

RAPORTY IChTJ. SERIA B nr 1/2025

**POSSIBLE METHODS OF REDUCTION
OF GREENHOUSE GASES EMISSIONS
FROM THE COMBUSTION OF FOSSIL FUELS
WITH USE OF RADIATION TECHNOLOGIES,
IN PARTICULAR IN DIESEL ENGINES
INSTALLED ON MARITIME TRANSPORT UNITS**

Andrzej Pawelec, Andrzej G. Chmielewski

Warszawa 2025

AUTHORS

Andrzej Pawelec, Andrzej G. Chmielewski
Institute of Nuclear Chemistry and Technology

© Copyright by the Institute of Nuclear Chemistry and Technology, Warszawa 2025

EDITORIAL OFFICE

Institute of Nuclear Chemistry and Technology
Dorodna 16, 03-195 Warszawa, Poland
phone: 22 811 06 56, fax: 22 811 15 32, e-mail: sekdyrn@ichtj.waw.pl
www.ichtj.waw.pl

Paper is published in the form as received from the Authors

Possible methods of reduction of greenhouse gases emissions from the combustion of fossil fuels with use of radiation technologies, in particular in diesel engines installed on maritime transport units

The greenhouse gases (GHG) emissions are of special interest nowadays and this also covers emission from shipping sector. As over 96% of global shipping sector is powered using heavy duty diesel engines, the research on various methods of greenhouse gases emissions mitigation for marine application are intensively performed.

The International Maritime Organization (IMO) has elaborated the strategy leading to reduction of greenhouse gases emissions from ships. According to the 2023 IMO Strategy on Reduction of GHG Emissions from Ships, carbon dioxide (CO₂) emissions from international shipping shall be reduced by at least 40% by 2030, compared to 2008, and net-zero GHG emissions shall be reached by or around 2050.

The most common option to meet the IMO greenhouse gases emission goals, discussed nowadays, is fuel switching for low-carbon emission fuels such as biodiesel, liquefied natural gas (LNG), ammonia, methanol and others. The other approach for carbon dioxide emission mitigation is application of post-combustion carbon capture technologies. These technologies were first developed and commercialized for their onshore applications; therefore, they are considered a ready to deploy and possible long-term solution option for CO₂ emission reduction from the marine sector.

There are known several methods of CO₂ capture, such as absorption, adsorption, chemical looping combustion, membrane separation, hydrate-based separation and cryogenic separation; however, not every one of them may be applied in marine conditions. Among them there are four main technologies considered for carbon capture applications at shipping industry: chemical absorption, adsorption, membrane separation and cryogenic separation. Although there are carried out intensive research on application of these methods in marine industry, at present only few demonstrational attempts were achieved. Although the post-combustion carbon capture methods are regarded as a perspective solution of marine carbon dioxide emission, there is still a lot of issues to be solved.

Apart from the known CO₂ emission mitigation technologies, a new one – electron beam induced carbon dioxide mitigation process was proposed. The process is based on the reaction of oxalates creation from CO₂ under electron beam irradiation in the presence of formates. The technology involves a two-step process, where in the first step, acidic pollutants such as sulfur dioxide (SO₂) and nitrogen oxides (NO_x) are removed in the hybrid electron beam flue gas treatment process, while in the second step, carbon dioxide is removed by irradiation in the presence of formates. The condensed effluents containing absorbed acidic pollutants or oxalates shall be stored onboard and unloaded at harbor, regarding that sodium and potassium oxalates are the commercial products and may be directed for further applications. The possible modification of the process may lead to the formation of sodium salt in ionic form which may be discharged to the sea.

The process is under development; however, its application for marine conditions is possible.

Metody redukcji emisji gazów cieplarnianych ze spalania paliw kopalnych z wykorzystaniem technologii radiacyjnych, w szczególności w silnikach wysokoprężnych instalowanych w jednostkach transportu morskiego

Obecnie szczególny nacisk kładziony jest na ograniczenie emisji gazów cieplarnianych. Dotyczy to również sektora żeglugowego.

Ponad 96% światowego sektora żeglugowego stosuje silniki wysokoprężne do napędu statków, dlatego prowadzone są intensywne badania nad różnymi metodami ograniczania emisji gazów cieplarnianych możliwymi do zastosowania w warunkach morskich.

Międzynarodowa Organizacja Morska (IMO) opracowała strategię prowadzącą do ograniczenia emisji gazów cieplarnianych ze statków. Zgodnie ze strategią IMO na rok 2023 glo-

balna emisja ditlenku węgla (CO_2) z żeglugi ma zostać do 2030 r. zmniejszona o co najmniej 40% w porównaniu z 2008 r., a poziom zerowy emisji netto gazów cieplarnianych ma zostać osiągnięty do około 2050 r.

Obecnie najczęściej rozważaną opcją osiągnięcia celów IMO jest zamiana paliwa na paliwa niskoemisyjne, takie jak biodiesel, LNG (skroplony gaz ziemny), amoniak, metanol i inne. Drugim podejściem jest zastosowanie technologii wychwytywania CO_2 ze spalin. Technologie te zostały opracowane i skomercjalizowane do zastosowań lądowych, ale uważa się, że są gotowe do wdrożenia i umożliwią długofalowe rozwiązanie problemu redukcji emisji CO_2 w sektorze morskim.

Znanych jest kilka metod wychwytywania CO_2 , takich jak absorpcja, adsorpcja, spalanie w pętli chemicznej, separacja membranowa, separacja na bazie hydratów i separacja kriogeniczna, jednak nie każdą z nich można zastosować w warunkach morskich. Pod kątem zastosowania w przemyśle żegludowym rozważane są cztery technologie: absorpcja chemiczna, adsorpcja, separacja membranowa i separacja kriogeniczna. Mimo prowadzenia intensywnych badań nad ich zastosowaniem w przemyśle morskim, dotychczas udało się przeprowadzić jedynie kilka prób demonstracyjnych.

Prowadzone są też prace nad nowymi technologiami, do których należy proces ograniczania emisji CO_2 indukowany wiązką elektronów. Proces ten jest dwuetapowy. W pierwszym etapie usuwane są kwaśne zanieczyszczenia, takie jak SO_2 i NO_x , natomiast w drugim etapie usuwany jest ditlenek węgla poprzez wytworzenie z niego szczawianów pod wpływem napromieniowania wiązką elektronów w obecności mrówczanów. Ciekłe produkty procesu zawierające wchłonięte zanieczyszczenia kwasowe lub szczawiany, po zatężeniu, będą gromadzone na statku i przekazywane w porcie do utylizacji z zastrzeżeniem, że szczawiany sodu i potasu są produktami handlowymi i mogą być użyte do dalszych zastosowań. Ewentualna modyfikacja procesu może prowadzić do powstania soli sodowych, które mogą być odprowadzane do morza.

