereby the fuel prices expected for 2031 have been used as basis for calculation. The levelized costs of CC (LCCC) are calculated for 2031 as well and assume a life-time of 20 years and a discount rate of 10 % (Willson, 2020).

The second case study is carried out for a small RoPax ferry with 830 DWT, driven by a hybrid diesel-electric–battery propulsion system with four four-stroke engines running on MGO, each delivering 1.200 kW (Willson, 2020). Two cases are assessed: No CC and CC from all engines. Since the results are similar, merely in a different scale due to the reduced size and different operating pattern, they are not addressed in further detail here. Willson (2020) is concluding, that the A3C process is a competitive alternative, noting that the LCCC of conventional amine processes are typically around 100 to  $150 f/t_{CO2}$ .

The decarbonICE project, on which no scientific papers have been published so far, is developing several conceptual designs for an onboard CC system with an integrated solution for long-term storage (MDC, 2021). The project is developing a CCC plant for the application on LNG and MGO/HFO fuelled ships, making it feasible for retrofit as well as for newbuildings. The captured CO2 is stored as dry ice onboard and will be shaped in a certain way, to so-called Carbon Decent Vehicles. These vehicles can be released into the sea, where they will sink with high speed and dig themselves into the seabed sediments. Therefore, the decarbonICE project is also including the development of a production system for manufacturing of the Carbon Decent Vehicles, a launching system for these, analysis to find the optimal shape for the vehicles and analysis of the CO2 storage in seabed sediments (MDC, 2021). Nevertheless, the storage in seabed sediments is seen critical, since the consequences of a concentrated gas leakage into the surrounding are not well researched until now and significant knowledge gaps exist in this regard (Harvey et al., 2012). Besides these environmental and technical issues, also a cost analysis and safety and risks assessments are addressed by the project (MDC, 2021). When the vessel is equipped with the decarbonICE technology and is using carbon neutral biofuels, the system could achieve carbonnegative shipping (MDC, 2021).

| Authors (Year)        | Title  | TRL <sup>1</sup>                                       | Ship type   |
|-----------------------|--|--|---|
| Willson (2020)        | Evaluation of the Marine<br>Application of Advanced<br>Carbon Capture Technology | 4  | Car carrier (10.200 DWT, 12.614 kW);<br>RoPax ferry (830 DWT, 4.800 kW)   |
| decarbonICE<br>(2021) | decarbonICE: On-board Ship<br>Technology   | 2  | Not specified   |
| Authors (Year)        | Main conclusion  | Additio  | nal Information   |
| Willson (2020)        | A3C process is feasible and cost<br>competitive for the application<br>onboard   | A3C pro<br>reduce e<br>impact o<br>capture-<br>economi | ocess is recuperating cold energy to<br>nergy demand; case studies evaluating<br>of different fuels (LNG/MGO) and<br>rates on the ship's design and stability;<br>ic estimations for all case studies |
| decarbonICE<br>(2021) | N/A  | CO <sub>2</sub> to l<br>includes                       | be stored as dry ice onboard, concept<br>sediment storage analysis of dry ice   |

### Table 4.11: Literature on CCC for the application onboard

<sup>1</sup> The TRL in this table is reflecting the state of the research described in the respective article/report. It is not indicating the TRL of the corresponding technology and is not used as basis for the assessment in chapter 5.

# 4.2 Pre-combustion capture

Pre-combustion CC is referring to the removal of  $CO_2$  from a synthesis gas (syngas). The syngas is either obtained by the gasification of carbonaceous fuels, e.g., coal, heavy oils or hydrocarbon fuels, or the catalytic reforming of natural gas with  $O_2$ . Fundamentally, the created syngas consists of CO and H<sub>2</sub>. With the utilisation of steam, the CO is converted into a syngas of CO<sub>2</sub> and H<sub>2</sub>, so that the resulting mixture is (almost pure) H<sub>2</sub> and CO<sub>2</sub>. In this gas mixture, the actual CC process is applied (Kanniche et al., 2010).

The capturing of  $CO_2$  from a syngas can occur via different technologies. Two mature CC technologies in pre-combustion are the absorption via chemical and physical solvents and the adsorption via chemical and physical sorbents. Apart from the difference that pre-combustion technologies capture  $CO_2$  from a syngas instead of combustion flue gases, the capture process via ab- or adsorption functions in the same way as described in the respective post-combustion chapter. In the consulted literature, the availability of data regarding individual pre-combustion technologies is scarce. Often there are no indications, which specific CC technology is used in the described appliances. This is restricting the distinction between the available pre-combustion technologies in the following subsections. The focus in this chapter lies on the syngas generation, as a mandatory prerequisite for the CC process. *Table 4.12* is summarising key data on precombustion CC.

 Table 4.12: Key data on pre-combustion absorption and adsorption

| TRL   | CAPEX           | OPEX            | Space           | ICE<br>compatible | # of<br>articles |
|-------|-----------------|-----------------|-----------------|-------------------|------------------|
| 9 (5) | Higher than MEA | Higher than MEA | Higher than MEA | Yes               | 1                |

## 4.2.1 Technology setup and operating principle

The principle of absorption and adsorption processes via solvents and sorbents from the syngas is working similarly as described in the respective subsections for post-combustion capture technologies. The same applies for the related regeneration, with a varying working principle of the desorption process in dependence to the applied sorbents and solvents. However, the general technology setup, which is required for the pre-combustion CC process, is far more complex.

As aforementioned, pre-combustion CC is applied in a syngas, produced from carbonaceous fuels. This process is referred to as gasification (Vaseghi et al., 2012). In the gasifier, the fuels are partially combusted, while  $O_2$  from an air separation unit (ASU) is added to the process (partial oxidation). The gasification is occurring under pressurised conditions and at high temperatures, caused by the partial combustion (Oresome Resources, 2010). Resulting from the gasification process, a pressurised gas stream rich of CO and  $H_2$  is leaving the gasifier. PM and sulphur contaminants from the partial combustion are also diluted in the gas mixture. The PM are subsequently separated from the gas by a downstream cyclone unit (Lip et al., 2016). A simplified technology setup of the entire pre-combustion CC process is shown in *Figure 4.9*.



Figure 4.9: Simplified schematic of the pre-combustion CC process

The  $O_2$  which is added in the gasification process is obtained from the separation of ambient air in an ASU. In the ASU, not only  $O_2$  is separated from ambient air also  $N_2$  is removed. Since  $N_2$  is the major component of the ambient air and does not contribute to the combustion process, it is separated. In this way, a high-concentrated stream of  $CO_2$  and  $H_2$  is produced in the gasification process. Beneficial for this  $N_2$  separation is that it simplifies the CC process and reduces the energy demand for the adsorption/desorption of  $CO_2$  (Kotowicz et al., 2019). The ASU can be any version of a potential air separator. Nowadays, membranes, absorption by chemicals and cryogenic processes are applied (Kotowicz et al., 2019).

In the further processing, the pressurised gas stream is forwarded to a water gas shift reactor (WGS), were the CO and H<sub>2</sub>-rich gas is mixed with water vapour, to convert CO to  $CO_2$  and H<sub>2</sub>O to H<sub>2</sub>. By this, the efficiency of the syngas production is increased and CO emissions are lowered. After the WGS, the emerged syngas stream is sent through a desulphurisation unit, to remove remaining sulphur contaminants. The desulphurisation is occurring through a selective separation of sulphur from the syngas, utilising either a suitable absorption or adsorption technology (Lip et al., 2016). The final syngas, after the separation of all contaminants, consists of almost pure H<sub>2</sub> and CO<sub>2</sub>, with a CO<sub>2</sub> content of about 40 % and a pressure of 65 bar (Vaseghi et al., 2012).

These conditions are highly favourable for the subsequent CC process, which is applied right after the desulphurisation of the syngas (Vaseghi et al., 2012). As mentioned above, the capturing of  $CO_2$  from the syngas can occur through the utilisation of similar absorption and adsorption technologies as described in the post-combustion chapter under 4.1.1 and 4.1.2. Different absorbents and adsorbents can be applied in pre-combustion  $CO_2$  capture due to the higher partial pressures of  $CO_2$  in the syngas. For such applications, physical sorbents are usually used (S. M. Nazir, personal communication, 13.05.2021). Finally, the CC unit is splitting the syngas stream into two separate gas streams: H<sub>2</sub> from the process is used as fuel, whereas the captured  $CO_2$  is compressed and stored.

## 4.2.2 Field of current application and TRL

The pre-combustion CC technology, as described in the section above, is mature and in commercial application worldwide. A lot of industrial applications for the gasification of carbonaceous fuels, natural gas reforming and the processing of natural gas are existing since several years already (i.e. TRL 9) (Global CCS Institute, 2012). In pre-combustion CC by absorption, most mature and highest rated on TRL 9 are the liquid physical absorbents, Rectisol and Selexol, used in natural gas processing and fuel gasification (Kearns et al., 2021).

In recent research,  $H_2$  is considered to be a promising fuel for the decarbonisation of ICEs (Babayev et al., 2021). Currently,  $H_2$  is utilised in fuel cells and gas turbines, but the conversion of carbonaceous fuels to  $H_2$  by pre-combustion capture processes is providing a base for the further  $H_2$  usage in ICEs (Lip et al., 2016). Although current diesel and fuel-oil-driven ICEs can be adapted for the usage of  $H_2$ , Beckmann & Pieper (2019) state, that the interest in research for  $H_2$  ICEs has dropped, since technological progress has been made with the development of fuel cells. However, Wermuth et al. (2020) report, that the successful use of  $H_2$  in a single-cylinder research ICE has been validated. Furthermore, MAN Energy Solutions is reporting that they see  $H_2$  as an attractive fuel to be used in ICEs and that concepts by MAN for the use of  $H_2$  in a dual-fuel system are currently under development. For ship applications, the future use of  $H_2$  is seen as a propulsion-fuel for vessels with a limited range (MAN Energy Solutions SE, 2021).

One step ahead is a joint-venture between the Belgian shipowner CMB and the Belgian engine manufacturer ABC, where dual-fuel as well as mono-fuel H<sub>2</sub> ICEs are to be commercialised. In their joint-venture, called BeHydro, the focus is put on short-distance vessels, e.g., tugs, ferries and other commercial crafts, as well as auxiliary engines for larger vessels (Mercator Media Ltd., 2019). Lately, the efforts in development by CMB resulted in the commission of a dual-fuel ship, driven by a H<sub>2</sub> ICE. The passenger ship called "Hydroville" is the first ever, fully seaworthy, vessel, that is propelled by an ICE running on H<sub>2</sub> (Van Hoecke et al., 2021). Based on this technological progress, the H<sub>2</sub> ICE has reached TRL 7. It has to be noted, that the H<sub>2</sub> combusted onboard the "Hydroville", is bunkered from shoreside supply and stored in fuel tanks, rather than being produced on the ship.

In conclusion, although the technology of pre-combustion CC for land-based applications for  $CO_2$  removal and  $H_2$  generation is mature, it is not applied in connection with ICEs so far. The functional interaction between pre-combustion CC from carbonaceous fuels and the subsequent combustion of  $H_2$  in ICEs still need to be proven. Nevertheless, the subsystem components of the pre-combustion CC technology have been validated, which is accrediting this technology a TRL of 5.

## 4.2.3 Costs

Rubin et al. (2015) examine estimates on additional costs which arise when a pre-combustion CC technology is used in connection with integrated coal gasification combined cycle (IGCC) power plants. The setup of the IGCC is similar as described under 4.2.1, with gas turbines as main consumer of the produced H<sub>2</sub>. The average power output of the investigated power plants is about 750 MW, with a base case efficiency of 41 %, without usage of a CC plant. When a pre-combustion CC plant is installed, the total efficiency decreases to 33 % (8 % reduction), with additional energy requirements for the capture of 25 %. Jansen, Gazzani, Manzolini, Dijk, & Carbo (2015) specify, that 44 % of the total 8 % efficiency penalty are caused by the WGS.

The CAPEX for the base case power plant increase by 93 % when a pre-combustion CC technology is installed. Further, the LCOE increase by 80 % with the use of CC in the system. The average costs of  $CO_2$  captured are estimated to be at 63 \$/tonne, when pre-combustion CC is applied in an IGCC power plant (Rubin et al., 2015).

To compare the cost figures of the pre-combustion technology with common post-combustion technologies, Rubin et al. (2015) applied the same cost estimation as used for pre-combustion CC technologies above, to compute the cost figures for coal-fired power plants equipped with post-combustion CC technologies. The average power output of the reference plants is about 750 MW

and the plant efficiencies are at 41.4 %, without a capture plant. With the installation of a CC plant, the total efficiency decreases to 31.6 % (9.8 % reduction). The additional energy requirements sum up to 32 % more energy input for the CO<sub>2</sub> capture (Rubin et al., 2015).

An increase in total CAPEX of 75 % is estimated between the base case power plant (without CC) and the same power plant when a post-combustion CC technology is installed. The LCOE are increasing by 62 %. However, the costs of  $CO_2$  captured are at 46 \$/tonne, with the usage of a post-combustion CC plant in coal-fired power plants (Rubin et al., 2015).

The statement of costs of the two cases above allows for a general cost comparison between the post-combustion and pre-combustion CC technology. It is clearly shown that the CAPEX as well as the LCOE for the post-combustion CC technology are lower than for a comparable pre-combustion CC technology. Lower costs per tonne of  $CO_2$  captured are also shown by the post-combustion CC technology, compared to the pre-combustion technology.

It has to be noted, that the study by Rubin et al. (2015) is not specifying the exact pre- or postcombustion technology which was used for the cost estimations. Furthermore, no specifications of the direct costs contributing to the CAPEX are provided. Therefore, the cost comparison in *Table 4.12* is just stating a general cost trend (e.g., higher/lower) between post-combustion and pre-combustion CC technologies.

# 4.2.4 Space requirements

In the available literature, no considerations regarding the space required for a pre-combustion CC plant are made. The technology has been developed for land-based applications, where the obtainable space is not regarded. However, one source mentioning the occupied space for a pre-combustion capture plant for a 600 MW IGCC plant could be identified. The capture technology used at this plant is a solvent-based absorption with subsequent stripping of the  $CO_2$ . The space requirements of the pre-combustion capture plant include the WGS reactors,  $CO_2$  absorption/stripping, drying and compression of the gas and sum up to  $6.000 - 8.000 \text{ m}^2$  (Global CCS Institute, 2012).

Provided that this figure can be scaled down linearly, the space demand for a pre-combustion CC plant of a 6 MW power plant (or engine), is between  $60 - 80 \text{ m}^2$ , tendentially even higher, since not all components of the equipment can be scaled down equally. Nevertheless, this is merely an estimate by the authors.

The actual components which are involved in the CC process, e.g., absorber and stripper, can be downsized in comparison to post-combustion capture, caused by the slower volume flow in the process. Further, to capture the same amount of  $CO_2$  as in post-combustion capture, the absorber (or adsorber, respectively) can be smaller in size, due to the higher partial pressure of  $CO_2$  in the syngas. However, components from the syngas generation, such as the gasifier or the WGS, are space demanding and are making up for the gained space from the capture units. Since the technology setup in pre-combustion CC is more complex than for post-combustion technologies, the demanded space for the CC equipment is assumingly higher than for the MEA benchmark process.

## 4.2.5 Advantages and drawbacks

One of the advantages of the concept of pre-combustion CC is the production of H<sub>2</sub>, which can be used for energy generation (Cormos et al., 2018). In this way, Jansen et al. (2015) see the potential of the pre-combustion CC technology to contribute to a faster implementation of H<sub>2</sub> as an alternative fuel. Based on the working principle of this technology, the CO<sub>2</sub> is captured at an elevated pressure, which is decreasing the energy consumption for the subsequent compression for CO<sub>2</sub> storage (Jansen et al., 2015). The energy demand for the capture and stripping process itself is significantly lower than in the post-combustion CC, due to the higher CO<sub>2</sub> content in the syngas, which is ultimately making the capturing more efficient (Eldardiry & Habib, 2018).