Zaproponowana technologia jest obecnie w fazie rozwoju, jednak dotychczasowe prace wskazują na możliwość jej zastosowania w warunkach morskich.

CONTENTS

1. INTRODUCTION	7
2. GREENHOUSE GASES EMISSIONS AND REDUCTION TARGETS IN MARITIME SHIPPING SECTOR	8
2.1. Carbon dioxide emission	8
2.2. Emissions of other greenhouse gases	9
2.3. IMO Strategy on Reduction of GHG Emissions from Ships	9
3. CARBON DIOXIDE MITIGATION TECHNOLOGIES	10
3.1. Carbon dioxide capture technologies	10
3.2. Carbon dioxide mitigation technologies for maritime applications	14
<i>3.2.1. Fuel switching</i>	<i>14</i>
<i>3.2.2. Other energy sources</i>	<i>16</i>
<i>3.2.3. Post-combustion carbon capture technologies</i>	<i>17</i>
4. ELECTRON BEAM INDUCED CARBON DIOXIDE MITIGATION PROCESS	18
5. CONCLUSIONS	21
6. LITERATURE	22

1. INTRODUCTION

There are around 90,000 merchant ships in service globally of various usage, size and carrying capacity. The maritime shipping sector carries about 80% of global trade by volume and 70% by value. In 2015, about 300 Mt of fuel was consumed by this sector, where high sulfur content fuels such as heavy fuel oil (HFO) covered 72%, more refined distillate fuels such as marine diesel oil (MDO) covered 26% and liquefied natural gas (LNG) covered 2% [1]. On the other hand, ferry transport is also an important component in the maritime industry and plays a critical role in transporting passengers with vehicles and cargo at the same time. In the past few years, greenhouse gases (GHG) emissions have been increasingly generated from passenger travel and freight transport.

The pollutants emitted by ships to the atmosphere are a result of various processes. The main emission originates from fuel combustion both complete (sulfur dioxide – SO_2 , nitrogen oxides – NO_x , carbon dioxide – CO_2) or incomplete (hydrocarbons including methane – CH_4 , carbon monoxide – CO , polycyclic aromatic hydrocarbons – PAHs, particulate matter – PM, etc.). Some pollutants such as ammonia and nitrous oxide (N_2O) are a result of exhaust gases treatment processes and heavy metals may originate from fuel, lubricating oil and engine wear. The shipping sector as a whole is responsible for about 15% of global nitrogen oxides emissions and 13% of sulfur oxides (SO_x) emissions, while annual emission of PM is estimated at 1.4 Mt [1].

During the previous studies, the intensity of exhaust emissions from ships was linked to the course of shipping routes and the location of ports. Based on the data obtained, for years pollution maps have been drawn up in connection with the density of ship traffic, recorded on the most frequently used routes on the open sea and in coastal zones. The highest emissions of exhaust gases from engines installed on ships are observed in these areas, while about 70% of ship emissions occur within 400 km of coastlines [2]. Figure 1 shows the main shipping routes [3].

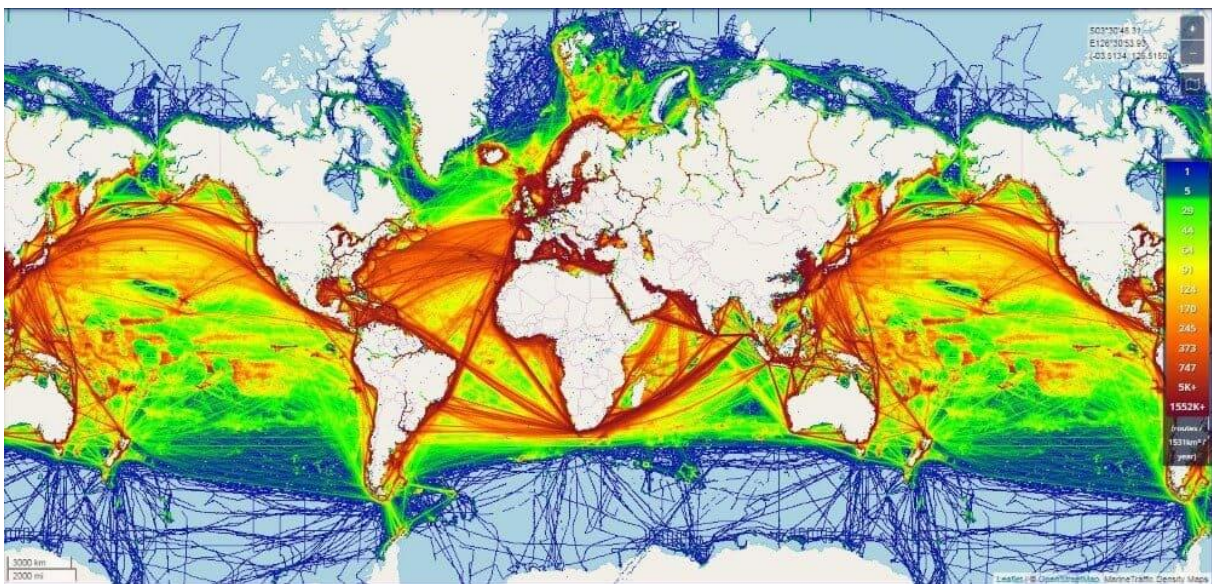


Fig. 1. Main shipping routes [3].

In 1973, the International Maritime Organization (IMO) introduced the International Convention for the Prevention of Pollution from Ships (MARPOL), where Annex VI, introduced in 2005, concerns air pollutants emission. According to this annex, SO_2 and NO_x emissions are strongly limited. From the 1st of January 2020, the sulfur content of maritime fuel is limited to 0.5%, or 0.1% in the IMO enforced Sulfur Emissions Control Areas (SECAs). Currently SECAs cover the North Sea, the Baltic Sea, and North America and the Caribbean, with plans to integrate Japan and the Mediterranean Sea as future SECAs. Alternatively, vessels may be equipped with onboard sulfur scrubbers or switch to low-sulfur fuels (such as hydrogen, LNG

or biofuels). In the case of NO_x permissible levels of emissions depend on vessel age and maximum engine operating speed. Reducing NO_x emission may be obtained either by combustion process modification (e.g., exhaust gas recirculation) or treatment of exhaust gases by selective catalytic reduction (SCR).

Nowadays, greenhouse gases emissions are of special interest and this also covers emission from shipping sector. Compilation of GHG emission reduction with emission control of other pollutants may lead to near-zero emission shipping. Therefore, the research on various methods of greenhouse gases emissions mitigation for marine application are intensively performed. This report presents the overview of the greenhouse gases emission mitigation technologies with special concern on the radiation induced processes.

2. GREENHOUSE GASES EMISSIONS AND REDUCTION TARGETS IN MARITIME SHIPPING SECTOR

Although carbon dioxide is the most important component of greenhouse gases emission from shipping, other important gaseous contributors are methane and nitrous oxide. Another important anthropogenic species being regarded as a greenhouse effect contributor is black carbon (BC). With the inclusion of BC emissions, the carbon dioxide equivalent (CO_2eq) emissions of shipping increase by 7% [2].

According to the International Maritime Organization, greenhouse gases emissions including carbon dioxide, methane and nitrous oxide from shipping (international, domestic and fishing) increased from 977 million tons of CO_2eq in 2012 to 1,076 million tons of CO_2eq in 2018. In 2012, CO_2 emission from shipping was 962 million tons, while in 2018 this amount was 1,056 million tons [4].

2.1. Carbon dioxide emission

According to Our World in Data service, global anthropogenic emission of CO_2 in 2022 was 37.15 billion tons (5.11 billion tons in Europe) [5]. Similar data (36.8 billion tons) was given by the International Energy Agency (IEA) [6]. At the same time, annual natural emission of carbon dioxide is estimated by the Intergovernmental Panel on Climate Change (IPCC) at 770 billion tons (210 GtC), where 120 GtC is emitted from land and 90 GtC from ocean [7].

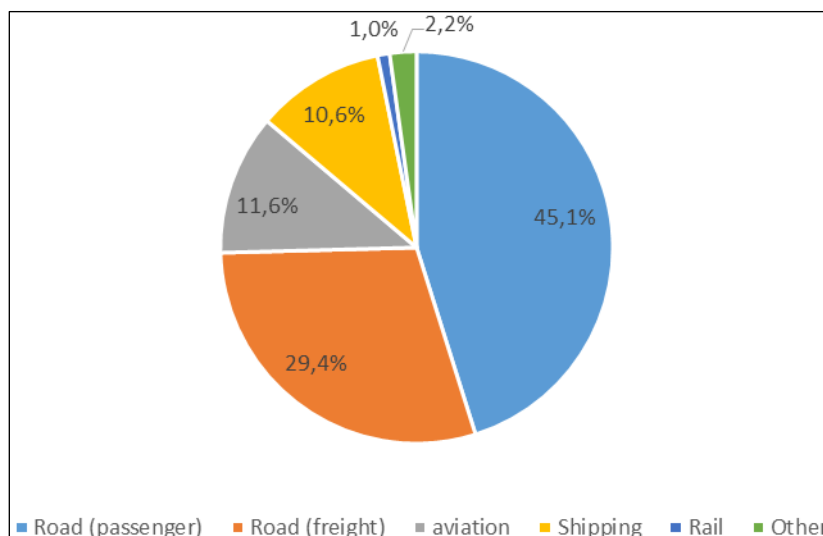


Fig. 2. Structure of carbon dioxide emission in transport sector.

According to the International Energy Agency, carbon dioxide emission in transport in 2022 was 7.98 Gt [6, 8], that stands for 21.7% of global anthropogenic emission of this compound. Based on data from 2018, Our World in Data service gives the following structure of global CO₂ emission in transport [9]: road – 74.5% (including passenger – 45.1% and freight – 29.4%), aviation – 11.6%, shipping – 10.6%, rail – 1.0%, and others (such as transport of liquids, gases and other materials via pipelines) – 2.2% (Fig. 2). Therefore carbon dioxide emission from shipping industry stands for 2.2% of global anthropogenic emission.

The annual CO₂ emissions from shipping sector according to the International Maritime Organization data [4] are presented in Table 1.

Table 1. Shipping based CO₂ emission in 2012-2018.

Year	Global anthropogenic CO ₂ emission [Mt]	Total shipping CO ₂ emission [Mt]	Share of shipping in global anthropogenic CO ₂ emission [%]
2012	34,793	962	2.76
2013	34,959	957	2.74
2014	35,225	964	2.74
2015	35,239	991	2.81
2016	35,380	1,026	2.90
2017	35,810	1,064	2.97
2018	36,573	1,056	2.89

2.2. Emissions of other greenhouse gases

According to Our World in Data service, global anthropogenic emission of methane in 2022 was 10.49 billion tons (5.11 billion tons in Europe). In the same period, global anthropogenic emission of nitrous oxide was 2.97 billion tons of CO₂eq in the world and 420.48 million tons in Europe [5]. Black carbon emission in 2019 was estimated at 5.8 million tons [10].

Black carbon emission in transport sector in 2019 was estimated at 1,342 million tons [10]. In the case of shipping sector, non-CO₂ greenhouse gases emission in 2018 was 20 million tons [4].

2.3. IMO Strategy on Reduction of GHG Emissions from Ships

The International Maritime Organization has elaborated the strategy leading to reduction of greenhouse gases emissions from ships. In 2018, the IMO adopted an initial strategy on the reduction of emissions of greenhouse gases from ships [11]. The initial strategy presented the IMO's vision on commitment to reducing GHG emissions from international shipping and was a base for further works. The initial strategy stated that a revised strategy would be adopted by 2023.

In July 2023, the Marine Environment Protection Committee (MEPC 80) adopted the 2023 IMO Strategy on Reduction of GHG Emissions from Ships [12]. The strategy identifies four levels of ambition for international shipping as follows:

- Carbon intensity of the ship to decline through further improvement of the energy efficiency for new ships.

The aim of this level of ambition is to review and improve the energy efficiency design requirements for ships.

- Carbon intensity of international shipping to decline.
The goal of this level of ambition is to reduce CO₂ emissions from international shipping by at least 40% by 2030, compared to 2008.
 - Uptake of zero or near-zero GHG emission technologies, fuels and/or energy sources to increase.
This level of ambition assumes uptake of zero or near-zero GHG emission technologies, fuels and/or energy sources to represent at least 5% striving for 10% of the energy used by international shipping by 2030.
 - GHG emissions from international shipping to reach net zero.
The aim of this level of ambition is to reach net-zero GHG emissions by or around 2050.
The 2023 IMO Strategy on Reduction of GHG Emissions from Ships also introduced indicative checkpoints to reach net-zero greenhouse gases emissions from international shipping:
 - to reduce the total annual GHG emissions from international shipping by at least 20%, striving for 30%, by 2030, compared to 2008;
 - to reduce the total annual GHG emissions from international shipping by at least 70%, striving for 80%, by 2040, compared to 2008.
- The review of the 2023 IMO GHG Strategy is foreseen for summer 2027 during MEPC 86. Finalization of the review with a view to adoption of the 2028 IMO strategy on reduction of GHG emissions from ships is foreseen for autumn 2028 (MEPC 88).