Disadvantageous for this technology is the high CAPEX, connected to the components for the syngas generation. Therefore, in comparison to post-combustion CC, pre-combustion capture is less economically favourable for the owner (Jansen et al., 2015). Further, as described under 4.3.4, the high space demand for the syngas generation as well as the capture-related plants, is another drawback of this system. This fact is limiting the possibility of retrofitting a pre-combustion CC technology. Provided that sufficient space is available for the additional components, retrofitting still might not be feasible since the pre-combustion CC technology requires a completely new system from fuel processing to energy conversion.

## 4.2.6 Research for the application onboard vessels

This thesis could not identify literature for the application of absorption or adsorption technology in combination with pre-combustion capture onboard seagoing ships. Only one concept for precombustion capture could be identified: the HyMethShip. The HyMethShip concept, which has been named as example for an approach towards a circular economy for carbon in chapter 2.2, applies membrane separation to separate  $H_2$  from the other syngas components. By the time this thesis was finalised only conference proceedings, presenting the scope and basic preliminary results of the technology have been published. The mains of the article used to describe the concept in the following, are summarised in *Table 4.13*.

The HyMethShip project aims to develop and assess a complete system, i.e., from bunkering of methanol throughout the propulsion, energy generation and temporary storage of captured  $CO_2$  onboard, until the  $CO_2$  is discharged to port facilities (Zelenka et al., 2019). This is also including economic and life-cycle assessments. The project includes the optimisation of a marine ICE for the combustion of H<sub>2</sub>, to make the technology feasible for a wide range of vessels. The core of the HyMethShip's propulsion system is the pre-combustion CC system (Zelenka et al., 2019), of which a schematic is shown in *Figure 4.10*.



#### Figure 4.10: Schematic of the HyMethShip CC system

In the mixing chamber (1) methanol and water from the storage tanks are mixed before being fed into the economiser (2) and afterwards into the evaporator/superheater (3). The resulting gas mixture is then fed to the membrane reformer (4), which is combining two process steps in one (Zelenka et al., 2019). The catalytic methanol reforming as well as the separation process of  $H_2$  via a membrane takes place under the same reaction conditions. All three (economiser, evaporator/superheater, membrane reactor) are utilising waste heat, generated by the combustion of  $H_2$  within an ICE. The membrane reactor (4) is splitting the mass flow into two streams. The  $H_2$ -selective carbon membrane allows generated  $H_2$  to be removed as permeate. The permeate stream mainly consists of  $H_2$  and water. Latter is removed by condensation and fed back into the process before the pressurised gaseous  $H_2$  is supplied to the engine. The other stream, the retentate, is cooled down to condense remaining water and methanol, which are fed back into the process. The remaining gaseous phase is containing the CO<sub>2</sub>, produced within the membrane reactor. By cooling down this gas stream to -45 to -55 °C, the CO<sub>2</sub> partially condenses and can be stored in liquid phase. The non-condensed stream of gases is led back into the process. The cold needed to condense the  $CO_2$  is generated by an absorption chiller, which is utilising waste heat for its operation. The technical key issues within this process are to control the energy transfer into the membrane reactor, to control the chemical composition and the partial pressures. (Zelenka et al., 2019). Difficulties in regards of these key issues are currently limiting this concept to achieve a higher TRL.

The HyMethShip system is expected to achieve 97 %  $CO_2$  capture-rate and practically eliminate sulphur, PM and  $NO_x$  emissions (Zelenka et al., 2019). Energy efficiency is expected to be more than 45 % higher than combusting renewable methanol directly and capture the  $CO_2$  after the combustion. To demonstrate the feasibility of the system, an onshore demonstration plant with an engine in the range of 1.000 to 2.000 kW will be developed. The project is planned to end and present results in 2021 (Zelenka et al., 2019).

| Authors (Year) | Title   | TRL <sup>1</sup>  | Ship type   |  |
|----------------|---|---|---|--|
|                | The HyMethShip Project:<br>Innovative Emission Free<br>Propulsion for Ships   | 3   | Not specified   |  |
|                |   |   |   |  |
| Zelenka et al. | Main conclusion   | Additional Information  |   |  |
| (2019)         | Potential to reduce GHG<br>emissions by 97 %;<br>elimination of polluting<br>emissions (SO <sub>x</sub> , NO <sub>x</sub> , PM) | Pre-combust<br>and cryogeni<br>from methan<br>H <sub>2</sub> ; 45 % hig<br>technology | ion CC by a combination of membrane<br>c separation technology; H <sub>2</sub> generated<br>iol, ICE optimised for combustion of<br>her energy efficiency than best |  |

#### Table 4.13: Literature on pre-combustion CC for the application onboard

<sup>1</sup> The TRL in this table is reflecting the state of the research described in the respective article/report. It is not indicating the TRL of the corresponding technology and is not used as basis for the assessment in chapter 5.

# 4.3 Oxyfuel combustion

Oxyfuel combustion is another approach towards the capture of  $CO_2$ . Rather than filtering the low concentrated  $CO_2$  out of a mixture of exhaust gases, this technology allows to produce exhaust gases consisting mainly out of  $CO_2$  and water vapour (Wilcox, 2012).

Table 4.14: Key data on oxyfuel combustion

| TRL   | CAPEX            | OPEX        | Space       | ICE<br>compatible | # of<br>articles |
|-------|------------------|-------------|-------------|-------------------|------------------|
| 7 (4) | ~1,7 - 3,8 x MEA | ~0,76 x MEA | Same as MEA | Yes               | 2                |

## 4.3.1 Technology setup and operating principle

By combusting the fuel in an  $O_2$ -enriched environment, reducing the portion of other gases usually contained within the combustion air, dilution of the  $CO_2$  in the exhaust is avoided. When the water vapour is condensed out, the remaining flue gas ideally consists of  $CO_2$  only. The  $CO_2$  can be captured, compressed and brought to the intended aggregate phase for storage (Wilcox, 2012). *Figure 4.11* is showing a schematic of the process described above.



Figure 4.11: Schematic of the oxyfuel combustion process

To achieve the combustion in pure  $O_2$ , an ASU is required to separate the  $O_2$  needed for the oxyfuel combustion from other gases contained within the air. However, a typical stream from an ASU still contains about 3 %  $N_2$  and 2 % argon, which are diluting the exhaust (Wilcox, 2012). Especially in retrofit applications, air slip into the exhaust can lead to further dilution. Furthermore, the initial investment for an ASU and its operating costs are high, making it often uneconomically for retrofitting (Wilcox, 2012).

Chemical looping combustion is an alternative technique to achieve oxyfuel combustion without the need for an ASU but is only feasible for the combustion of solid fuels such as coal (Wilcox, 2012). Instead of adding gaseous  $O_2$  to the combustion process, metal oxides are used as  $O_2$  transporter. In the combustion chamber, the metal oxide is reduced, supplying the required  $O_2$  for the oxidation of the fuel. After the combustion, the metal ions are separated from the exhaust stream by a cyclone filter and are transported into an air reactor, where they are oxidised and afterwards added to the combustion process again (Wilcox, 2012).

The combustion of fuel in an oxygen-enriched environment causes the reaction-speed to increase, since non-reactive atoms like  $N_2$ , which are delaying the reaction, are absent (Kang et al., 2018).

Further these non-reactive atoms would act as a thermal buffer by absorbing some of the heat released during the combustion. Their absence is resulting in a faster and hotter combustion of the fuel, which is having a negative impact on the thermal efficiency of the engine (Li et al., 2020). Therefore, different strategies are developed to keep the combustion at manageable temperature and pressure levels and to increase the efficiency of the engine.

In coal-fired power plants, where oxyfuel combustion is already applied to reduce the  $NO_x$  emissions, around 70 % of the exhaust gases are recycled to dilute the  $O_2$ -enriched environment in the combustion chamber. This lowers the temperature of the combustion process to levels similar to conventional combustion in air (Wilcox, 2012). Exhaust gas recycling (EGR) is an effective measure to lower the combustion temperature in ICEs as well. Nowadays it is mainly utilised in order to reduce the formation of  $NO_x$  during combustion (Verschaeren et al., 2014).

The drawback of EGR is the deliberate reduction of the engine's efficiency, which can be avoided when water is injected into the combustion chamber to control the temperature. The injection of water is even increasing the thermal efficiency of the engine (Kang et al., 2018; Li et al., 2020; Wu et al., 2014). The water injected into the combustion chamber is taking up heat from the combustion and is evaporating. The increased volume of the water becoming gaseous is raising the pressure within the combustion chamber, resulting in a higher energy output and efficiency of the engine. *Figure 4.12* is showing a schematic of the Internal Combustion Rankine Cycle (ICRC) engine developed by Wu et al. (2014), which is utilising waste heat from the exhaust and cooling water of the engine to heat up the water injected into the combustion chamber. Their simulation is showing that the injected water is capable to moderate the peak combustion temperature and increase the efficiency of the engine. Further, the simulation results indicate that a higher temperature of the injected water is leading to a higher efficiency of the combustion, since the water is evaporating faster. The conducted experiment resulted in a thermal efficiency increase from 32,1 % to 41,5 % (Wu et al., 2014).

To determine the best strategy for water injection for a maximum efficiency-gain, further research has been conducted by Kang et al. (2018). The research investigated the best amount and temperature of injected water as well as the best timing to inject the water. Too much injected water is deteriorating the combustion process since it is consuming too much heat. The same is caused by too early water injection, resulting in a direct interaction between flames and water and thereby reducing the combustion efficiency. The optimum injection strategy has been determined as "1:1.11 fuel-to-water ratio, 365°CA timing, and 160°C temperature" (Kang et al., 2018) improving the cycle efficiency by 5,2 %.

Even though oxyfuel combustion is applied for coal combustion in power plants to increase the efficiency, it is still under research for the application in ICEs. Current research is focussing on the optimisation of the combustion process, to gain the best efficiency and reduce the use of O<sub>2</sub>. Since this field is still under research and no demonstration plants are in place till today, no reliable evaluation of costs for such a technology setup including an ICE is available. For land-based power plants, the costs for electricity produced with oxyfuel combustion are higher than from conventional coal fired plants, but including CC the overall costs might be lower than for post-combustion capture (Wilcox, 2012).



Figure 4.12: Schematic of an ICRC engine with water injection

## 4.3.2 Field of current application and TRL

Oxyfuel combustion, particularly chemical looping, has mainly been researched for the combustion of solid and gaseous fuels in power plants for energy generation. Several projects have developed pilot plants, achieving the demonstration state with a TRL of 7 (ZEP, 2017). However, due to an unforeseen development of the electric energy market and the emission trading market, oxyfuel combustion is not commercially competitive and therefore further efforts for most of the pilot plants have been stopped (F. Johnsson, personal communication, 03.05.21). As described above, oxyfuel combustion processes for ICEs are still under development and have barely reached TRL 4 (Wu et al., 2014).

Cryogenic ASUs are mature in the  $O_2$  production and therefore have achieved TRL 9 in industry applications (ZEP, 2017). However, these ASUs are energy intensive and further development is required to increase the energetic efficiency of such. Besides cryogenic ASUs, vacuum-pressure-swing-adsorption (TRL 6) and membranes (TRL 5) are being researched for  $O_2$  separation (Abanades et al., 2015).

## 4.3.3 Costs

Due to the low TRL of oxyfuel combustion processes in ICEs, currently no predictions on the costs of such technology are available. Therefore, this study assumes that the costs of oxyfuel combustion in combination with an ICE can be compared to the costs of oxyfuel combustion for a gas-fired power plant.

Gibbins and Chalmers (2008) compared the costs for equipping a gas-fired power plant with three alternative CC technologies: post-combustion capture by amine solvent, pre-combustion capture with PSA and oxyfuel combustion. The CAPEX of the power plant without CC were estimated to 500 \$/kW, for post-combustion capture to 870 \$/kW, for pre-combustion capture to

1180 \$/kW and 1530 \$/kW for oxyfuel combustion (Gibbins & Chalmers, 2008). Concluding, the CAPEX for oxyfuel combustion are 3,8 times higher than for post-combustion capture with MEA.

Contradictory to this, the variable expenses, the costs of  $CO_2$  avoided, for oxyfuel combustion (102  $t_{CO2}$ ) are lower than for pre-combustion capture (112  $t_{CO2}$ ) but not as low as for post-combustion capture (58  $t_{CO2}$ ) (Gibbins & Chalmers, 2008). This means, that the variable expenses of oxyfuel combustion are 1,7 times higher than for post-combustion capture with MEA.

Gardarsdottir et al. (2019) carried out a comparison of several CO<sub>2</sub> capture technologies, including absorption by MEA as reference, and oxyfuel combustion for CC from cement production. Their results show that the CAPEX for an absorption process with MEA would increase the total plant costs by 76 M€ and by 128 M€ for an oxyfuel combustion process, respectively. This means, the CAPEX for oxyfuel combustion are 1,7 times higher than for adsorption with MEA. The annual OPEX for the MEA process is estimated to 76 M€ and 58 M€ for oxyfuel combustion, respectively (Gardarsdottir et al., 2019), i.e., the annual OPEX of oxyfuel combustion is 0,76 times the one of the MEA process. The costs of CO<sub>2</sub> avoided for the oxyfuel process (42,4 €/t<sub>CO2</sub>) are about half of the costs for the MEA CC process (80,2 €/t<sub>CO2</sub>).

The interviewed experts agreed with these findings, stating that oxyfuel combustion has the highest investment costs in comparison to other CC technologies, but lower operational costs (F. Johnsson, personal communication, 03.05.21; F. Normann, personal communication, 04.05.21; S. M. Nazir, personal communication, 06.05.21). The experts added that the required ASU and a completely different setup for fuel combustion are the main reasons for the high capital investments.

## 4.3.4 Space requirements

Since research in oxyfuel combustion is focussing on the application in land-based power plants, space requirements are not considered in the available literature. The interviewed experts estimated that the space occupied by the required ASU and intermediate storage of  $O_2$  is similar to the overall space required for an absorption CC process working with MEA as solvent (F. Johnsson, personal communication, 03.05.21; F. Normann, personal communication, 04.05.21).

## 4.3.5 Advantages and Drawbacks

The main advantage of oxyfuel combustion is the comparably easy capture of  $CO_2$ , since the exhaust stream ideally consists of  $CO_2$  and water vapour only (Wilcox, 2012). Further, due to the absence of  $N_2$  in the combustion,  $NO_x$  emissions can almost be avoided completely (Wilcox, 2012).

Disadvantageous are the high investment costs and the electricity demand of the required ASU (F. Johnsson, personal communication, 03.05.21; F. Normann, personal communication, 04.05.21). The high efforts necessary to avoid a slip of air into the combustion process and the need to replace the engine are the main reasons for this technology is not being considered as feasible for retrofit applications (Wilcox, 2012; F. Johnsson, personal communication, 03.05.21; F. Normann, personal communication, 04.05.2021).

Since oxyfuel combustion processes are not requiring heat for regeneration, such as chemical absorption processes, they might be competitive in processes where only little waste heat is available, by achieving significantly lower costs of captured  $CO_2$  (Gardarsdottir et al., 2019).

## 4.3.6 Research for the application onboard vessels

Currently, there are no publications available presenting concepts for the application of oxyfuel combustion onboard internationally trading vessels. Wang et al. (2017) evaluated the feasibility of different CC technologies for vessels and concluded that oxyfuel combustion could potentially be applied onboard, once it is ready for commercial use. Nevertheless, they also state that new materials for engine components might be required, to withstand the high combustion temperatures. Further, the high-power demand for the ASU might be disadvantageous for the application of this technology onboard. Additionally, the need to install the equipment in restricted sites is evaluated as a serious problem for the application onboard vessels (H. Wang et al., 2017). The safety issues connected to the production and storage of large amounts of O<sub>2</sub>, which are requiring the installation in restricted sites, are seen as a major problem for marine applications by interviewed experts as well (F. Normann, personal communication, 04.05.21).