3. CARBON DIOXIDE MITIGATION TECHNOLOGIES

There are different approaches considered for carbon dioxide emission reduction. The most common strategies are:

- enhancement of energy efficiency and promotion of energy conservation;
- increase usage of low-carbon fuels such as natural gas, hydrogen or biogas;
- usage of renewable energy, such as solar, wind or hydropower;
- application of geoengineering approaches such as afforestation and reforestation;
- development of clean coal technologies (gasification, fluid bed combustion);
- development of nuclear power;
- CO₂ capture and storage (CCS).

Each strategy has its own advantages and limitations that define its applicability and most of them require complex solutions at national level. Moreover, it is not possible to adopt a single strategy for all cases and mostly combination of different approaches is applied. Among these strategies, only CO₂ capture and storage can reduce CO₂ emissions from existing large emission sources, such as conventional power plants or industrial facilities such as refineries or cement kiln plants.

3.1. Carbon dioxide capture technologies

Carbon dioxide is formed during combustion processes and the type of combustion process determines choice of an appropriate CO₂ capture process. Generally, carbon capture (CC) may be realized in three main ways depending on different combustion processes: post-combustion, pre-combustion and oxy-fuel combustion [13].

Pre-combustion CO₂ capture processes involve fuel (coal or natural gas) prior combustion processing. In the case of coal, the gasification process is conducted under low oxygen level forming a syngas that consists mainly of CO and H₂ (reaction 1). The syngas may undergo further reaction with steam for higher hydrogen yield (reaction 2). In the case of natural gas, containing mostly methane, it may be also converted to syngas (reaction 3) and the content of H₂ can be also increased by the reaction with water vapor (reaction 2).



Carbon dioxide is subsequently captured and hydrogen is burned for energy generation. The concentration of carbon dioxide in syngas obtained with application of pre-combustion capture processes is usually high (>20%), that results in more efficient separation of this compound. The pre-combustion capture processes are suitable to be applied to integrated gasification combined cycle (IGCC) power plants using coal as fuel, but it involves a 7-8% efficiency loss [14]. Moreover, this technology requires a gasification facility that increases complexity and cost of the plant.

Post-combustion capture processes remove CO₂ from the flue gas after combustion of the fuel in conventional boilers; therefore, these technologies are the preferred option for retrofitting existing power plants. However, the major problem for these technologies is large amount of flue gas with low CO₂ concentration (7-14% for coal-fired plants and about 4% for gas-fired plants) and the presence of contaminants such as SO₂ or NO_x. Therefore, the cost of construction and operation of such a facility is high. According to the recent research, application of the post-combustion processes would increase the cost of electricity by 32% in the case of gas-fired plants and 65% for coal-fired plants [15].

Oxy-fuel combustion is a novel approach to the problem of carbon dioxide capture. In this technology, fuel is combusted in oxygen instead of air. This not only reduces the amount of flue gases, but also prevents the generation of thermal NO_x. In this technology, the major components of the flue gas are CO₂ and water vapor and the main pollutants are SO₂ and particulates that may be easily removed. The flue gas, after pollutants and water removal, may contain up to 80-98% of CO₂ that can be directly compressed, transported and stored. Despite these advantages, air separation process for oxygen generation is a significant drawback. Moreover, the flame temperature has to be lowered by flue gas recycling. At the moment no industrial oxy-fuel plant is in operation and two demonstrational coal-fired oxy-fuel plants of 25 MWe and 250 MWe are under development [14].

Regardless of the selected combustion process, carbon dioxide has to be separated from flue gas. There are several methods of CO₂ capture, such as absorption, adsorption, chemical looping combustion, membrane separation, hydrate based separation and cryogenic separation [13, 14]. The main features of these methods are discussed below.

Absorption

Absorption is the most matured carbon dioxide capture method and may be adapted to various conditions. It may be applied to various combustion processes, including pre-combustion, post-combustion and oxy-fuel capture. Therefore, it is the most commonly used CCS method.

In this technique, a liquid sorbent is used for CO₂ separation from flue gas. During the process, CO₂ rich gas flows through the absorber, where it is absorbed into the liquid phase. Then the liquid containing carbon dioxide is guided to regeneration, where desorption process takes place. The captured CO₂ can be compressed and stored or utilized and then the regenerated solvent can be recycled to the process.

Both physical and chemical absorption processes may be used for carbon capture. In the case of physical absorption, low temperature and high pressure conditions are used in absorption stage and regeneration is realized by increasing temperature or decreasing pressure, or both. In physical absorption, weak van der Waals forces are used to carbon dioxide capture, therefore the absorbents of high CO₂ solubility, such as Rectisol, Selexol, Purisol and propylene carbonate, are used [13]. For high pressure conditions, physical absorption is appropriate for carbon dioxide capturing in a pre-combustion stage of the IGCC plants, however a lot of energy is required to pressurize the flue gases.

In the case of chemical absorption, lower partial pressures are used, therefore it is suitable for post-combustion carbon dioxide capture processes. The regeneration process is made by stripping or heating and/or depressurization. There are many types of sorbents used in this process, such as carbonate solutions, ammonia solutions, amine-based solutions, ionic liquids, amino acid salts, phase changing absorbents, microencapsulated and membrane absorptions, nanofluids

and phenoxide salt solutions [16]. However, the most typical sorbents are monoethanolamine (MEA), diethanolamine (DEA) and potassium carbonate. According to the literature [14], MEA is the most efficient sorbent for CO₂ absorption and the efficiency of the process exceeds 90%.

Among the advantages of the absorption the most important are maturity of the technology, high CO₂ selectivity and high capture efficiency. Moreover, the process is versatile and easy adaptable to various conditions. On the other hand, it has some drawbacks, such as high energy requirements for solvent regeneration, strong corrosion and high costs. From the environmental point of view, there shall be mentioned high toxicity and high absorbent loss causing environmental emissions.

Although the absorption is widely used in CCS processes, intensive research and development works are still carried out in the world. The most important subjects of these works are the application of process promoters and corrosion inhibitors, solvent blends, novel solvents such as nanofluids or phase changing solvents, as well as environmental impact of the process [16].

Adsorption

Carbon dioxide capture with the use of adsorption is also a widely used method, where CO₂ is bound on the surface of a solid sorbent. There are known two types of the adsorption process where adsorption-desorption process is carried out by swinging the pressure (PSA – pressure swinging adsorption) or temperature (TSA – temperature swinging adsorption).

In the PSA process, carbon dioxide is adsorbed on the surface of a solid adsorbent at high pressure and desorption process takes place at low (usually atmospheric) pressure, where the adsorbent is being regenerated and CO₂ is released for subsequent transport and storage. According to the literature [14], PSA is a commercially available technology and its efficiency at power plants may be higher than 85%.

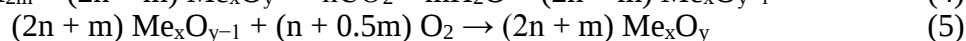
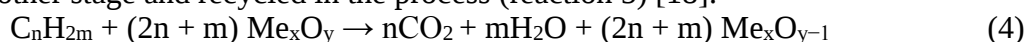
In the case of the TSA process, CO₂ is adsorbed at low temperature and released by increasing the temperature using hot air or steam injection. Although the regeneration time is longer than in the case of PSA, this method allows to achieve CO₂ purity above 95% with recovery efficiency higher than 80% [14].

The main criteria for adsorbent selection are large specific surface area, high selectivity and adsorption capacity, high regeneration ability, easy handling and material stability. There are known various types of adsorbents, such as metal-organic frameworks (MOFs), zeolites, mesoporous silica, clay, porous (activated) carbons, porous organic polymers (POPs), hydro-talcite, organic-inorganic hybrids and metal oxides. These sorbents operate in different adsorption-desorption temperatures. MOFs, zeolites, silica, clay, porous carbons, organic polymers (POPs) and organic-inorganic hybrids operate at lower temperatures (< 473 K), while metal oxides and hydrocalcite operate at intermediate temperatures (473-673 K). There are also known lithium zirconate sorbents that operate at high temperatures, over 673 K [17].

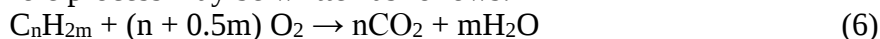
Adsorption requires less energy consumption than absorption-based methods, however still large amount of energy is consumed in the process. The advantage of this method is high purity of captured carbon dioxide. On the other hand, the drawback of this method is high cost of high-effective sorbents. Cheaper sorbents such as zeolites, silica, clay or porous carbons have lower adsorption potential [17].

Chemical looping combustion

Chemical looping combustion (CLC) is a novel technique that uses solid particles, usually metal oxides, to transport oxygen from air to burn the fuel. During the process, the metal oxide is reduced, while the fuel is being oxidized to CO₂ and water (reaction 4). The metal is then oxidized in another stage and recycled in the process (reaction 5) [18].



Similar to oxy-fuel combustion, the products of the combustion are only carbon dioxide and water that may be easily separated, however the process uses solid oxygen carriers instead of gaseous oxygen. The whole process may be written as follows:



Natural or synthetic oxygen carriers may be used in the process. Among the natural oxygen carriers are substances such as ilmenite, ferrous and manganese ores, calcium sulfate

and others. Among the synthetic ones, the most common reported are NiO, CuO, Mn₃O₄, Fe₂O₃, CoO and combined oxides [19].

There are three basic constructions of reactors considered for application of chemical looping combustion in practice [18]:

- dual fluidized bed reactors,
- swing reactors (packed bed reactors),
- rotary (rotating bed) reactors.

In the case of fluidized bed reactors, a set of two reactors is applied, where one of them is a fuel reactor and the second is an air reactor. The fuel is burned in the fuel reactor with the help of oxygen carriers, while the oxygen carriers are regenerated in the air reactor. Solid oxygen carriers circulate between the reactors and the process is continuous.

In the case of swing reactors, the process is semi-periodical. The system consists of a set of two reactors placed in parallel, both filled with solid oxygen carriers. While the first reactor is fed with fuel and combustion takes place, the second one is in regeneration mode (air reactor). After the oxygen carrier in the fuel reactor is depleted, the roles of the reactors are reversed.

The rotary reactor is constructed similarly to rotary heat exchangers. The reactor is a ring divided into four sections: air section, fuel section and two curtain sections. The combustion takes place in the fuel section, while the oxygen carrier regeneration takes place in the air section. The reactor circulates between the sections allowing for oxygen transport to the fuel section. Such construction allows for continuous operation with a packed bed.

Although the idea of chemical looping combustion seems very promising, up to now only several pilot plants have been constructed. The biggest (1 MW power) of them was constructed in Darmstadt (Germany) [19].

Membrane separation

Membrane separation technology is based on the phenomenon where a semipermeable membrane allows to separate the components of a mixture by rejecting unwanted substances and allowing the others to pass through the membrane. The process is based on the differences in diffusion process of different gases [20, 21]. In the case of CO₂ separation, flue gas is compressed to 100-300 kPa [13] and directed to membrane modules. Carbon dioxide passes through the membrane to permeate and the rest of the mixture is removed with retentate.

The separation of the flue gas with the use of membranes may be realized in a one- or two-stage process, where membrane modules are placed in series. The main problem of carbon dioxide capture, especially from post-combustion off gases, is low concentration of this component. Therefore, in order to achieve high purity and high recovery of CO₂ in the one-stage process, high selectivity of the applied membrane is required. In the case of the two-stage membrane process, high purity and recovery are more easily reached. In this configuration gas recycling may be also applied to enhance the recovery. However, the two-stage membrane process is more expensive because more membrane modules are used and more power is consumed (more compressors are needed). Moreover, gas recycling increases the required membrane area.

The membranes used for CO₂ separation may be divided for organic, inorganic and mixed matrix membranes (MMMs). The organic membranes are made mostly of polymeric materials, such as polyacetylene, polyaniline, polyamides, polyimides, polyetherimides, polycarbonates, poly(phenylene oxides), poly(ethylene oxides), polysulfones and cellulose acetate. In the case of inorganic membranes, materials such as activated carbon, zeolites, silica and metal-organic frameworks are used. Moreover, ceramic membranes made of aluminum oxide (Al₂O₃), titanium oxide (TiO₂) or carbon nanotubes (CN) are also under research [22].

Due to their mechanical properties, polymeric membranes are easy to processing, however it is hard to obtain both high selectivity and permeability. On the other hand, inorganic membranes present high selectivity or permeability, but they are thick and fragile. Therefore the mixed matrix membranes made by mixing organic and inorganic materials were invented. These membranes are under intensive research [22].

Membrane separation technique offers advantages over conventional CO₂ capture techniques, such as simple equipment, lower energy consumption, easy operation, high flexibility, low capital and operating costs, and minimal environmental impact. On the other hand, current

commercially available membrane modules present low selectivity and the trade-off between selectivity and permeability still remains an important limitation in membrane separation technologies. Moreover, a major challenge in coal-fired power plants is the low CO₂ concentration in the flue gases and the membranes have a shorter lifespan under exposition to acid gases (NO_x and SO₂) contained in flue gases.

Although a significant gap is observed between lab scale research and real field applications, membrane separation seems to be a promising CO₂ capture technology.