The feasibility study by Li et al. (2020) investigates the conversion of a conventional diesel-driven inland water ship to a propulsion drive powered by oxyfuel combustion. Thereby, the main focus was to reduce the consumption of  $O_2$  and at the same time, to attain the original energy output of the engine. However, the study is limited on the conversion and optimisation of the engine and feasible solutions regarding space requirements and possibilities onboard, as well as economical aspects are not considered. The concept contains the onboard storage in bottles of the required  $O_2$ , rather than producing it by an ASU (Li et al., 2020). The main insights of the study are summarised in *Table 4.15*.

| Authors<br>(Year)   | Title  |   | TRL <sup>1</sup>  | Ship type  |
|---------------------|--|---|---|--|
|                     | A feasibility study of implementation of oxy-fuel<br>combustion on a practical diesel engine at the<br>economical oxygen-fuel ratios by computer<br>simulation | -   | 2   | Inland vessel (40 kW)  |
|                     | Main conclusion Addi   |   | itional information   |  |
| Li et al.<br>(2020) | Optimisation of combustion process is not<br>sufficient to regain power of original engine;<br>O <sub>2</sub> excess is required                               | Resea<br>optim<br>powe<br>when<br>comb<br>exces<br>regain | arch con-<br>nisation f<br>or of the<br>convert<br>oustion e<br>s the eng<br>n the orig | ducts several<br>measures to regain the<br>original diesel engine<br>ed to an oxyfuel<br>ngine; without O <sub>2</sub><br>gine is not able to<br>ginal power |

 Table 4.15: Literature on oxyfuel combustion for the application onboard

<sup>1</sup> The TRL in this table is reflecting the state of the research described in the respective article. It is not indicating the TRL of the corresponding technology and is not used as basis for the assessment in chapter 5.

# 5 Comparative assessment

This chapter is applying the method as presented in section 3.3 to evaluate which of the technologies described in the preceding chapter is the most promising for the application onboard ships. The assessment is referring to data provided in chapter 4 where the origin and interpretation of the data are explained in more detail. Due to a lack of comparable figures, the ranking is based on a discussion for each criterion. Therefore, the structure of this chapter is oriented on the stages and criteria assessed. For each criterion, tables are summarising the ranking and main facts behind the ranking of each technology.

# 5.1 Technologies included

To preselect technologies to be included in the main assessment, two excluding criteria were defined in the method section. Since it is quite likely that newbuild ships will be equipped with ICEs for energy conversion throughout the upcoming decade and further, the need for technologies being able to decarbonise this drive technology is urging. Therefore, technologies that are not able to run in combination with an ICE are excluded from the assessment. Moreover, the assessment is limited to technologies that have achieved TRL 4 or higher, i.e., these technologies are still under development but have proven their functionality as a whole system in lab-scale. The TRL provided here is referring to the technology in general, it does not evaluate the state-of-the-art for the technology in combination with an ICE. Apart from the general CC technologies that have been described in detail in chapter 4, *Table 5.1* is also including initiatives for the application onboard, which have achieved TRL 3 or higher. Several identified articles and reports are based on simulations of the CC process for onboard application, but no proof-of-concept tests have been conducted, i.e., they are still at TRL 2 and not included here.

*Table 5.1* shows the considered technologies, their ability to run in combination with an ICE, the TRL and the main literature sources used for the assessment. The technologies marked with an " $\times$ " are fulfilling the criteria and are considered further in stage 1 of the assessment.

| CC technology   | ICE<br>compatible | TRL | Key literature                                  | Stage 1 |
|---|-------------------|-----|---|---------|
| Post-combustion capture   |                   |     |   |         |
| Absorption by MEA-<br>solvent                                     | Yes               | 9   | Luo & Wang (2017);<br>Feenstra et al. (2019)    | ×       |
| Absorption by ammonia-<br>solvent (NH <sub>3</sub> )              | Yes               | 6   | Awoyomi et al. (2019);<br>Awoyomi et al. (2020) | ×       |
| Absorption by piperazine<br>(PZ)                                  | Yes               | 6   | Feenstra et al. (2019)                          | ×       |
| Absorption by NaOH and<br>CaO                                     | Yes               | 3   | Zhou & Wang (2014)                              |         |
| Adsorption by solid<br>sorbents (in general)                      | No                | 6   | Ben-Mansour et al. (2016)                       |         |
| Adsorption by alumina<br>supported K <sub>2</sub> CO <sub>3</sub> | Yes               | 3   | Erto et al. (2018)                              |         |
| Membrane separation   | Yes               | 5   | Siagian et al. (2019)                           | ×       |
| Cryogenic separation<br>(A3C process)                             | Yes               | 4   | Willson (2020)                                  | ×       |
| Pre-combustion  |                   |     |   |         |
| Absorption/Adsorption   | Yes               | 5   | Lip et al. (2016)<br>Kotowicz et al. (2019)     | ×       |
| HyMethShip  | Yes               | 3   | Zelenka et al. (2019)                           |         |
| Oxyfuel combustion  |                   |     |   |         |
| Oxyfuel combustion in<br>ICEs                                     | Yes               | 4   | Kang et al. (2018);<br>Wu et al., (2014)        | ×       |
| Chemical-looping  | No                | 6   | Wilcox (2012)                                   |         |

#### Table 5.1: Overview of CC technologies considered for the assessment

In general, almost all CC technologies can be adapted in some manner to run in combination with an ICE. Out of the considered technologies, only chemical looping is not able to be applied in combination with ICEs, since it is based on the cycling of particles to transport O<sub>2</sub>.

It needs to be pointed out that there are numerous other solvents which could be used in postcombustion CC. Apart from the MEA benchmark solvent, the assessment is taking  $NH_3$  and PZ into consideration as well. Studies for all these solvents have been carried out to evaluate the application onboard vessels. The absorption process using NaOH and CaO by Zhou & Wang (2014) is developed for onboard appliances, but has not yet achieved TRL 4.

Post-combustion adsorption in general is developed quite far (TRL 6) for the application in industrial processes, but this technology is not effective to capture  $CO_2$  from such low concentrations as prevalent in the exhaust gases of ICEs, i.e., it is not feasible to run in combination with ICEs. Nevertheless, Erto et al. (2018) conducted proof-of-concept tests for an adsorption process using alumina supported K<sub>2</sub>CO<sub>3</sub> as sorbent, to be applied onboard a small ferry. The problems that occur in this research are similar to the problems found by other researchers for adsorption technology and are hindering the technology to achieve a higher TRL.

Membrane technology has not yet been researched for the application onboard, but its general characteristics allow it to be applied in surroundings with a confined space. Membrane appliances for separation of  $CO_2$  are still under development (TRL 5) and require extensive flue gas pre-treatment to capture  $CO_2$ . However, with such pre-treatment they are feasible to run in combination with ICEs.

CCC has been tested in pilot-scale for CC from industrial processes and power plants and achieved TRL 6 for such appliances. However, these tests do not consider the constraints of the application onboard a vessel. The study by Willson (2020) assessed the appliance of the A3C process for shipboard application in combination with ICEs. Hence, the A3C process is included in the assessment to represent cryogenic separation, since it is a feasible way to apply CCC onboard, although the TRL is lower than for other CCC technologies.

All pre-combustion technologies have in common, that they convert fuel into a syngas. The  $H_2$  fraction out of this syngas is used as fuel for a connected engine, i.e., the ICE needs to be able to run on  $H_2$ . Such  $H_2$  engines are still under development and have currently achieved TRL 7. Although, the pre-combustion CC process is mature in coal-fired power plant applications, it has not yet been applied in combination with ICEs. Since the subsystems of the pre-combustion CC technology have been validated, it is assigned TRL 5. Like in chapter 4.2, ab- and adsorption technology for pre-combustion capture is assessed in common in stage 1 of the assessment.

Whereas pre-combustion ab- and adsorption processes remove  $CO_2$  and other pollutants from the syngas stream, leaving an almost pure stream of H<sub>2</sub> for combustion, the membrane-reactor of the HyMethShip concept works conversely. The H<sub>2</sub> contained in the syngas is removed as permeate, leaving a  $CO_2$ -rich retentate stream. The difficulties to control the process in the membrane-reactor, combining several steps of the common pre-combustion capture process, are currently limiting the HyMethShip concept to achieve a higher TRL, resulting in an exclusion from the assessment (TRL < 4).

Similar to pre-combustion capture technologies, oxyfuel combustion requires a specialised ICE that is able to combust fuel in an oxygen-enriched environment. Difficulties in keeping the parameters of oxyfuel combustion in a manageable range require further development, before the oxyfuel combustion process can achieve a higher TRL. Nevertheless, ICEs for oxyfuel combustion have achieved TRL 4. Therefore, the technology is considered in stage 1 of the assessment. The required ASU is not a limiting factor since those are already commercially available (TRL 9).

# 5.2 Stage 1: Feasibility for shipboard application

Stage 1 of the assessment is evaluating the technologies, which have passed the excluding criteria, regarding their feasibility for the application onboard ships. This stage is not deciding which technology is the most feasible for marine applications, rather it addresses which technology is impacting the ships safety and vice versa which technology is impacted by the movement of the ship. Further, the impact of the fluctuating energy demand, for instance during manoeuvring, and the tolerance towards impurities in the fuel and exhaust are assessed. The results of stage 1 are summarised in *Table 5.2*.

| Technology                    | (1.1)<br>Safety and<br>stability | (1.2) Ship's<br>movement and<br>vibration | (1.3)<br>Fluctuations<br>in energy<br>demand | (1.4)<br>Impurities in<br>fuel/exhaust | Overall<br>score |
|-------------------------------|----------------------------------|---|--|--|------------------|
| Cryogenic separation<br>(A3C) | 1                                | 2   | 3  | 1                                      | 7                |
| Absorption by NH <sub>3</sub> | 3                                | 5   | 1  | 2                                      | 11               |
| Membrane separation           | 2                                | 1   | 3  | 7                                      | 13               |
| Absorption by PZ              | 3                                | 5   | 3  | 4                                      | 15               |
| Oxyfuel combustion            | 4                                | 3   | 2  | 6                                      | 15               |
| Absorption by MEA             | 3                                | 5   | 3  | 5                                      | 16               |
| Pre-combustion                | 5                                | 4   | 4  | 3                                      | 16               |

 Table 5.2: Results for stage 1 of the assessment

A detailed description of the conducted ranking can be found in the following subsections. Since only the TOP 3 technologies are considered in more detail in the second stage of the assessment, oxyfuel combustion as well as absorption by MEA or PZ will not be regarded in stage 2. The safety issues related to the large amounts of high concentrated  $O_2$  as well as the high fuel requirements disqualified oxyfuel combustion as a feasible solution for the shipboard application in this assessment. Although pre-combustion CC technologies can be adapted to a wide range of fuels, it is not able to work under unsteady conditions as they are usually occurring onboard vessels. When a failure occurs in the pre-combustion CC plant, this may lead to a complete loss of propulsion, which is further disadvantageous in regard to the safety of ship and crew.

The general drawbacks of the absorption process are leading to the exclusion of the solvents PZ and MEA for the second stage of the assessment. Only ammonia-solvents will be included in the second stage, due to the individual advantages regarding energy demand and the resistance towards solvent degradation by impurities in the exhaust gas. Furthermore, membrane and cryogenic separation will be considered for the second stage of the assessment, both being advantageous for appliances, where only a limited amount space is available.

## 5.2.1 Safety and stability (1.1)

While evaluating the impact on the ship's safety and stability, several factors are to be considered. Firstly, additional hazards originating from the CC process, which may affect the safety of crew and ship need to be taken into account. This section will rather identify the main hazards connected to each technology, than to carry out an extensive risk assessment, that would be required to evaluate the full scope of the risk connected to each technology. *Table 5.3* is showing the ranking according to the discussed factors below.

Oxyfuel combustion for ICEs demands large amounts of high concentrated  $O_2$ . The required  $O_2$  either needs to be bunkered and stored or produced onboard the ship. However, both scenarios include the storage of  $O_2$  in concentrations far above 30 %, making the handling very delicate (F. Johnsson, personal communication, 03.05.2021). The threat is related to the highly oxidising effect of  $O_2$ , which requires protection of all metal surfaces against the contact with the  $O_2$  stream. Even though, the  $O_2$  is not hazardous to the ships personnel when a leakage occurs, the high fire and explosion risk is the main threat, connected to this technology. Fire is in general a major threat to vessels, due to the limited firefighting capabilities onboard and the high temperatures weakening the vessel's steel structure (Azzi et al., 2011).

Another factor to consider is the so-called "safe return to port" regulation, which is compulsory for passenger ships (H. Kim et al., 2016). While this regulation does not apply for cargo vessels, its reasoning still urges the need for a back-up propulsion system. Hence, one needs to consider the case, how a ship's propulsion system will be affected by a failure of the CC system. Whereas in post-combustion capture the CC plant can be bypassed easily, oxyfuel and pre-combustion capture are requiring a different fuel system and combustion engines. If there is a failure in the fuel system, it may cause the ship to lose its propulsion completely and thereby posing a major threat to ship and crew.

Pre-combustion capture relies on the conversion of fuel into syngas, out of which the CO<sub>2</sub> is separated and the remaining H<sub>2</sub> is used as fuel. If a failure occurs in the syngas production or treatment process, this may cause the production of H<sub>2</sub> to be stopped, leading to a loss of fuel to drive the propulsion and auxiliary generators. H<sub>2</sub> is highly explosive, i.e., the amount produced and stored in advance should be kept as small as possible to limit the risk. In addition to these threads, which are similar to the ones posed by oxyfuel combustion, the impact of the ab- or adsorption plant for CO<sub>2</sub> removal from the syngas needs to be considered. Even though the equipment can be designed smaller than for post-combustion CC due to the lower gas-flow and higher CO<sub>2</sub> concentration, a negative impact on the ship's stability, as described in the following, might not be avoided. It can be concluded that the potential negative impact of the pre-combustion CC technology is higher than for oxyfuel combustion.

The hazards of post-combustion technologies are mainly related to the used solvent. Either the solvent is harmful or toxic to the environment (e.g., ammonia) or the degradation products formed by the solvent in contact with the flue gases are harmful. While precautionary measures can reduce the total risk, the use of such solvents still leads to an increased risk for the ship's personnel.

A fact being valid for all CC technologies, is that the installation of such plants is resulting in additional weight of the ship. Whereas the additional weight can be addressed in the design of a newbuilding, e.g., by additional ballast water tanks, the impact on the ship's stability might be an exclusion criterion in retrofit appliances. In general, all weight added above the metacentric height (GM) is negatively impacting the stability of the vessel (Brian, 2003). Since the sources of the flue gas, the ship's engines, are placed in the back of the vessel, the CC equipment needs to be installed here as well. This is impacting the weight distribution and could also affect the trim of the vessel, which may cause an increased fuel consumption. Furthermore, the additional weight added by fixed installations needs to be deducted from the ship's transport capacity and is therefore reducing the economic value of the vessel. In conclusion, technologies being compact and having a reduced weight are potentially less impacting to the ship's stability.

The post-combustion absorption plants using chemical solvents are bulky and weight intensive. The main weight is contributed by the absorber, the stripper and the cross-heat exchanger. Even though, the absorber column could be split into a series of columns to reduce the height of the equipment, it is likely impossible to avoid a negative impact on the stability of the vessel. Additionally, the liquid solvent can have a negative impact on the stability. The large amounts of solvent in the absorber and stripper could start to swing from one side of the column to the other, once the ship is moving due to weather conditions, e.g., wind, waves and swell. The free surface of the liquid column above the GM poses a threat to the stability of the vessel at sea (Brian, 2003). Regarding the vessel's safety and stability, all absorption technologies have the same impact and are therefore all ranked the same.

Typically, before a ship is built or major changes are applied to an existing ship, the construction drawings need to be approved by the classification society. For the approval of the classification society, calculations proving evidence of a sufficient stability are required. Technologies like membrane and cryogenic separation might be advantageous, since they allow a compact design of the CC plant and can be placed near the GM of a vessel, thus reducing the negative impact on stability. The free surface of liquids is significantly reduced in case of MC and even erased for MGS and CCC. However, all current membrane separation technologies require extensive pretreatment of exhaust gases, to protect the membranes from degradation. This leads to an increase in weight.

| Technology                    | (1.1) Impact on safety and stability  | Score |
|-------------------------------|---|-------|
| Cryogenic separation<br>(A3C) | Compact unit, allows to reduce the impact on the stability of the vessel; CC can be bypassed in case of failure; no additional risk for ships personnel   | 1     |
| Membrane separation           | Very compact design, allows reduced size and flexible placement<br>of plant to reduce impact on stability; current technologies require<br>intensive pre-treatment of flue gases, adding weight; CC can be<br>bypassed in case of failure; no additional risks for ships personnel    | 2     |
| Absorption by MEA             | Equipment size and weight is negatively impacting stability of the vessel: free surface of solvent in absorber and stripper negatively  |       |
| Absorption by NH3             | impacting stability; solvent and/or by-products hazardous for   | 3     |
| Absorption by PZ              | environment and crew; CC can be bypassed in case of failure   |       |
| Oxyfuel combustion            | High risk due to large amounts of highly concentrated O <sub>2</sub> ;<br>technical defects may cause loss of propulsion; not possible to<br>bypass   | 4     |
| Pre-combustion                | High risk due to production of highly explosive H <sub>2</sub> ; technical defects in syngas production or treatment may cause loss of propulsion; not possible to bypass; negative impact on ship's stability due to heavy equipment (ab-/adsorption) and free surfaces (absorption) | 5     |

### Table 5.3: Impact on safety and stability (1.1)

## 5.2.2 Ship's movement and vibration (1.2)

In the preceding criterion, the impact of the CC technology on the ship's movement was reviewed. Criterion 1.2 is evaluating the impact of the ship's movement and vibration, caused by the ICE as well as the weather conditions impacting a vessel. The results of the assessed impacts are summarised in *Table 5.4*.

For an optimal absorption of  $CO_2$  by the solvent, the contact surface between the flue gas stream and the solvent has to be maximised. This requires an equal distribution of the exhaust gases over the complete diameter of the absorber column. When a vessel is tilting to one side, the absorber is exposed to this movement as well. The gas flow in the absorber is going to shift to the "upper" side of the absorber, since the gases are lighter than the surrounding solvent. This problem of absorption applications onboard vessels was found by Einbu et al. (2021) and needs to be faced by including additional gas distribution zones in the packing of the absorber, resulting in a further increase of the total height of the absorber. This problem occurs in absorption applications in general, whether post- or pre-combustion. Pre-combustion absorption plants might be less affected, since the diameter of the columns is smaller due to a lower gas flow, which has to be treated.

The vessel's movement may also impact the metal beads used for the moving-bed in the A3C process presented by Willson (2020), but this has not been considered yet. Anyhow, this issue could be easily fixed by adding additional structures to avoid the movement of the beads. The potential impact of the vessel's movement on membrane separation and oxyfuel combustion is not considered in the consulted literature, but is deemed to be insignificant, due to the absence of free-moving liquids or solids. The same applies for pre-combustion capture, when applying adsorption for CC from the syngas.

The impact of vibrations caused by an ICE and the weather conditions affecting the vessel have not been considered in the available literature either. Whereas vibrations in specific frequencies could increase the mass transfer in absorption appliances (Ellenberger & Krishna, 2002), it can lead to serious damage on a ships' equipment and structure (Wärtsilä, 2021a). The CC technology installed onboard is affected by this threat, which may cause mechanical and/or structural damages or an increased maintenance effort. Therefore, systems with a limited number of moving parts (e.g., membranes) are less affected by vibrations. The oxyfuel combustion system is even causing its own vibrations, when considering that a special engine is required for this appliance. In the A3C process, an increased wear and tear might be caused but the CC process itself is not threatened by ship vibrations.

The impact of vibrations on the pre-combustion CC process is dependent on the technology which is applied. In general, the syngas production process is including lots of sensors and moving parts, which could be damaged by the vibration. When applying absorption, the impact is similar as for absorption technology in post-combustion applications. In case adsorption is applied for CC from the syngas, the impact of vibrations might be increased. The currently most mature technology, TSA with rotating bed, involves heavy moving parts. Problems with the sealing of the rotating bed might be further increased by wear and tear in result of the vibrations.

| Technology   | (1.2) Impacts by ship's movement and vibration   | Score |
|--|--|-------|
| Membrane separation                                | Largely not impacted by ship movement, limited number of<br>moving parts which could be damaged by vibration   | 1     |
| Cryogenic separation<br>(A3C)                      | Moving bed could be affected by vessel's movement, but easy to<br>avoid; vibration might increase the wear and tear  | 2     |
| Oxyfuel combustion                                 | Not impacted by ships' movement; system requires new engine,<br>which generates its own vibrations   | 3     |
| Pre-combustion                                     | Syngas production not affected by ship's movement, but by<br>vibrations; same problem of shifting exhaust gas flow in absorber<br>column as in post-combustion adsorption, but potentially less<br>severe (absorption); not impacted by ship's movement, but<br>affected by vibrations due to high number of heavy weighted<br>moving parts increasing wear and tear (adsorption); problems with<br>seals might be increased by wear and tear due to vibration<br>(adsorption) | 4     |
| Absorption by MEAAbsorption by NH3Absorption by PZ | Exhaust gas flow in absorber column is shifting when ship is<br>moving, impacting distribution of gases in the absorber column;<br>additional distribution zones required  | 5     |

#### Table 5.4: Impacts by ship's movement and vibration (1.2)

## 5.2.3 Fluctuations in energy demand (1.3)

In difference to industrial and power plants, who's operation is mostly steady, shipboard engines are often operating in an unsteady state since the energy demanded onboard is fluctuating. Depending on the required speed, operation mode and energy demanded by auxiliaries, an alternating amount of energy needs to be converted from fuel, resulting in a varying mass flow of  $CO_2$  to be captured. Especially during manoeuvring, the power demand and corresponding  $CO_2$  flow is changing fast. *Table 5.5* is summarising how the technologies are affected by fluctuations in the exhaust gas flow.

Post-combustion CC technologies do not affect the ship's engines itself but are faced with a fluctuating exhaust gas flow. For an absorption-based CC plant, the diameter of the absorber is dependent on the volume flow of exhaust fumes. The whole process needs to be dimensioned to reliably capture  $CO_2$  at high loads, which typically occur during a vessel's sea-passage. Whereas the energy demand for regeneration of amine-solvents is increasing with the amount of captured  $CO_2$ , the energy demand for regeneration of ammonia-solvents remains low, even with increasing amount of exhaust fumes to be treated (S. M. Nazir. personal communication, 06.05.21). In general, the large quantity of solvents being recirculated, heated and cooled within the process is the main reason for the inertia of the system. In certain operation modes (e.g., during manoeuvring), when the mass flow of  $CO_2$  is fluctuating, the system would be required to run on a high load to reliably capture  $CO_2$  from the exhaust fumes, like it is done with  $SO_x$  scrubbers nowadays.

The effect of a varying  $CO_2$  mass flow has not been considered in research on membrane and cryogenic separation yet. It is quite probable, that these technologies would require to run on full load during manoeuvring, same as the absorption plant, to be able to capture the  $CO_2$  reliably. In oxyfuel combustion processes, a buffer of  $O_2$  is required to manage the fast load changes, but apart from this, only the cooling energy for the condensation of water from the exhaust fumes would need to be adjusted.

Contradictory to post-combustion CC technologies, pre-combustion CC technologies are having a large impact on the ship's energy conversion process, since they produce H<sub>2</sub>, which is required as fuel. Due to the high heat and involved masses of the syngas production process, the system is only feasible to operate energy efficient in a steady-state operation. The pre-combustion CC technology is not able to adjust to a fluctuating demand in H<sub>2</sub> fuel, as it would be necessary during manoeuvring. To address this deficiency a buffer of H<sub>2</sub> would be required, which could pose an increased risk and requires additional equipment for the compression of the gaseous H<sub>2</sub>, to reduce the volume. Alternatively, a dual-fuel engine could be installed, which is able to run on  $H_2$  and the fuel used as feedstock for the H<sub>2</sub> generation. Such an engine would be able to run on ordinary fuel when the operation mode does not allow the generation of syngas for  $H_2$  production. The drawback of a dual-fuel engine is, that the carbon contained in the fuel is emitted but cannot be captured. Another possibility could be the installation of batteries onboard, acting as a buffer for electric energy. This allows the pre-combustion CC plant and the connected auxiliary engine to operate in steady-state, excessive energy is stored in the battery and used when a lack of electric energy occurs. Of course, this is only a feasible solution when the vessel is driven by an electric propulsion motor. In conclusion, pre-combustion CC requires additional technical effort to overcome the limitation to steady-state operation. Currently researched H<sub>2</sub>-fueled engines are developed as dual-fuel engines, resulting in the emission of CO<sub>2</sub> during unsteady operation.

Apart from post-combustion absorption using  $NH_3$  and oxyfuel combustion, none of the other technologies showed to be more advantageous against these. Excluding pre-combustion CC, all technologies included in this assessment are able to reliably capture  $CO_2$  under varying conditions. Pre-combustion capture technologies are not able to run under such unsteady process conditions. The included WGS reactor is only able to operate under steady-state conditions, requiring a steady load of the connected engine.

| Technology                    | (1.3) Impacts by fluctuation in energy demand  | Score |
|-------------------------------|--|-------|
| Absorption by NH <sub>3</sub> | Low energy demand, independent of CO2 to be captured   | 1     |
| Oxyfuel combustion            | Can easily adapt to different loads  | 2     |
| Membrane separation           |  |       |
| Cryogenic separation<br>(A3C) | All these technologies are assumed to be able to capture $CO_2$ reliably, even when the mass-flow is fluctuating but need to   | 3     |
| Absorption by MEA             | operate at full load to do so, causing an increased energy demand.   |       |
| Absorption by PZ              |  |       |
| Pre-combustion                | Only able to operate in steady-state; additional equipment required<br>to deliver energy required in unsteady operation modes; dual-fuel<br>engine would result in emission of CO <sub>2</sub> | 4     |

### Table 5.5: Impact of fluctuations in energy demand (1.3)

# 5.2.4 Impurities in fuel and exhaust gases (1.4)

Marine fuels often contain impurities that are emitted into the atmosphere, when combusting the fuel. The most common contaminant is sulphur, which is also addressed by regulations of the IMO. Since the beginning of 2020, the so-called IMO sulphur cap is limiting the sulphur content in the exhaust gases released into the environment to 0,5 % outside and 0,1 % inside SECA zones, respectively (IMO, 2019a). However, only the content of sulphur in the emitted exhaust fumes, but not the content in the fuel itself is limited by this regulation. Due to the lower prices of fuel oils containing sulphur, it is economically beneficial to install exhaust gas treatment equipment onboard. This allows to continue to use sulphurous fuels, while meeting the requirements. Such

an effect could also be beneficial for the installation of CC equipment onboard, i.e., CC technologies that allow the use of low-priced fuels, will have lower OPEX. *Table 5.6* is summarising how all considered technologies are affected by impurities in fuel and exhaust fumes. It also shows the corresponding ranking for this criterion, of course.

PM emissions from marine ICEs could negatively affect CC technology. PM emissions mainly result from the incomplete combustion of carbon and incombustible fuel components (Corbett & Winebrake, 2008). The soot captured from exhaust gases could accumulate in the CC plant, which can reduce its efficiency and increase costs due to degradation.

 $NO_x$  emissions are not directly resulting from the combusted fuel itself. These are actually formed due to the high temperatures during the combustion, in particular by the N<sub>2</sub> contained within the combustion air.  $NO_x$  emissions are addressed by regulations of the IMO and limit the allowed quantity, depending on a vessel's year of manufacture and the engine's rotation speed (IMO, 2019c). Although the  $NO_x$  formation is dependent on an engine's design, the choice of fuel can have an impact as well. For example, LNG is combusting at a lower peak temperature, which results in a reduced formation of  $NO_x$  emissions. A method commonly used to reduce  $NO_x$ formation is exhaust gas recycling (Verschaeren et al., 2014). Replacing a part of the combustion air by recycled exhaust gases reduces the concentration of  $N_2$  and lowers the combustion temperature due to a decreased  $O_2$  concentration. A side effect, beneficial for CC, is that the concentration of  $CO_2$  in the exhaust gases is increased and the total amount of exhaust fumes is decreased. This allows reduced equipment sizes and also increases the efficiency of the CC plant (Luo & Wang, 2017).

Higher-grade fuels have an increased ratio of  $H_2$  to carbon (H/C-ratio), i.e., the CO<sub>2</sub> produced per energy unit is lower. This allows to reduce the size of the CC equipment (E. Malmgren, personal communication, 12.05.21). Furthermore, higher-grade fuels contain less contaminants, which is reducing the need for other exhaust gas treatment systems. LNG mainly consists of CH<sub>4</sub> and has almost no contaminants, such as sulphur. The high H/C-ratio and the absence of contaminants requiring exhaust gas treatment makes LNG a fuel, being of high interest for CC applications (Awoyomi et al., 2020; Feenstra et al., 2019; H. Lee et al., 2020).

In general, all CC technologies included in this assessment require a pre-treatment of the exhaust gas, but some technologies are more sensitive to impurities in the exhaust fumes than others. Out of all considered technologies, membrane separation requires the most intense pre-treatment. The current membrane technology is very sensitive to water,  $SO_x$  and  $NO_x$ , which are causing a fast degradation of the membrane.

The principle of the oxyfuel combustion process is to reduce exhaust gas components such as water and  $CO_2$ . To conclude, all fuel impurities will be counterproductive to meet this target and need to be addressed by aftertreatment. Hence, the oxyfuel combustion process is fairly limited in the choice of fuels.

Amine-solvents (e.g., MEA) and PZ in absorption processes could theoretically be applied without a pre-treatment of exhaust gases, when a loss of solvent by degradation is accepted. All solvents are selective to acids, which allows them to bind  $CO_2$ , but also  $SO_2$  and  $NO_2$ . Since the chemical affinity of solvents towards  $SO_2/NO_2$  is higher than towards  $CO_2$ , the capture-rate is reduced. Furthermore, bonds between solvents and  $SO_2/NO_2$  are permanent. This is leading to a degradation of the solvents. Degraded solvent has to be replenished, which is increasing the OPEX and produces a hazardous sludge of degraded solvent. To limit the degradation effect, either a pre-

treatment is needed, or the technology can only be used in combination with high-grade fuels, such as LNG.

An additional problem is the oxidation of solvents with  $O_2$  contained in exhaust gases. Thereby, PZ is less affected by degradation (due to oxidation of solvents) than MEA. The oxidative degradation of MEA results in formation of NH<sub>3</sub>, being hazardous to the environment when emitted (Mertens et al., 2013).

In pre-combustion capture, the fuel is converted to produce a syngas. Impurities such as ashes, which cannot be converted, have to be filtered out before prior processing. In power plant applications, where the syngas is produced from coal containing a lot of ashes, this is achieved by a cyclone filter (Figure 4.9). Impurities that are converted and therefore contained in the syngas, might need to be addressed in case the CC technology is harmed by those or when their emission into the environment should be avoided. This can be done by including additional syngas treatment equipment before the CC unit, as it is seen in Figure 4.9 for desulphurisation. Similar to post-combustion applications the required effort is depending on the solvent/sorbent, which is applied for CC from the syngas by ab-/adsorption. The common solvents in pre-combustion absorption are degraded by SO<sub>x</sub> and NO<sub>x</sub>, i.e., those contaminants need to be removed from the syngas to reduce the solvent loss. Common adsorbents are degraded by these contaminants as well, some are even sensitive to water contained in the syngas flow. However, contaminants that are not affecting the CC process can be left in the H<sub>2</sub> stream, i.e., they would be emitted together with the exhaust gases of the combustion process. Overall, a wide range of fuels can be used when applying pre-combustion CC, but additional syngas treatment may be required to avoid degradation of the solvent or sorbent.