Hydrate-based separation

Hydrate-based carbon dioxide separation is a new technology that uses the phenomenon that CO₂ contained in the flue gas forms hydrates when exposed to water under high pressure. The mechanism is based on the differences of phase equilibrium of CO₂ with other gases, where CO₂ can form hydrates easier than other gases such as N₂ [14, 23]. The CO₂ hydrate may be later dissociated by depressurization and/or heating and carbon dioxide can be recovered. The method is supposed to be very efficient, as one volume of CO₂ hydrate can hold up to 160 volumes of CO₂ which makes this method a potential way of carbon dioxide storage [24].

As the water is the only raw material of the process, there are no pollutants released to the environment. Moreover, the reported cost of this technology is expected to be much lower than other carbon capture technologies. According to the literature the cost of hydrate-based CO₂ separation in the IGCC plant is calculated at 8.75 USD/t CO₂, while for the chemical absorption method with the use of monoethanolamine is 49 USD/t CO₂, and in the case of the pressure swing adsorption method is as high as 57 USD/t CO₂ [25].

Although first reports about this technology are very promising, it is currently in the early R&D phase.

Cryogenic separation (cryogenic distillation)

Similar to other conventional distillation processes, cryogenic distillation is based on the difference of boiling points of gaseous mixture components. The gas is cooled down at high pressure until CO₂ condensation, that allows to separate it from other components of flue gas. The process is usually realized by a series of compression, cooling and expansion steps, that leads to obtaining of liquid CO₂ that can be further stored or sequestered [26]. There are known also processes utilizing sublimation and desublimation of CO₂ [14].

The advantages of cryogenic distillation are connected mostly with the product of the process. The obtained product is of high purity (over 99%) and is liquid, that allows for transport via pipeline or tanker for further storage or utilization. Also the process is very effective – the amount of recovered CO₂ can reach even 90-95% of the carbon dioxide contained in flue gas.

On the other hand, the cryogenic distillation process requires high amount of energy, that makes it costly. The process would be more cost-effective in the case of oxy-fuel combustion processes than in the case of post-combustion processes.

3.2. Carbon dioxide mitigation technologies for maritime applications

As over 96% of global shipping sector is powered using heavy duty diesel engines [2], it is very hard to obtain IMO greenhouse gases emission goals. The most common option discussed nowadays is fuel switching for low-carbon emission fuels, such as biodiesel, LNG, ammonia, methanol and others. There are discussed also other power sources, such as wind power, electricity and nuclear power. Carbon capture technologies are also under consideration and intensive research is being conducted in this field.

3.2.1. Fuel switching

Liquefied natural gas

Nowadays, LNG is the major alternative marine fuel on the market with about 3% share in marine fuels. Natural gas is liquefied by cooling to -162°C in order to increase energy density (up to 600 times). There is a huge interest in the application of this fuel in the marine sector. At first, LNG has been used for the propulsion of LNG carrier vessels over 40 years ago. The first

LNG fueled ship, other than an LNG carrier, was constructed in 2000. Up to 2017, there were 117 such vessels in operation and new ones are still constructed [27].

As natural gas has a higher hydrogen to carbon ratio than liquid heavy fuel oil (HFO) or marine diesel oil (MDO), combustion of this fuel results in up to 30% lower CO₂ emission. Moreover, the emission of other pollutants such as SO_x, NO_x and PM is considerably reduced. As LNG does not contain sulfur, SO_x emissions are near zero (some emissions may occur from lubricants and ignitions in dual fuel engines). Lower combustion temperatures in LNG fueled engines may result in 75-90% reduction of NO_x emissions compared to HFO fueled engines [27].

On the other hand, some unburned methane slip occurs. As methane is also regarded as a greenhouse gas of global warming potential 36 times stronger than CO₂, this phenomenon reduces the overall GHG abatement effect.

The main advantage of LNG is that it is the first alternative fuel implemented in maritime industry on broad scale. However, application of this fuel does not meet the IMO goals. According to the IEA estimation, shifting 50% of the fleet to LNG will result in 10% (or less, taking into account methane slip) abatement of GHG in global shipping industry [2].

Biofuels for diesel engines

As liquefied natural gas requires major modifications of the propulsion unit, application of diesel-like biofuels may allow to reduce carbon dioxide emission without such major engine alterations. There are few biofuels available on the market today, such as straight vegetable oil (SVO), hydrotreated vegetable oil (HVO) and fatty acid methyl ester (FAME), however the production of biofuels for transport application is limited [2, 27].

There are also more advanced biofuels for international shipping applications, such as Fischer-Tropsch diesel (FT-Diesel) and pyrolysis oil. FT-Diesel is produced by the gasification of biomass followed by Fischer-Tropsch liquefaction, while pyrolysis oil is produced by pyrolysis of bio-waste or cellulosic feedstocks.

Another option is the production of HVO fuel from waste oils and fats by hydrogenation. E-diesel may be also produced by the synthesis of hydrogen and CO₂ using Fischer-Tropsch liquefaction.

Biofuels applicable in diesel engines contain very little sulfur, therefore their application will allow to achieve NO_x, SO_x and GHG emission reduction targets. Moreover, biofuels are biodegradable, that may avoid large contamination problems in the case of accidental spills. On the other hand, the price of biofuel may be an important barrier. The IEA estimates the price of FAME at 1040 USD/t and the price of HVO at 542 USD/t, while fossil fuels prices are 482 USD/t for MDO and 290 USD/t for HFO (2016 calculations) [27].

LNG type fuels

Another type of low-carbon fuels are LNG type fuels, such as biogas, biomethane, hythane and methanol [2, 28].

Although biogas may be potentially applied in marine engines, there are some issues with using it in internal combustion engines as [28]:

- high CO₂ content that limits power output,
- acidic H₂S (hydrogen sulfide) content leading to damage of the engine,
- high moisture of the gas that can impact ignition (during ICE start-up),
- biogas composition variation due to instability of biotechnological process,
- possible damage of engine parts during combustion due to the presence of siloxanes.

Moreover, the application of biogas requires purification [29] and/or post-combustion processing of flue gas due to the presence of such impurities as SO₂. Therefore, the application of biomethane obtained by separation of methane from biogas is much more efficient [28].

Apart from biogas purification, biomethane may be obtained from biomass through gasification and methanation and from renewable hydrogen and CO₂ by synthesis (the Sabatier process) [2]. Such obtained methane is similar to fossil LNG and may be used in respective engines.

The drawbacks of biomethane application in marine engines are:

- not enough raw material for shipping industry,

- high production cost in comparison to fossil fuels,
- lack of infrastructure and supply chains.

Hythane is a novel approach to carbon dioxide emission mitigation by mixing compressed natural gas (methane) with hydrogen. The main problem of such fuel is the different liquefaction temperatures of methane (-162°C) and hydrogen (-253°C), that would result in the separation of these gases. However, the research on the injection of hydrogen for addition to natural gas in LNG engines are in progress [2].

Application of methanol fuel for ships is currently the subject of intensive research. Methanol combustion in marine engines allows to reduce both CO_2 and other pollutants emissions compared to heavy fuel oil or marine diesel oil. According to the literature [27], the first methanol powered ship “Stena Germanica” (Swedish car ferry) allows for emission reduction of SO_x by 99%, NO_x by 60%, particulates by 95% and CO_2 by 25%.

Methanol for marine engine usage may be produced from natural gas, by catalytic hydrogenation of a waste CO_2 stream or from biomass. Therefore, taking into account the lifecycle of this fuel, the CO_2 emission depends on the generation method. In the case of a biomass origin of methanol, CO_2 emissions are regarded as biogenic and are discounted. On the other hand, methanol obtained from natural gas causes lower CO_2 emissions to the atmosphere, but GHG emissions calculated for lifecycle are around 10% higher than from HFO or MDO. Moreover, the cost of methanol is higher than liquid fossil fuels and LNG.

Other fuels

There are also other fuels under concern to be applied in marine engines, such as dimethyl ether (DME) and ammonia [2].

Similar to LNG, dimethyl ether is a gaseous fuel that requires moderate pressure for liquefaction. It is manufactured from methanol by dehydration. Diesel engines need relatively mild modifications for this fuel application, however research on the application of this fuel for marine diesel engines is at early stage.

Ammonia is also concerned for application as a marine fuel and may be used for internal combustion engines. This carbon-free fuel is produced from hydrogen and nitrogen in the Haber-Bosch process. However, the carbon dioxide emissions may occur during ammonia production depending on the source of electricity used for the process. Ammonia is corrosive and hazardous (it may cause permanent injuries of eyes, alkali burns, etc.). The combustion of ammonia produces N_2O that is also concerned as a greenhouse gas. Therefore, the emission control of N_2O is essential when ammonia is used as a fuel.

3.2.2. Other energy sources

Among the other energy sources, the most matured is nuclear energy. Besides it, electric energy from both batteries and fuel cells is considered. Other options such as wind or solar energy, due to high instability, are regarded as auxiliary power demands.

Nuclear propulsion for military and submarine purposes has been used since 1955. For civil purposes, such propulsion is used in icebreakers and other selected ships. Nuclear propulsion is achieved via a small onboard nuclear plant. The steam obtained with the use of nuclear reaction heat drives steam turbines and turbo generators. Nuclear fuel offers very high energy density with very low emissions of greenhouse gases and other air quality emissions. Moreover, the ships may operate for long periods without refueling and the operational costs of such a system are very low. On the other hand, this type of propulsion is hard to accept by a society. Due to safety risks, many countries do not allow nuclear ships to enter their ports.

Electric propulsion system may be powered from both batteries and fuel cells. The batteries are heavy and have limited capacity, although they can be adapted for shorter routes. Moreover, the costs of batteries are foreseen to decrease. Battery propulsion system may be used as an auxiliary system or may be applied for hybridization of smaller vessels to achieve fuel savings.

Application of fuel cells is a more promising solution, however the most important problem is availability of hydrogen and its low volumetric energy density, that requires significant additional infrastructure. On the other hand, also methane, methanol and ammonia may be utilized

in fuel cells with high efficiency. The electric motors for propulsion may have as high efficiency as 95%. Combined with up to 45% efficiency of fuel cells, it gives a significant efficiency. Diesel engines require 44% more fuel than fuel cells with the same output power. The first civilian ship using fuel cell technology was the “Viking Lady”. Main propulsion was provided by LNG in a diesel engine, with a fuel cell for supplementary propulsion. The emissions were reduced by 100% for SO_x, by 85% for NO_x and by 20% for CO₂ [27].

Although the works on commercialization of fuel cells for marine application are very intensive, the required capital costs for new infrastructure are a barrier to global commercialization. Moreover, the hydrogen price is an order of magnitude higher than that of conventional fuels. Therefore, the electric propulsion for marine application will not be commercially available in the near future.

3.2.3. *Post-combustion carbon capture technologies*

At present, low-carbon fuels (excluding liquefied natural gas) and other power sources for shipping applications are at early stage of development. Moreover, application of these propulsion systems requires also adaptation of marine engines and construction of shoreside infrastructure. Therefore, the possibility of their commercialization in the near future is limited.

The other approach for carbon dioxide emission mitigation is application of post-combustion carbon capture technologies. These technologies were first developed and commercialized for their onshore applications, therefore they are considered as ready to deploy and possible long-term solution option for CO₂ emission reduction from marine sector.

There are four main technologies considered for carbon capture applications at shipping industry: chemical absorption, adsorption, membrane separation and cryogenic separation [30]. Some authors also consider calcium looping process as a fifth option [31]. According to the medium spent in the process, three types of technologies may be distinguished: heat-driven, electricity-driven, and material-driven.

Chemical absorption technology is a heat-driven process, as heat is used for desorption of captured CO₂ and the sorbent is recirculated to the process. The potential CO₂ purity and capture rate are estimated to be high. Due to the fact that the waste heat from the exhaust gas can be readily available to the capture unit, this process is advantageous for shipping application. Moreover, the maturity of this technology is the highest among all carbon capture technologies considered for marine applications. Therefore, chemical absorption is regarded as reference technology.

Depending on the system applied, adsorption may be a pressure swing or temperature swing process, making the system electricity- or heat-driven. The potential CO₂ purity and capture rate are linked, however the obtained carbon dioxide purity is rather low (about 80%) [32]. Another disadvantage is a large footprint, that is not desirable due to the limited space available on ships.

The membrane process is a compact and electricity-driven technology with a reasonable energy consumption. However, as in the case of adsorption CO₂ purity and capture rate is linked, the obtained carbon dioxide purity is low (about 60%) [32]. Higher purity requires a multistage system of membrane modules, that increases energy consumption and space requirements.

Cryogenic separation is a typical electricity-driven technology. Although the potential purity of separated CO₂ is very high (up to 99.9%) with a high capture rate, the energy consumption is much higher than in other cases, that makes this technology economically unprofitable.

Calcium looping technology is based on chemical reaction of calcium oxide with carbon dioxide, leading to CO₂ binding with a high amount of heat generation in the process [33]. Otherwise than in previously mentioned carbon capture methods, this technology is material-driven. Although the energy requirements are very low, the high operation temperature, large space requirements for fresh and used solid sorbent in the process as well as onshore sorbent regeneration facilities make this technology much less feasible than other options.

Due to the specificity of marine application, especially to avoid affecting nautical properties of the ship, the possibility of selected carbon capture technology application depends on criteria such as:

- CO₂ capture rates;
- capital and operational costs;
- suitability of the process for onboard application;
- equipment footprint, space and weight;
- requirements of chemicals and process water;
- presence of impurities and wastewater for treatment;
- ship modification level and maintenance scheme;
- CO₂ onboard storage and unloading infrastructure.