Using ammonia-solvents in a post-combustion absorption process in combination with sulphurous fuels allows the integration of  $SO_x$ -removal into the CC process (Awoyomi et al., 2019). By sequestering sulphur to  $NH_3$ , a saleable by-product, ammonia-fertiliser, is produced. This can be seen as beneficial in some cases, but also requires extra storage and additional equipment, e.g., to filter the ammonia-fertiliser out. A problem in this regard might be, that such filter equipment could not be selective between the fertiliser and other components, which are also washed out from the exhaust stream.  $NH_3$  is resistant towards oxidation by  $O_2$  contained within the flue gas stream and is therefore not subject to oxidative degradation.

The A3C process proposed by Willson (2020) requires a flue gas inlet temperature of 30 °C, i.e., cooling of the gas stream is required before entering the cryogenic separation plant. Willson (2020) proposes a direct contact cooler which could be equipped to work like a scrubber and thereby remove sulphur emissions, PM as well as condense the gaseous water, which is contained in exhaust fumes. The remaining water and NO<sub>2</sub> are removed by the cooler-dryer, the first stage of the A3C process, to avoid a contamination of the captured CO<sub>2</sub>. Thus, upgrading the direct contact cooler to function as a scrubber allows the use of conventional marine fuel oils.

### Table 5.6: Impact of impurities in fuel/exhaust (1.4)

| Technology                    | (1.4) Impacts by impurities in fuel/exhaust  | Score |
|-------------------------------|--|-------|
| Cryogenic separation<br>(A3C) | Direct contact cooler required for cooling, can be upgraded to<br>function as scrubber; core process is not affected by impurities in<br>fuel or exhaust; no degradation due to impurities in exhaust gases                            | 1     |
| Absorption by NH <sub>3</sub> | Pre-treatment required if degradation of solvent should be<br>avoided; sulphur contained in exhaust gases can be converted to<br>saleable by-product, when desired; solvent is not degraded by<br>oxidation                            | 2     |
| Pre-combustion                | Additional pre-treatment required if degradation of solvent/<br>sorbent should be avoided; absence of O <sub>2</sub> in syngas avoids<br>degradation; wide range of fuels applicable, when additional syngas<br>treatment is installed | 3     |
| Absorption by PZ              | Pre-treatment required to avoid degradation of solvent; impurities<br>in exhaust gases are leading to solvent degradation and production<br>of hazardous waste; not as much affected by oxidation as MEA                               | 4     |
| Absorption by MEA             | Pre-treatment required to avoid degradation of solvent; impurities<br>in exhaust gases are leading to solvent degradation and production<br>of hazardous waste; oxidation of MEA is producing NH <sub>3</sub><br>emissions             | 5     |
| Oxyfuel combustion            | Principle of oxyfuel combustion requires clean fuel; all<br>contaminants need to be addressed by additional an aftertreatment<br>system  | 6     |
| Membrane separation           | Current-state technology is strongly affected by impurities in<br>exhaust gases; water contained in exhaust fumes is degrading<br>membranes; extensive pre-treatment is required to avoid damage<br>to the membranes                   | 7     |

# 5.3 Stage 2.a: Most promising technology for newbuildings

Stage 2.a aims to evaluate which technology is most promising for the appliance onboard newbuild vessels. Therefore, the three technologies deemed as the most feasible for the application onboard vessels in stage 1, are evaluated in relation to typical constraints set out by the application onboard. Furthermore, financial aspects which are of high interest for shipowners, are included as well. The ranking for each criterion is based on a discussion of facts that are presented in chapter *4. Table 5.7* is summarising the results of stage 2.a, showing that the absorption process using aqueous NH<sub>3</sub> as solvent has achieved the lowest score, i.e., it is the most promising technology for newbuildings.

| Criteria                  | Absorption by NH <sub>3</sub> | Cryogenic<br>separation (A3C) | Membrane separation |
|---------------------------|-------------------------------|-------------------------------|---------------------|
| (2.1) Space requirements  | 3                             | 2                             | 1                   |
| (2.2) Additional weight   | 3                             | 2                             | 1                   |
| (2.3) Energy requirements | 1                             | 3                             | 2                   |
| (2.4) Capture-rate        | 2                             | 1                             | 3                   |
| (2.5) Investment costs    | 2                             | 1                             | 3                   |
| (2.6) Operational costs   | 1                             | 2                             | 3                   |
| (2.7) Maturity level      | 1                             | 3                             | 2                   |
| Overall score             | 13                            | 14                            | 15                  |

#### Table 5.7: Results of stage 2.a of the assessment

## 5.3.1 Space requirements (2.1)

The limited space is the main obstacle for the installation of CC equipment onboard a vessel. Space occupied by the CC plant and all related installations cannot be utilised for the transportation of goods, which is the purpose of a vessel and defines its economic value. Since the EEDI calculation is including the amount of cargo transported, less cargo capacity will also negatively impact the attained EEDI. Therefore, a CC unit for the application onboard ships should take up as little space as possible.

Post-combustion absorption units require an absorber and a stripper, both being large in size and having a high weight. Furthermore, to reduce the energy required for the regeneration of the solvent, a space consuming lean-rich heat exchanger is required. Out of the three technologies considered for the second stage of the assessment, the absorption process using ammonia solvent is requiring the most amount of space.

The size of the A3C unit is only varying slightly when a higher  $CO_2$  flow needs to be captured. The moving-bed of metal beads as well as heat exchangers and refrigeration unit contribute to its size, but it is the weight of the entire unit that is reflecting the maximum capture capacity. The A3C setup proposed by Willson (2020) consists of a compact unit, rather than several bulky columns as it is required for the absorption process.

Membrane technologies are developed for appliances, where only little space is available. Nowadays, membrane technology is applied onboard vessels for fresh water production and wastewater treatment (Wärtsilä, 2021b, 2021c). The membrane structure allows to fit a big surface for the separation in a confined space. Same as for current membrane applications onboard, it is probable that the required pre-treatment is going to occupy more space than the membranes themselves. However, the use of cleaner fuels allows to reduce the necessary pre-treatment equipment, so that it is likely to be less space consuming. Therefore, the membrane technology is rated best in terms of space requirements in *Table 5.8*.

| Technology                    | (2.1) Space requirements  | Score |
|-------------------------------|---|-------|
| Membrane separation           | Made for applications within a confined space                                 | 1     |
| Cryogenic separation (A3C)    | Compact design, size does only vary slightly with higher CO <sub>2</sub> flow | 2     |
| Absorption by NH <sub>3</sub> | System consists of several bulky components                                   | 3     |

Table 5.8: Space requirements (2.1)

## 5.3.2 Additional weight (2.2)

A vessel's design allows for a specified amount of cargo and provisions to be loaded, the so-called DWT. When retrofitting a CC plant to an existing vessel, the weight of the installation needs to be deducted from the DWT and is thereby reducing the ship's capacity. In the design of newbuildings, the additional weight can be addressed by the design of the hull. Nevertheless, the lower the weight of the technical installations onboard, the higher the DWT allowed with the same hull design. Hence, also the attained EEDI can be improved due to a higher capacity of the vessel.

As mentioned above, the weight of the A3C plant is dependent on the amount of flue gas to be treated. The required heat exchangers, refrigeration unit and the bed of moving metal beads are the main contributors to the weight of the entire plant. Although, the technology allows a compact design, the required equipment is very heavy. To capture 3,7  $t_{CO2}$ /h Willson (2020) estimated the weight of the plant to be about 100 t.

Absorption plants consist of several components, which are increasing in size with a growing volume flow and lower  $CO_2$  concentration in flue gases. When scaling up the weight estimations of Feenstra et al. (2019) to the same amount of  $CO_2$  captured as in the case study by Willson (2020), it results in a total weight of about 150 t for the entire CC plant.

No weight figures regarding membrane separation could be attained from the consulted literature nor from all interviewed experts. However, with a very high certainty it can be assumed, that the weight of the membrane separation unit is going to be lower than for the other technologies considered in this assessment. The low weight of the membrane unit allows the assumption, that even with an inclusion of the required pre-treatment equipment the total weight is still less than for the A3C process. When cleaner fuels are used the effort for pre-treatment can be reduced, i.e., the weight of the equipment is further reduced. Therefore, membrane separation is ranked best in this category, as seen in *Table 5.9*.

| Technology                    | (2.2) Additional weight  | Score |
|-------------------------------|--|-------|
| Membrane separation           | Not addressed in consulted literature, but with high certainty lower than for other technologies | 1     |
| Cryogenic separation (A3C)    | About 100 t to capture 3,7 $t_{CO2}/h$ ; weight is corresponding to the CO <sub>2</sub> flow     | 2     |
| Absorption by NH <sub>3</sub> | About 150 t to capture 3,7 t <sub>CO2</sub> /h; several heavy-weighted components are required   | 3     |

Table 5.9: Additional weight (2.2)

# 5.3.3 Energy requirements (2.3)

All types of energy required for a CC unit onboard a vessel needs to be converted from fuel, e.g., to electric and thermal energy. The more energy is required by a CC unit, the more CO<sub>2</sub> is produced due to the increased fuel consumption and is thereby negatively affecting the carbon reduction rate of the CC technology. Furthermore, the fuel consumption is the main cost driver in the operation of vessels and an increasing energy demand would thereby directly impact the OPEX (Gohari et al., 2018). For these reasons, the technology having the most energy-efficient operation is ranked best in this category.

The principle of the A3C process relies on very low temperatures (-100 °C) to solidify the CO<sub>2</sub> contained in the flue gases for separation. Therefore, the refrigeration unit has a high power demand. Further, the A3C process is not able to utilise waste heat. The simulation conducted for the case study by Willson (2020) approximated the energy demand for the capture of 3,7  $t_{CO2}$ /h to 1.700 kW. The OPEX, mainly derived from the fuel consumption, for the CC have been estimated to be 70 % lower than for the benchmark process of absorption with MEA.

To effectively operate a membrane separation plant, the partial pressure difference of  $CO_2$  has to be as high as possible, i.e., the flue gases need to be compressed or the inner pressure of the membrane needs to be reduced by creating a vacuum. Both possibilities require energy, but no figures on this could be obtained from the consulted literature. Apart from this, energy is also required for the intense pre-treatment, which is necessary for this particular technology. When MC membranes are used, the waste heat available onboard can be utilised for the regeneration of the solvent. Out of all considered technologies, membrane separation is estimated to have the lowest energy demand when excluding the pre-treatment. It is likely, that the energy demand of the compulsory pre-treatment is higher than the one of the membrane separation unit itself. Therefore, including the compulsory pre-treatment reduces the energy-efficiency drastically. The authors estimate the total energy demand to be similar to the absorption process by NH<sub>3</sub> but due to the uncertain data basis membrane separation is ranked on the second place.

The advantage of an absorption process using  $NH_3$  is the possibility to utilise the engine's waste heat for the regeneration of the solvent. Thereby, the reboiler duty, the energy required for regeneration of the solvent, is reported to be only 27 % of the energy required for the regeneration of MEA solvents (Awoyomi et al., 2020). Another energy-saving advantage of  $NH_3$  solvents is connected to the ability to desorb  $CO_2$  at an elevated pressure, thus reducing the energy demand for the compression of captured  $CO_2$ . Due to these benefits, the absorption process is ranked best in this category, as summarised in *Table 5.10*.

| Technology                    | (2.3) Energy requirements   | Score |
|-------------------------------|---|-------|
| Absorption by NH <sub>3</sub> | Only 27 % reboiler duty of MEA; possibility to utilise waste<br>heat; desorption at elevated pressure allows energy savings in<br>compression of CO <sub>2</sub>                                | 1     |
| Membrane separation           | No figures provided in literature; additional energy required<br>for intense pre-treatment and to create pressure difference for<br>separation; only small amount of waste heat can be utilised | 2     |
| Cryogenic separation (A3C)    | Not possible to utilise waste heat; large amount of electric<br>energy required for refrigeration unit  | 3     |

## Table 5.10: Energy requirements (2.3) Image: Comparison of the second secon

# 5.3.4 Capture-rate (2.4)

In general, all capture technologies can achieve a capture-rate of 99 %, but this is not seen as economically feasible in the consulted literature. Due to severe cost increases to capture the last 10 % of CO<sub>2</sub>, most research is carried out to achieve a capture-rate of 90 %. The increase in costs for a complete capture mainly results from the required equipment size to capture CO<sub>2</sub> with a very low partial pressure. However, technical and energetic efforts required to achieve a higher capture-rate differ for all technologies, which are considered in this assessment. *Table 5.11* shows the ranking of these technologies for this criterion.

The separation process in membranes is driven by a partial pressure difference (Siagian et al., 2019). A certain pressure difference is required to force  $CO_2$  through the membrane, i.e., with a decreasing  $CO_2$  concentration in the flue gas, the pressure of the flue gas would need to be increased to achieve the required partial pressure difference. This results in an increased energy demand. Furthermore, the material strength of the membrane needs to be improved to withstand a higher pressure. Moreover, at a certain pressure level also other flue gas components might pass through the membrane. Current membrane applications for water purification, which have been named as example before, are therefore only separating a part of the water (Wärtsilä, 2021b, 2021c).

The absorption process is driven by an equilibrium of the partial pressure between bonded and unbonded  $CO_2$  (Dugas & Rochelle, 2008). To achieve a higher capture-rate, the absorption column height would need to be increased significantly. In order to bind more  $CO_2$ , the solvent at the upper end of the absorption column has to be very lean. This would require a higher regeneration rate, which in turn results in a higher reboiler duty and a larger stripper column. Further, the slow kinetics of the absorption process using NH<sub>3</sub> may require an even larger absorber.

Cryogenic separation processes, such as the A3C process, rely on very low temperatures to solidify the CO<sub>2</sub>. Due to the low the gas stream temperature, the CO<sub>2</sub> solubility is decreased, which allows an increased capture-rate with less effort than required by the other technologies. The usage of a higher moving-bed of metal beats in the A3C process is a feasible approach to increase the capture-rate to 99 % (Willson, 2020). Therefore, the A3C process is judged best in this category.

| Technology                    | (2.4) Capture-rate   | Score |
|-------------------------------|--|-------|
| Cryogenic separation<br>(A3C) | Low temperature is decreasing solubility in flue gas stream; higher<br>bed of metal beads can capture 99 % of CO <sub>2</sub> contained in flue gas<br>stream                        | 1     |
| Absorption by NH <sub>3</sub> | Significantly higher absorber and stripper required; power<br>consumption for regeneration process will increase significantly;<br>economically unfeasible                           | 2     |
| Membrane separation           | Higher pressure required to achieve a better capture-rate; material<br>strength of membranes may no longer be sufficient to withstand<br>increased pressure; economically unfeasible | 3     |

### Table 5.11: Capture-rate (2.4)

## 5.3.5 Investment costs (2.5)

The payback period is the most important criterion for ship owners to decide in which energy efficiency measure to invest (DNV GL, 2015). If a taxation of  $CO_2$  emissions from shipping becomes reality, the initial investment would be the most important factor for shipowners to calculate the payback period. The longer a payback period, the higher the financial risk connected to the investment, since the development of the market can only be foreseen for a short period of time. Shipowners would therefore prefer a technology, with the lowest investment costs and the shortest payback period.

The costs of membranes for  $CO_2$  separation could not be ascertained from available literature. However, such required membranes are difficult to produce and a high-tech solution, which is quite likely reflected in a high price. The current membrane technology is requiring intensive pretreatment, which is adding further investment costs. Due to a low concentration of  $CO_2$  in the exhaust gases of ICEs, currently available literature suggests that one membrane unit might not be sufficient, i.e., a CC unit for the application in combination with ICEs would comprise of two or even more membrane units (Khalilpour et al., 2015; Siagian et al., 2019). Additional costs result from the necessary pre-treatment and its installation. Membrane technology is therefore deemed to have the highest investment costs out of the three technologies.

Awoyomi et al. (2020) designed an absorption unit using aqueous-ammonia as solvent for an LNG-fuelled engine delivering 10.305 kW continuous-rated power. The estimation of the CAPEX predicts costs of about 35 million US-dollars, which includes the  $CO_2$  compression and liquefaction. Since the related simulation was conducted for CC onboard a  $CO_2$ -tanker, costs for the storage tanks have not been included. However, absorption plants allow a trade-of between CAPEX and OPEX (Einbu et al., 2021). Reducing the size of the installed absorber is lowering the initial costs but involves a higher recirculation rate of the solvent and higher reboiler duty. This leads to a higher power consumption, which is the main contributor to the OPEX.

The case study conducted by Willson (2020) for the application of the A3C process onboard involves an LNG-fuelled engine with 12.614 kW. The CAPEX for the complete CC process includes the inlet cooler, refrigeration process as well as costs for liquefaction and tanks for intermediate  $CO_2$  storage onboard. The estimate comprises costs of about 11,5 million pound sterling. Since this is significantly lower than the CAPEX for an absorption plant for the treatment of exhaust gases generated by a less powerful engine, the A3C process is ranked highest in *Table* 5.12.

| Technology                    | (2.5) Investment costs  | Score |
|-------------------------------|---|-------|
| Cryogenic separation (A3C)    | About half of investment costs of an absorption plant   | 1     |
| Absorption by NH <sub>3</sub> | High investment costs; CAPEX/OPEX trade-of allows to lower investment costs when plant size is reduced                              | 2     |
| Membrane separation           | No figures available; potentially very expensive due to<br>high-tech technology; additional costs due to required pre-<br>treatment | 3     |

### Table 5.12: Investment costs (2.5)
### 5.3.6 Operational costs (2.6)

Lower operational costs are contributing to a shorter payback-period, which is more attractive for shipowners (DNV GL, 2015). Operational expenses include costs for power consumption, chemicals and maintenance. Hence, the main contributor to the operational costs is the fuel consumed for additional power generation onboard. *Table 5.13* shows the ranking for this criterion.

Same as for the CAPEX, no figures on the OPEX for membrane separation were available in the consulted literature either. However, energy requirements for the separation itself are estimated to be low and might even be lower than for the compulsory pre-treatment. In comparison to all other technologies considered in this assessment, the main cost driver for membrane technology are maintenance costs, due to short lifespan of membranes, which are currently available. These membranes are expensive, which is why this technology is evaluated to have the highest OPEX, even though the required energy for the core process might be the lowest.

The case study conducted by Willson (2020) for the application of the A3C process onboard, is estimating the OPEX to be about 1,15 million pound sterling, with fuel costs for energy generation contributing to about 80 % of the overall OPEX. Referring to conventional industrial processes, it is stated that the A3C process can cut the OPEX by 70 %.

The absorption process using aqueous-ammonia solvent can attain the lowest OPEX, due to low chemical costs and a low energy demand (Awoyomi et al., 2020). In comparison to the benchmark absorption process with MEA solvent, the OPEX can be reduced by 73 % (Awoyomi et al., 2020).

| Technology                    | (2.6) Operational costs                                  | Score |
|-------------------------------|--|-------|
| Absorption by NH <sub>3</sub> | Low chemical costs; low energy costs; 73 % lower OPEX    | 1     |
|                               | than MEA benchmark process                               | 1     |
| Cryogenic separation (A3C)    | About 80 % of total OPEX originate from increased energy |       |
|                               | demand; 70 % lower OPEX than conventional processes in   | 2     |
|                               | industry applications                                    |       |
| Membrane separation           | Low energy demand of core process, but high maintenance  |       |
|                               | costs due to short lifespan of membranes are main cost   | 3     |
|                               | contributor  |       |

Table 5.13: Operational costs (2.6)

### 5.3.7 Maturity level (2.7)

The maturity level in this assessment is evaluated according to the TRL of the included technologies. The achieved results can be found in *Table 5.14*. A higher TRL makes a commercial application in the nearby future more likely and figures on cost estimates are getting more precise, since more experience regarding these technologies has been gained.

Even if cryogenic gas separation is already commercially applied in the industry (Abanades et al., 2015), the A3C process is not fully developed yet. Nevertheless, due to mostly mature technology in the industry, A3C has the potential to achieve a higher TRL soon.

Membrane technology for  $CO_2$  separation is nowadays mainly applied in the fossil fuel industry for gas-sweetening, where it is already a mature technology. However, for exhaust gas treatment only pilot plants exist so far and problems affecting membranes' lifespan still need to be solved before an application at a larger scale is getting feasible (L. L. Baxter et al., 2019; Sustainable Energy Solutions, 2021b).

Absorption processes using liquid sorbents are applied for CC in commercial applications and have thereby achieved TRL 9. Nowadays, research is focussing on the development of sorbents, which require less energy and are less affected by degradation. Pilot plants using aqueous ammonia solvents are already in place, where research is conducted to reduce the loss of solvent (ammonia slip) and to increase the capture efficiency.

| Technology                    | (2.7) Maturity level  | Score |
|-------------------------------|---|-------|
| Absorption by NH <sub>3</sub> | TRL 6; pilot plants in place, research to increase capture  | 1     |
|                               | efficiency and reduce ammonia-slip                          | -     |
| Membrane separation           | TRL 5; issues regarding short lifespan of membranes (due to |       |
|                               | degradation by exhaust gas components) still need to be     | 2     |
|                               | resolved, before reaching higher TRL                        |       |
|                               | TRL 4; potential to achieve a higher TRL soon, due to       |       |
| Cryogenic separation (A3C)    | cryogenic gas separation already being mature in onshore    | 3     |
|                               | industry  |       |

#### Table 5.14: Maturity level (2.7)

### 5.4 Stage 2.b: Most promising technology for retrofitting

Integrating CC technology into the design of a newbuild vessel allows to accommodate all requirements of a CC plant. When a CC plant is installed as a retrofit solution, it needs to be integrated into the design of an existing vessel. The more changes are necessary, the higher will be the costs of such an investment into a CC technology. Therefore, this assessment stage is considering additional criteria, which are of high interest when installing CC technology onboard an existing vessel. The scores achieved in the three criteria of this stage are added to the scores attained in stage 2.a, since all criteria of the foregone stages are important characteristics for retrofit applications as well. The outcome of this stage is shown in *Table 5.15*.

| Table 5.15: Results of stage 2.b d | of the assessment |
|------------------------------------|-------------------|
|------------------------------------|-------------------|

| Criteria                    | Absorption by NH <sub>3</sub> | Cryogenic<br>separation (A3C) | Membrane separation |
|-----------------------------|-------------------------------|-------------------------------|---------------------|
| Stage 2.a                   | 13                            | 14                            | 15                  |
| (2.8) New engine            | 1                             | 1                             | 1                   |
| (2.9) Conversion of fuel    | 1                             | 2                             | 3                   |
| (2.10) Repowering           | 1                             | 3                             | 2                   |
| Overall score $(2.a + 2.b)$ | 16                            | 20                            | 21                  |

Due to a low power consumption and the advantages of ammonia solvents in connection with sulphurous fuels, this assessment is judging the considered absorption process as best choice for retrofitting. The high energy demand of the A3C process makes it likely that the existing energy system is not able to provide all additional energy, which is required by the refrigeration unit. Membrane separation systems need intense pre-treatment to reduce the membranes' degradation. A conversion to clean fuels, such as LNG, could reduce the necessary pre-treatment, but still cannot avoid it completely.

### 5.4.1 New engine (2.8)

CC technologies such as pre-combustion capture and oxyfuel combustion are requiring extensive changes to the engine. In pre-combustion capture applications, an engine needs to be able to combust H<sub>2</sub>. The conversion of a conventional marine diesel engine is probably uneconomical (i.e., prohibitively expensive) or even impossible (from a technical point of view). Therefore, pre-combustion capture technology would require a replacement of the entire engine, which would significantly increase the costs for the installation of CC technology. The same applies to oxyfuel combustion, which also requires an engine replacement.

However, all technologies, which are considered in stage 2 of this assessment, are post-combustion capture technologies and thereby do not affect the engine. Post-combustion technologies can be retrofitted relatively easy into an existing exhaust gas aftertreatment system, e.g., like  $SO_x$ -scrubbers today. Since none of these reviewed technologies has a negative impact regarding this particular criterion, all are rated to a score of 1.

### 5.4.2 Conversion of fuel and fuel system (2.9)

In general, the same applies for this criterion, as for criterion 2.8. All technologies included in this assessment can capture  $CO_2$  resulting from any kind of fossil fuel combustion, but also all require pre-treatment to do so. In criterion 1.4 (5.2.4), it has been discussed how impurities in a flue gas stream would affect all CC technologies and which technologies require more effort in pre-treatment when low-grade marine fuels are combusted. The ranking for this criterion, shown in *Table 5.16*, is therefore referring to criterion 1.4.

| Technology                    | (2.9) Conversion of fuel and fuel system   | Score |
|-------------------------------|--|-------|
| Cryogenic separation<br>(A3C) | Pre-treatment required for cooling can be upgraded to function as<br>scrubber; core process is not affected by impurities in fuel or<br>exhaust; no degradation due to impurities in exhaust                                 | 1     |
| Absorption by NH <sub>3</sub> | Pre-treatment required to avoid solvent degradation; sulphur<br>contained in exhaust can be converted to saleable by-product, when<br>desired; solvent is not degraded by oxidation  | 2     |
| Membrane separation           | Currently available technology is strongly affected by impurities in<br>exhaust gases; water contained in exhaust gas is severely degrades<br>membranes; extensive pre-treatment is required to avoid damage to<br>membranes | 3     |

Table 5.16: Conversion of fuel and fuel system (2.9)

### 5.4.3 Repowering (2.10)

If it is likely that the installed power system onboard is not able to meet the power demand of an additional CC plant, repowering is required. The installation of additional engines to convert fuel into electricity, is increasing the CAPEX as well as the OPEX, due to an increased fuel consumption and higher maintenance expenditures. Depending on the vessel, this might make the installation of CC onboard uneconomically or even technically unfeasible. *Table 5.17* is summarising the results for this criterion.

With regard to the energy requirements assessed in criterion 2.3, the A3C system has a high electricity demand to drive the refrigeration unit and no waste heat can be utilised. The auxiliary generators installed on the case study vessel considered by Willson (2020) have been sufficient to provide the energy required for the A3C process, but were required to run continuously. Hence, the CC plant would need to be shut down to carry out maintenance or in case of a breakdown of one of the auxiliary engines. Due to this limitation, the study recommends upgrading the power system by an additional auxiliary engine, to ensure redundancy in case one engine needs to be taken out of service.

The energy demand of the membrane separation process is deriving from the compression of the flue gas, to achieve the partial pressure difference, which drives the separation process. In addition, the excessive pre-treatment of the membrane process requires electric energy, but no figures regarding the energy demand of a membrane unit could be found in consulted literature. Overall, the energy demand of membrane separation and absorption by NH<sub>3</sub> is estimated to be similar. In case MC technology is applied, little waste heat can be utilised, i.e., electric energy is representing the biggest share of the consumed power. Depending on the vessel and the fuel used (impacts the effort required for pre-treatment), repowering might become necessary or can be avoided.

It is quite likely that the energy demand required for regeneration of the aqueous ammonia solvent in an absorption process could be assured by the engine's waste heat (Awoyomi et al., 2020). The electric energy demand of the process derives from pumps for transfer of the solvent and blowers to overcome the pressure drop of the absorber. The possibility to desorb  $CO_2$  in the stripper at an elevated pressure allows to further reduce the electrical energy demand for compression of the captured carbon emissions. Therefore, the bulkiest unit is judged to have the highest energy efficiency and is most likely not requiring repowering of a ship's energy system.

| Technology                    | (2.10) Repowering  | Score |
|-------------------------------|--|-------|
| Absorption by NH <sub>3</sub> | Waste heat is likely to be sufficient for regeneration; desorption at elevated pressure allows energy savings in compression of CO <sub>2</sub> ; electricity required for pumps and blowers | 1     |
| Membrane separation           | No figures found in consulted literature; energy required for intense<br>pre-treatment and to create pressure difference for separation; only<br>little waste heat can be utilised           | 2     |
| Cryogenic separation<br>(A3C) | Expected that repowering is required; not possible to utilise waste<br>heat; large electricity demand for refrigeration unit   | 3     |

#### Table 5.17: Repowering (2.10)

## 6 Discussion

The comparative assessment revealed post-combustion CC by absorption with aqueous ammonia solvents as the most promising solution for newbuildings, as well as retrofit solutions. This chapter is critically reviewing the outcome of the assessment and is discussing under which conditions CC technology is a feasible solution, to reduce the carbon intensity of international shipping. Apart from factors that are already acknowledged in existing literature, often disregarded ones – which are quite relevant for the useability of CC technology onboard vessels – are taken into consideration as well. Finally, an outlook for future research is arguing for the need of studies on a common basis to allow the comparability of data for different CC technologies and elaborates how such data could impact the outcome of this thesis.

### 6.1 Feasibility of carbon capture for vessels

The literature review, which has been conducted for data collection in this thesis, revealed a wide variety of technologies being researched for CC from power plants and industrial processes, but also for the capture of  $CO_2$  from the exhaust of marine ICEs. At current state-of-the-art, this thesis assessed post-combustion capture by absorption with aqueous ammonia solvents to be the most promising technology for appliances onboard, both for newbuildings as well as for retrofitting of existing vessels. The following discussion is elaborating to what extend these results are valid for the complete commercial fleet and under which conditions other CC technologies are more favourable.

The selection of the optimal CC technology for a specific vessel depends on several factors. **Firstly**, it depends on the power of the vessel's engine and the space available onboard a ship. The post-combustion absorption process is the technology that has the highest space requirements out of the technologies included in the assessment, in which the high space requirements have just been addressed by a low ranking of the technology. In reality, the high space demand might be an excluding criterion for several shipowners. Especially for smaller vessels absorption technology might not be a feasible solution since the occupied space and the additional weight would reduce the vessel's transport capacity by a higher percentage as it is the case for bigger vessels. The reduced cargo capacity is negatively impacting the EEDI of the vessel, i.e., the capture-rate has to be higher than the EEDI reduction-rate aimed for (Sanghyuk Lee et al., 2021).

When the space is confined, other CC technologies such as the A3C process or membrane separation might be more advantageous. Even though the OPEX are higher, whether due to the energy demand or required maintenance, the lower space requirements would result in less cargo capacity loss and therefore increase the potential revenue of the ship.

The power of the vessel's engine has a direct impact on the size of the required CC plant. The more powerful the engine, the more fuel needs to be combusted for energy conversion. The resulting higher flue gas flow and corresponding mass of CO<sub>2</sub> require a larger CC unit, which is able to handle these. In absorption plants, the diameter of the absorber column is reflecting the exhaust gas flow, i.e., the space required by the CC unit is in relation to the power of the ship's engine. Generally, the ship's installed power is proportional to its size and thereby the space available for the installation of the CC technology. For ship types that have an over-proportional installed power (e.g., tugboats), the A3C technology may be more advantageous. The size of the unit, which is increasing slightly with a higher exhaust gas flow, rather it is the weight of the unit, which is increasing (Willson, 2020).

A fact that has neither been considered in this thesis nor in the assessment, since it is common for all CC technologies, is the space required for intermediate storage of the captured CO<sub>2</sub> onboard the vessel. Most of the reviewed literature on research for the onboard appliance of CC, is proposing a compression and liquefaction of CO<sub>2</sub> to reduce the volume of the captured emissions. The required size of the tanks depends on several factors: ship's engine(s), fuel choice, fuel consumption, capture-rate and voyage duration. The impact of the ship's engine and the related amount of fuel consumed has been discussed before. The more CO<sub>2</sub> is produced and subsequently captured, the more  $CO_2$  needs to be stored in the shipboard tanks. To reduce the amount of produced  $CO_2$ , a fuel with a higher H/C-ratio can be chosen. This will reduce the amount of  $CO_2$ produced per unit of energy converted and thereby also decrease the required tank size (E. Malmgren, personal communication, 12.05.21). Ultimately, the required tank size is dependent on the voyage duration of the vessel, i.e., how often the vessel is able to unload the captured  $CO_2$ (JSTRA et al., 2020; Willson, 2020). This in turn is strongly dependent on the available infrastructure for the discharge of CO<sub>2</sub>. All these factors together decide whether the space required for the CC technology or the intermediate storage of CO<sub>2</sub> are requiring more space. Further it has to be noted, that the weight of the captured  $CO_2$  is exceeding the mass of the consumed fuel, i.e., the vessel is getting heavier during the voyage (Willson, 2020). This may lead to a further reduction of the cargo capacity and must be considered during loading.

The advantage of the absorption process using NH<sub>3</sub> solvents is the low energy demand. However, when the available space for the CC plant is limited and the size of the absorption plant needs to be reduced, this would negatively impact the energy efficiency and increase the overall energy demand. This possibility for a trade-off between the size of the entire plant and the energy demand during operation has been concluded as an option for a CAPEX/OPEX trade-off by Einbu et al. (2021). A confined space could lead to an increase of the OPEX for absorption plant, making other technologies more favourable. In summary, the more space is available onboard, the higher will be the energy efficiency of the absorption technology and hence, the lower the OPEX.

Secondly, having addressed the increase of the OPEX due to a decreased energy efficiency, another factor is favouring the application of CC in general for larger  $CO_2$  sources (i.e., larger vessels): economies of scale. Feenstra et al. (2019) found that the costs to capture one tonne of CO<sub>2</sub> are decreasing in average by 28 % when the capture-rate is increased from 60 to 90 %, even though the CAPEX are increasing with a higher capture-rate. Further, combining their results for a 1.280 kW and a 3.000 kW vessel with the results attained by Luo & Wang (2017) for a 17 MW vessel, a rapid drop in costs can be observed in the lower range of engine power. The decrease in costs is getting lower when the engine power is increasing, due to the corresponding increase of the exhaust gas amount and equipment size being linear (Feenstra et al., 2019). In general, the economies-of-scale effect can be observed for all CC technologies, since it is the initial investment that is responsible for the biggest share of the costs per tonne of  $CO_2$  captured. The investment into a new technology as well as the costs for the installation of the same onboard a vessel, are not growing proportionally to the size of a plant, i.e., in relation to the size of the CC unit, larger units might be able to achieve lower costs. The lower costs in relation to the potentially captured  $CO_2$ are therefore leading to decreased costs per tonne of captured CO2. The high CC costs for small vessels could make a conversion to renewable fuels more cost effective than the installation of a CC plant.

When considering the use of a fuel with a higher H/C-ratio (e.g., LNG), to reduce the size of the capture unit and storage tanks, one also needs to be aware, that this could increase the costs per tonne of captured  $CO_2$ . On one hand, higher grade fuels may be more expensive and at the same time the amount of total  $CO_2$  produced and captured is decreasing. On the other hand, higher

grade fuels also contain less contaminants, thus reducing the required effort for the pre-treatment of exhaust gases, before entering the CC unit. In conclusion, the choice of fuel is a trade-off between fuel costs and additional costs for required aftertreatment. Hereby parallels can be seen to the currently applied SO<sub>x</sub>-scrubber technology, which allows the use of low-cost fuels with the drawback of a necessary exhaust gas aftertreatment system.

**Thirdly,** the integration of any CC technology into the technical installations onboard is increasing the complexity of the entire system. Post-combustion absorption technology is a complex system by itself, consisting of several components. Synchronising the CC process with the surrounding equipment is getting more difficult with increasing complexity. The costs for the integration into the overall process are often overlooked (S. M. Nazir, personal communication, 06.05.21).

When installed onboard a vessel, the plant needs to be operated, serviced, and repaired by the ship's crew. The crew needs to be highly skilled, to be able to carry out these tasks responsibly and ensure a safe operation of the plant (E. Malmgren, personal communication, 12.05.21). Nevertheless, damage to the plant could occur due to negligence or due to a technical failure. Complicated plants containing large amounts of harmful substances, such as NH<sub>3</sub>, might therefore not be the best choice for the shipboard application. The A3C process consists of a single unit. Its principle is relatively simple and would therefore be more preferable for onboard applications.

On the downside, the A3C process has a high electric energy demand and is not able to utilise waste heat of the engine. The high energy demand is increasing the OPEX and furthermore makes it likely that the energy system of an existing ship will not be capable to supply the required power, making the retrofit of additional auxiliary engines necessary. Therefore, also the fuel consumption of the vessel is increasing, decreasing the carbon reduction potential of the A3C process.

**Fourthly**, the main advantage of the absorption process using NH<sub>3</sub> solvents are the low OPEX due to the low energy demand and chemical costs. The waste heat of the engine is sufficient to deliver the thermal energy required for the regeneration of the solvent (Awoyomi et al., 2020). However, this assumption needs to be seen critical. Often studies are assuming that the complete waste heat is available for the regeneration of the solvent and thereby are able to achieve high energy efficiency and low OPEX (Awoyomi et al., 2020; Feenstra et al., 2019; Luo & Wang, 2017). This ignores the fact though, that waste heat from the engine's exhaust as well as cooling water is already partially utilised for heating and fresh water generation (Zihan & Xiaoliang, 2021).

Another energetical advantage of using  $NH_3$  in an absorption process lies in the ability of the solvent to release  $CO_2$  at an elevated pressure, i.e., energy and equipment required for the compression of  $CO_2$  prior intermediate storage can be reduced (Awoyomi et al., 2020). Even though  $CO_2$  is leaving the A3C process in gaseous phase, it has been cooled down already, thus reducing its volume and the energy and equipment demanded for compression and liquefaction (Willson, 2020). Such energetical advantage does not exist for membrane separation, where the gaseous  $CO_2$  is leaving the CC unit as gas at a pressure close to atmospheric pressure (Haider et al., 2018).

Fifthly, the fact that makes absorption technologies the most promising technology in short-term, is its high maturity level. Amine-based absorption processes have reached TRL 9 for industrial processes ashore. The number of articles considering the application of this technology onboard vessels is by far the highest, showing that research for CC application is currently focussing on post-combustion absorption processes. In general, all interviewed experts see post-combustion absorption processes as the most promising technology in the near future (F. Johnsson, personal

communication, 03.05.21; F. Normann, personal communication, 04.05.21; S. M. Nazir, personal communication, 06.05.21). Specifically, the question is less about which technology will be applied and more about which solvent will be used in absorption processes (F. Johnsson, personal communication, 03.05.21). Currently, research is ongoing to increase the resilience of solvents towards degradation, increase the capture efficiency and reduce the energy demand for regeneration (Osman et al., 2021). Such research might identify solvents being more beneficial than aqueous ammonia solvents and thereby could reduce the disadvantages of the general process.

**Overall**, post-combustion capture by absorption with aqueous ammonia solvents might not be a feasible solution for small ships, but due to its high energy efficiency and low OPEX it is the most promising solution for CC onboard large vessels.

### 6.2 Method

Rather than adopting a well-established assessment method like a *multiple-criteria decision analysis* (MCDA) or a *techno-economic assessment* (TEA), the authors of this thesis decided to develop an own, specialised method (*Figure 3.1*). The data retrieved by literature review and expert interviews was found to be insufficient to conduct a proper MCDA or TEA, mainly due to the incomparability of certain data and related uncertainties. Moreover, the given timeframe limited the authors in further data collection to allow for an MCDA or TEA. This section will critically discuss the structure as well as the execution of the developed assessment method. The potential impact of certain criteria on the outcome and the effect of a different evaluation of technologies in these criteria will be discussed as well.

In chapter 4, which is forming the basis for the assessment, a wide variety of CC technologies is presented, each having several variations. To limit the number of technologies that are assessed, two excluding criteria are introduced. Firstly, all technologies that are not feasible to run in combination with an ICE are excluded. It is reasonably probable, that vessels built before 2030 will be equipped with ICEs running on fossil fuels (Bullock et al., 2020). In this thesis, CC technology is evaluated as a bridging solution until better, fossil free alternative drive technologies for vessels are available. This includes the retrofitting of CC to existing and future vessels, to reduce their carbon intensity. Promising technologies, like the combination of fuel cells with CC (H. Lee et al., 2020), still need further research, especially regarding their feasibility for the application onboard, before the data basis is sufficient for a comparison with CC in combination with ICEs.

In the second step, all technologies that have not yet achieved TRL 4 are excluded. Climate change mitigation measures are required urgently and therefore also solutions to decarbonise shipping need to be implemented. Limiting the technologies to TRL 4 or higher ensures that these technologies have been validated as a complete system in lab-scale and entered the development phase. In regard of the soon availability of CC technology as climate change mitigation measure, a higher TRL limit would be even more contributing, but limits the variety to very few technologies. On one hand, the limitation to TRL 4 or higher may exclude CC technologies, that could have performed better than the ones included in the assessment. On the other hand, the data available for the technology concepts with a TRL below 4 is not sufficient to compare them appropriately, making an assessment with the inclusion of such technologies subject to high uncertainties. Furthermore it has to be noted, that the conducted literature review may not have identified all concepts existing for CC. There might be a variety of other concepts for CC, currently at TRL 2 or lower, which could not be identified by the authors. The probability that technologies

having achieved TRL 4 have been missed by the conducted literature review, is much lower, since several scientific papers are published addressing these technologies. Therefore, the limitation to TRL 4 and higher allows to ensure, that all technologies passing the excluding criteria are considered for the assessment.

For the assessment of the technologies which have passed the excluding criteria, a ranking system is applied. Based on a discussion of their properties, the technologies are ranked according to their performance and scores are assigned according to the achieved rank. Thereby, the assessment attempts to find differences between the technologies, to justify a higher ranking of one technology in comparison to another. However, in certain cases such reasoning for a differentiation could not be found. In these cases (e.g., criterion 1.1 (5.2.1)), the concerned technologies are ranked the same and assigned the same score, i.e., the range of the scores is reduced. A sensitivity analysis for the first stage of the assessment showed, that the three best technologies are not affected, even if the full range (1 - 7) is applied.

The applied ranking system is assigning scores according to the rank achieved and thereby does not reflect the severity of the difference between the technologies. For some criteria, the difference between the technology ranked first and the one ranked second was minor, whereas the technology ranked third had major drawbacks in regards of the criterion. To reflect this, a scoring system using a scale from 1 - 10 and assigning a score relative to the performance of the technology, rather than to the achieved rank, can be more precise. However, to be able to apply such a scoring system, a sufficient data quality is required, which is not the case in this thesis.

Besides the excluding criteria, all criteria of the assessment have been given the same weight, i.e., all criteria are evaluated to have the same importance. Indeed, it is depending on the stakeholder's perspective (e.g., shipowner, authorities or classification societies) whether certain criteria are evaluated to have a higher impact than others. To include the stakeholder's perspective a questionnaire could have been sent out, asking relevant stakeholders to evaluate the importance of the criteria from their perspective. Such approach is chosen by Hansson et al. (2019), to weight the criteria included in the conducted MCDA according to different perspectives. However, this thesis has been limited by the allowed timeframe and therefore such extensive data collection has not been possible. Nevertheless, a ranking with weighted criteria to include different stakeholder's perspectives can be conducted in future work, based on the method developed in this thesis.

The main uncertainties in the assessment derive from the mostly incomparable data in the reviewed literature. The authors adopted the approach from the consulted literature to present performance data in relation to the benchmark process *post-combustion chemical absorption by MEA solvent*, even though the benchmark process is not standardised. Due to a missing standard, this may result in an incomparability of data. Although a research is presenting results in relation to the benchmark process, different assumptions and process boundaries could be applied.

Further uncertainties arise from the fact, that most of the research for CC technologies is currently conducted for shoreside industrial and power plants. Criteria being of high importance for the shipboard application, e.g., occupied space and weight, are not addressed in such research, since they are of minor importance for shoreside applications, at current TRL. Therefore, in certain cases, the authors had to take assumptions based on the consulted literature.

Whereas results of research for the application onboard of ships have been published for *absorption* by  $NH_3$  and the A3C process, comparable literature has not been available for *membrane separation*. Thereby, the mandatory pre-treatment for membrane separation was subject to high uncertainties,

since no data regarding this pre-treatment are available in the consulted literature. It is certain, that the weight and occupied space of the membrane CC unit itself are by far lower than for an absorption plant or the A3C process. Based on this, it is assumed that the membrane technology is less space and weight intense than the other TOP 3 technologies, even if the mandatory pre-treatment is included. Therefore, membrane separation is ranked best in the criteria 2.1 (space requirements) and 2.2 (weight). Future research could show that this assumption has been wrong, i.e., the required pre-treatment makes the membrane technology heavier and more space consuming than the A3C process (currently on the second rank for both criteria). A sensitivity analysis for this case reveals, that the A3C process would achieve the same score as the absorption by NH<sub>3</sub>, in case membrane separation needs to be rated down in one of the criteria. If membrane separation must be rated down in both criteria, the A3C process would gain the lowest score overall, i.e., the A3C process would also affect the outcome of stage 2.b of the assessment. Absorption by NH<sub>3</sub> and the A3C process would achieve the same score, meaning they are deemed to be equally promising as retrofit solution for CC.

Since all the TOP 3 technologies are post-combustion CC technologies, none of them mandatorily requires a change of the fuel or fuel system in regard to criterion 2.9. Nevertheless, membrane technology would benefit more from a change towards a higher-grade fuel than the other technologies assessed. The ranking for criterion 2.9 is therefore done according to the discussion of facts for criterion 1.4 (impurities in fuel and exhaust gases). This could be interpreted as giving this criterion double weight, since the same argumentation is applied twice. However, this is not the case since the scores assigned for criterion 1.4 are not considered anymore in stage 2 of the assessment. Stage 2 of the assessment is evaluating the performance of the TOP 3 technologies independent from the scores assigned to the technologies in stage 1. The same applies to criterion 2.7 (maturity level), where the ranking is performed according to the TRL achieved by the technologies, although this has been an excluding criterion already.

### 6.3 Future outlook

The assessment conducted in this thesis is based on currently available data and is thereby reflecting the current state of research. This section addresses, how future research and development could impact the outcome of the assessment and further, what needs to be achieved to make CC onboard vessels become reality.

This thesis reviewed literature and collected data on CC technologies ashore and onboard. Thereby, it was found that the parameters of CC from industrial processes and power plants vary in several factors from the application onboard vessels. Besides the low concentration of  $CO_2$  in the exhaust of ICEs, the confined space onboard and the impact of the weight are criteria not considered in the design of shoreside processes. The articles and reports published on research for the application onboard take different base assumptions and have different system boundaries, making a quantitative comparison of technologies subject to high uncertainties. Further uncertainties derive from the low TRL of CC technology for small and mobile sources, such as vessels. Due to the missing comparability and the high uncertainties, the assessment was based on a qualitative evaluation of data.

To allow a quantitative comparison of CC technologies onboard, future research should address the constraints of the application onboard on a common basis. Rather than evaluating what space is required to achieve a certain capture-rate, such research should be based on a given space and evaluate, what capture-rate can be achieved with this space constraint. Furthermore, a common basis should include the same source of exhaust and the same available energy (thermal as well as electric), considering that the waste heat of the engine is already partially utilised onboard current vessels. A TEA based on simulations (e.g., using Aspen) of the identified CC processes on such a common basis could resolve this issue, since it would be based on unbiased figures rather than qualified assumptions comparable data. Further research for each of the identified technologies will also improve the data quality, since with a higher TRL also the certainty of the data is rising. As already addressed in the method discussion, new insights and an improved data quality might change the outcome of the assessment, when assumptions taken in the current assessment are disproved.

Looking into the future one might wonder, what needs to be achieved to make CC onboard vessels happen. Before CC technology will be applied onboard seagoing vessels, its function has to be proven ashore (F. Normann, personal communication, 04.05.21). The extent to which CC technology is applied ashore will have significant impact on the development of the infrastructure for storage and utilisation of captured  $CO_2$  emissions (F. Normann, personal communication, 04.05.21). The more commonly CC is applied ashore, the better infrastructure will be in place and thereby decrease the expenses to use this infrastructure.

Until today, only a few large-scale applications for CC exist and some of these have already been discontinued for economic reasons. The oxyfuel combustion in combination with CC at the lignite-burning power plant Schwarze Pumpe in Germany was discontinued due to economical, as well as regulatory reasons (F. Johnsson, personal communication, 03.05.21). In May 2020, the Petra Nova project, a large-scale application of post-combustion capture from the exhaust of a coal-fired boiler, was paused due to the low oil prices, making the operation of the plant economically unfeasible (NRG Energy Inc., 2021). The fact is "that the non-abatement alternative is, and always has been, the cheaper option" (Helle & Koefoed, 2018). It is not the technology that is hindering the implementation of CC, it is the lack of policy promoting the implementation of abatement technologies by a carbon emission pricing that makes CC economically reasonable or at least is lowering the risk for such investments (Helle & Koefoed, 2018). Once the technology is applied continuously in large-scale, the technology- and cost-learning-effect could significantly reduce the costs of CC technology for future applications (Helle & Koefoed, 2018).

However, in the current state the mature CC technology (i.e., post-combustion absorption) is economically not competitive, but currently less mature technologies could have lower costs, making them profitable even with low carbon emission prices. While absorption technologies are the most promising technology in the short term due to their high TRL, the future of CC technology is seen in less energy consuming and more efficient processes (S. M. Nazir, personal communication, 06.05.21).

## 7 Conclusion

Based on the knowledge retrieved from literature and expert interviews, the thesis presents a broad spectrum of CC technologies including information on the process setup, current applications, costs, space requirements as well as specific advantages and drawbacks of each technology. Furthermore, the research conducted for the application of the identified technologies onboard has been reviewed and the findings of these are presented in a summarised form.

The conducted assessment considers a variety of constraints and criteria for the applicability of these CC technologies onboard vessels. Safety concerns towards ship and crew as well as peculiarities of the shipboard application (e.g., ship's movement and vibration, fluctuating energy demand) and circumstances set out by marine fuels are regarded. As specific constraints of the shipboard application, the occupied space, additional weight and energy demand have been identified and assessed. Additionally, the costs related to each CC technology as well as the maturity level and feasible capture-rate have been considered. For retrofitting CC technologies onboard, measures regarding the conversion of the fuel system, the potential replacement of the installed engine and constraints in the available power to operate the CC unit were examined.

Three post-combustion CC technologies have been identified as most feasible for the application onboard in combination with ICEs and are reviewed in detail: absorption by NH<sub>3</sub>, cryogenic separation (A3C) and membrane separation. All were found to be promising solutions for onboard CC. Cryogenic separation offers the highest economically feasible capture-rate but is lacking maturity and additionally shows the highest energy demand. Whereas membrane separation is deemed the least space consuming and weight adding technology, it demands extensive pre-treatment of the flue gases, which is also related to an intense energy demand of this technology. Absorption by NH<sub>3</sub> was found to be the most space consuming technology in the comparison, but it shows a low power consumption and has advantages in connection with sulphurous fuels, apart from that, it also achieved the highest TRL so far. Out of these three technologies, the assessment deems the absorption process using aqueous ammonia solvent as the most promising technology for the shipboard appliance, both for newbuilding and retrofit solutions.

In general, CC represents a potential solution to reduce the carbon intensity of international shipping. Due to the size of the required installation for capture and intermediate storage, CC might be a more attractive solution for larger vessels. For smaller vessels, the costs of CC might be higher than for a shift towards renewable fuels. Similar to shoreside applications, where batteries and zero-carbon fuels are intended for small emitters and CC is researched for large point sources, such technology mix could also be feasible for the marine transportation sector. Nevertheless, CC in combination with fossil fuels can only be a transitional solution, to overcome the time until renewable propulsion options are developed, since it is not feasible to capture 100 % of the emissions with CC technologies. In combination with renewable fuels, CC onboard ships with storage could result in negative  $CO_2$  emissions.

It must be pointed out, that this study was limited by the available data in the literature, mostly incomparable due to different base assumptions. Future research for the application of CC onboard should be carried out on a common basis. To determine which technology is the most suitable for the intended ship, the available space and energy need to be considered, when calculating which technology can achieve the highest capture-rate under certain circumstances. In any case, the potential of various solutions to reduce carbon-emission, not limited to CC, must be assessed for the specific case, to decide which technology is the most suitable.

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# Appendix

| A 1 | The global carbon cycle                    | II |
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| A 2 | Literature provided by interviewed experts | VI |

## A1 The global carbon cycle

To understand how CC as mitigation measure can contribute to mitigate climate change, one needs to understand the biochemical cycle of carbon in the Earth's ecosystem. Therefore, this section is going to introduce the basics of the model of the global carbon cycle including the impact by anthropogenic  $CO_2$  emissions on the cycle.

Biochemical cycles control the exchange and transformation of elements between the different components of the Earth's ecosystem. A number of biotic and abiotic processes is responsible for the mass flow between atmosphere, ocean, land as well as the lithosphere (Ciais et al., 2013). These processes are dependent on the surrounding environment, the climate and the impact of humankind on the environment (e.g., change of land-use). The cycle is impacted by the environmental changes, such as the rising concentration of  $CO_2$ , but at the same time it does impact the concentration of GHGs by itself. Besides the carbon cycle, there are cycles for other GHGs (e.g., methane-cycle, nitrogen cycle) which can interfere each other (Ciais et al., 2013).

GHGs are part of the gaseous phase of the cycles, such as the  $CO_2$  within the atmosphere is part of the global carbon cycle. The global carbon cycle can be seen as a number of carbon reservoirs within the Earth system which are connected by exchange streams (Ciais et al., 2013). Within the carbon cycle two domains can be divided: the fast and the slow domain.

The fast domain connecting atmosphere, ocean, surface ocean sediments and on-land vegetation, soils and freshwater (Ciais et al., 2013). It is characterised by large exchange fluxes and "quick" reservoir turnovers. The time for the turnover of a reservoir, defined as the mass of the reservoir divided by the exchange flow, spans from a few years (atmosphere) up to millennia for carbon reservoirs connected to land vegetation, soil and a variety of areas in the ocean. The slow domain is characterised by slow turnover times of 10.000 years and longer. It connects the long-term carbon stores in rocks and sediments (Ciais et al., 2013).

The natural exchange between the fast and the slow domain is achieved by volcanic  $CO_2$  emissions, chemical weathering of rocks, erosion and sediment formation at the seabed. This exchange is happening very slow and can be seen as constant over the last few centuries (Raymond & Cole, 2003). From the analysis of ice cores, it was found that the fast domain was in a steady state as well before the beginning of the industrial era (defined as 1750) since only small variations in the atmospheric  $CO_2$  concentration occurred (Pongratz et al., 2009). By the start of the industrial era the extraction of fossil fuel and the combustion for energy generation began to transfer significant amounts of carbon from the slow to the fast domain (Ciais et al., 2013), creating a major impact on the global carbon cycle.

*Figure A1.1* shows a simplified schematic of the global carbon cycle, published by the IPCC in 2013 in connection to the *Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. The size of the carbon reservoirs is given in PgC (1 PgC =  $10^{15}$  grams carbon) and the different exchange fluxes are given in PgC per year (PgC yr<sup>-1</sup>). The exchange fluxes are based on an average of the global emissions for the period from 2000 until 2009. The black numbers are estimates of the reservoir masses and exchange fluxes before the industrial era and the red numbers are indicating changes in reservoirs since 1750 as well as annual anthropogenic fluxes (Ciais et al., 2013).

A major part of the carbon reserved within the atmosphere is contained by  $CO_2$  (Ciais et al., 2013). Smaller amounts are found in form of  $CH_4$  and carbon monoxide (CO). It is estimated that the amount of carbon within the atmosphere increased by approximately 240 Pg until 2011 since the beginning of the industrial era.



Figure A1.1: Simplified scheme of the global carbon cycle. Reprinted with permission of the IPCC\*

Within the terrestrial ecosystem, carbon is stored in vegetation living biomass and in dead organic matter in litter and soils (Ciais et al., 2013). Additional amounts of carbon are stored within wetland soil as well as permafrost soils. By photosynthesis,  $CO_2$  is taken up from the atmosphere and fixed in biomass. It is released back into the atmosphere by respiration of plants and animals as well as microbiological decomposition within the soil. Disturbance events like forest fires are contributing to a release of  $CO_2$  into the atmosphere (Ciais et al., 2013). By erosion, a part of the terrestrial-stored carbon is transported into rivers. From rivers and lakes, the carbon is whether outgassed to the atmosphere or transported into the ocean. A smaller part is buried within organic sediments in the rivers and lakes (Ciais et al., 2013).

In the ocean, carbon is mainly found in form of dissolved inorganic carbon which is including dissolved  $CO_2$  (carbonic acid) bicarbonate and carbonate ions (Ciais et al., 2013). Atmospheric  $CO_2$  is dissolved within the surface ocean by gas exchange, driven by the partial pressure difference of  $CO_2$  in the ocean and the atmosphere. Another fraction of carbon within the ocean is present

in form of dissolved organic carbon. The marine biota does only represent a small fraction of the organic carbon found in the ocean (Ciais et al., 2013).

Within the ocean, carbon is transported by three mechanisms (Ciais et al., 2013). The first of these is the so-called solubility pump, a combination of two processes. The formation of deep water in high latitudes and the solubility of  $CO_2$  in seawater being inverse to the temperature of the water. The circulation of water within the oceans is driven by the fact that water is getting denser when cooling down. In high latitudes the surface ocean is cooling down which is also enhancing the solubility of  $CO_2$  within the seawater. The denser seawater is dropping down together with the dissolved oxygen forming deep water. When the deep water is getting warmer or is forced to the surface, the solubility of  $CO_2$  is reduced and excess gas is gassed out to the atmosphere (Ciais et al., 2013).

The second mechanism, the 'biological pump', is responsible for the sedimentation of carbon within the ocean (Passow & Carlson, 2012). In the beginning of this process, the dissolved inorganic carbon is taken up by phytoplankton and converted into fixed carbons. The carbon fixed within these organisms can be recycled as part of the nutrient cycle or starts sinking to the seabed once the organisms died. The biggest part of the sinking carbon compounds is whether consumed by zooplankton or remineralised by decomposition of bacteria. Only a small part of the sinking particles is escaping these processes and is sequestered within the seabed sediments (Denman et al., 2007).

The third process is the 'marine carbonate pump' (Ciais et al., 2013). The carbon bound by the formation of calcareous shells by organisms within the surface ocean is remineralised while sinking. The created dissolved inorganic carbon is increasing the partial pressure of  $CO_2$  within the surface waters of the ocean and thereby is driving towards a release of  $CO_2$  into the atmosphere. It is therefore working counter the biological pump in respect of carbon storage within the ocean (Ciais et al., 2013).

Having explained the natural global carbon cycle, the effect of anthropogenic emissions needs to be taken in account. As already described above, the extraction and combustion of fossil fuels is transferring carbon from the slow into the fast domain (Ciais et al., 2013). Besides the fossil fuel combustion, cement production is releasing carbon stored within rock into the atmosphere. Further anthropogenic emissions are generated by the change of land use. Even though, this amounts to about 9 PgC/yr (averaged for time period 2000 to 2009) transferred from the slow domain into the atmosphere, the atmospheric carbon pool does only increase by 4 PgC in average per year (Ciais et al., 2013). The overall net ocean and land flux are negative, i.e., the ocean and the land are acting as so-called carbon sinks, taking up more carbon than they emit (Ciais et al., 2013).

However, the buffering impact of the ocean is limited and further land use change is reducing the ability of terrestrial ecosystem to take up carbon (Ciais et al., 2013). The study of Solomon et al. (2009) shows that, even if  $CO_2$  emissions are completely eliminated today, it will take at least 1000 years before the Earth's mean temperature starts to cool down. Besides other effects, the buffering influence of the ocean is one reason.  $CO_2$  will be released again when the partial pressure of  $CO_2$  in the atmosphere is sinking, causing a relatively stable  $CO_2$  concentration in the atmosphere (Solomon et al., 2009).

"Figure 6.1 | Simplified schematic of the global carbon cycle. Numbers represent reservoir mass, also called 'carbon stocks' in PgC (1 PgC = 1015 gC) and annual carbon exchange fluxes (in PgC yr-1). Black numbers and arrows indicate reservoir mass and exchange fluxes estimated for the time prior to the Industrial Era, about 1750 (see Section 6.1.1.1 for references). Fossil fuel reserves are from GEA (2006) and are consistent with numbers used by IPCC WGIII for future scenarios. The sediment storage is a sum of 150 PgC of the organic carbon in the mixed layer (Emerson and Hedges, 1988) and 1600 PgC of the deep-sea CaCO<sub>3</sub> sediments available to neutralize fossil fuel CO<sub>2</sub> (Archer et al., 1998). Red arrows and numbers indicate annual 'anthropogenic' fluxes averaged over the 2000-2009 time period. These fluxes are a perturbation of the carbon cycle during Industrial Era post 1750. These fluxes (red arrows) are: Fossil fuel and cement emissions of  $CO_2$  (Section 6.3.1), Net land use change (Section 6.3.2), and the Average atmospheric increase of  $CO_2$  in the atmosphere, also called ' $CO_2$  growth rate' (Section 6.3). The uptake of anthropogenic  $CO_2$  by the ocean and by terrestrial ecosystems, often called 'carbon sinks' are the red arrows part of Net land flux and Net ocean flux. Red numbers in the reservoirs denote cumulative changes of anthropogenic carbon over the Industrial Period 1750-2011 (column 2 in Table 6.1). By convention, a positive cumulative change means that a reservoir has gained carbon since 1750. The cumulative change of anthropogenic carbon in the terrestrial reservoir is the sum of carbon cumulatively lost through land use change and carbon accumulated since 1750 in other ecosystems (Table 6.1). Note that the mass balance of the two ocean carbon stocks Surface ocean and Intermediate and deep ocean includes a yearly accumulation of anthropogenic carbon (not shown). Uncertainties are reported as 90% confidence intervals. Emission estimates and land and ocean sinks (in red) are from Table 6.1 in Section 6.3. The change of gross terrestrial fluxes (red arrows of Gross photosynthesis and Total respiration and fires) has been estimated from CMIP5 model results (Section 6.4). The change in air-sea exchange fluxes (red arrows of ocean atmosphere gas exchange) have been estimated from the difference in atmospheric partial pressure of CO<sub>2</sub> since 1750 (Sarmiento and Gruber, 2006). Individual gross fluxes and their changes since the beginning of the Industrial Era have typical uncertainties of more than 20%, while their differences (Net land flux and Net ocean flux in the figure) are determined from independent measurements with a much higher accuracy (see Section 6.3). Therefore, to achieve an overall balance, the values of the more uncertain gross fluxes have been adjusted so that their difference matches the Net land flux and Net ocean flux estimates. Fluxes from volcanic eruptions, rock weathering (silicates and carbonates weathering reactions resulting into a small uptake of atmospheric CO<sub>2</sub>), export of carbon from soils to rivers, burial of carbon in freshwater lakes and reservoirs and transport of carbon by rivers to the ocean are all assumed to be preindustrial fluxes, that is, unchanged during 1750-2011. Some recent studies (Section 6.3) indicate that this assumption is likely not verified, but global estimates of the Industrial Era perturbation of all these fluxes was not available from peer-reviewed literature. The atmospheric inventories have been calculated using a conversion factor of 2.12 PgC per ppm (Prather et al., 2012)."

<sup>\*\*</sup> Figure 6.1 from Ciais, P., C. Sabine, G. Bala, L. Bopp, V. Brovkin, J. Canadell, A. Chhabra, R. DeFries, J. Galloway, M. Heimann, C. Jones, C. Le Quéré, R.B. Myneni, S. Piao and P. Thornton, 2013: Carbon and Other Biogeochemical Cycles. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, pp. 465–570, doi:10.1017/CBO9781107415324.015. Full original legend:

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## DEPARTMENT OF MECHANICS AND MARITIME SCIENCES CHALMERS UNIVERSITY OF TECHNOLOGY

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