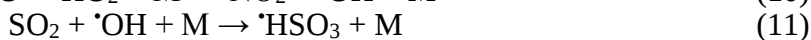
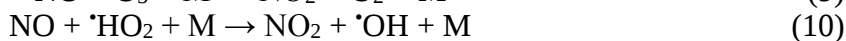
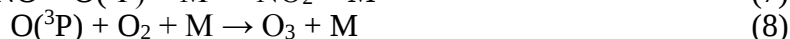
In the work [31], the authors discussed three main scenarios of carbon capture strategy for ships: original ship configuration (without CCS), a retrofitted ship with a 70% CO₂ emission capture rate and a new build ship with a 90% CO₂ emission capture rate. The simulation showed that the application of CCS system on both retrofitted and new ships is feasible, however the operation of CCS system requires a certain amount of energy. The calculations showed that in the case of a retrofitted ship with a 70% carbon dioxide removal efficiency (calculated for original stream of flue gas, i.e., without CCS), fuel consumption will increase by 70%, while in the case of a new ship with a 90% CO₂ removal rate, fuel consumption may increase even twice. Not less important are the capital and operational costs, however these costs are lower than biodiesel fuel application for the same emission mitigation levels.

4. ELECTRON BEAM INDUCED CARBON DIOXIDE MITIGATION PROCESS

The electron beam flue gas treatment process (EBFGT) was originally invented in Japan in the 1970's for SO₂ removal from ore sintering plants. However, steel crisis in Japan interrupted technology development for a few years. During the next twenty years, the process was intensively developed in several research centers in the world in Germany, USA, Japan and Poland. The results of the research led to the design and construction of industrial scale EBFGT plants. Two such installations were constructed by Ebara Corporation in China (Chengdu and Hangzhou) and the third one was constructed in Poland (Pomorzany) in the late 1990's and early 2000's [34].

The electron beam flue gas treatment process idea is based on oxidation of SO₂ and NO (nitric oxide) to higher oxides under electron beam irradiation and further creation of ammonium sulfate and ammonium nitrate in reaction with water vapor and ammonia. The whole process is realized in four main steps: cooling and humidification of flue gases, ammonia injection, irradiation, by-product filtration and storage.

During the research carried on in the Institute of Nuclear Chemistry and Technology (INCT), the process was adopted for treatment of flue gases from marine diesel engines. This technology, called hybrid electron beam flue gas treatment process, is based on a combination of two processes: electron beam irradiation and wet absorption. In the first step, the flue gases are irradiated and pollutants such as SO₂ and NO_x are oxidized to higher oxides, which then react with the water vapor present in the flue gases, resulting in the formation of sulfuric acid (H₂SO₄) and nitric acid (HNO₃) – reactions 7-14. In the second step, these acids are absorbed into aqueous solution. The combination of both processes allows for simultaneous removal of both SO_x and NO_x with high efficiency.





In the above reactions M is a third inert body in the reaction system.

After the laboratory studies, the concept of hybrid electron beam flue gas treatment process was tested in real conditions in pilot scale. The project was realized in Riga Shipyard (Latvia) [35, 36]. The main goal of this project was to demonstrate the ability of hybrid electron beam flue gas treatment technology for efficient removal of SO₂ and NO_x from marine diesel engine flue gases.

The source of flue gas was a tugboat “Orkāns” of Riga Shipyard equipped with two-stroke diesel engines berthed at the pier. The gas from the engine was directed to the irradiation device, that was a mobile accelerator of Fraunhofer FEP (Germany) with electron energy of 125 kV and beam current of 100 mA. After the irradiation, the flue gas was directed to the absorber, that was a countercurrent gas-liquid flow packed scrubber. A closed loop system was selected for water circulation in the scrubber. The circulating water was stored in two tanks filled with 3 m³ of seawater. After the treatment, flue gas was released to the atmosphere. The scheme of the pilot hybrid electron beam flue gas treatment plant is presented in Fig. 3.

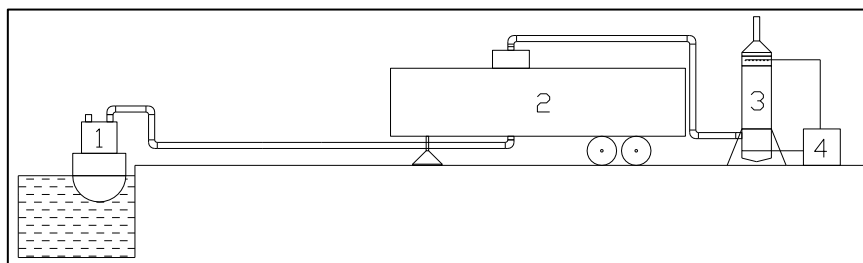


Fig. 3. General scheme of the pilot hybrid electron beam flue gas treatment plant: 1 – flue gas source, 2 – mobile accelerator, 3 – scrubber, 4 – seawater tank.

The construction and operation of the pilot hybrid electron beam flue gas treatment plant located in Riga Shipyard showed ability of the technology to be used in marine conditions. The results of the experiments proved that the combination of accelerator technology with wet scrubbing process is a good solution for simultaneous treatment of SO_x, NO_x and PM from marine diesel engine flue gases.

The method of acidic pollutants removal with the use of electron beam leads to oxidation of both pollutants, increasing their solubility and reactivity. In the case of carbon dioxide removal, a reductive pathway is proposed. Unfortunately, due to CO₂ chemical stability, the existing methods of its conversion into less oxidized chemical species typically require a source of energy to drive one- or multiple-electron transfer reactions [37].

The modified hybrid electron beam flue gas treatment process elaborated during the previous research may be adopted for electron beam induced carbon dioxide mitigation process. The idea of electron beam induced carbon dioxide mitigation process is based on the reaction of aqueous CO₂ with water radiolysis products (e⁻_{aq}, ·OH, H·) in the presence of formates as radical scavengers, resulting in creation of oxalates [38].

Since the process described above does not occur in the presence of acidic compounds, a two-step process was proposed. In the first step, acidic pollutants such as SO₂ and NO_x are removed in the hybrid electron beam flue gas treatment process, while in the second step, carbon dioxide is removed by irradiation in the presence of formates. The scheme of the process is presented in Fig. 4.

The raw flue gases are introduced through the inlet channel (1) to the first stage reactor (2), where they are irradiated with an electron beam from accelerator (3). As a result of irradiation, SO₂ and NO_x are oxidized to higher oxides and, together with the gas, directed to the scrubber (4), where they are absorbed in an aqueous sodium hydroxide solution containing sodium chloride (NaCl) and the oxidant (eq. NaClO₂). The solution containing the absorbed pollutants

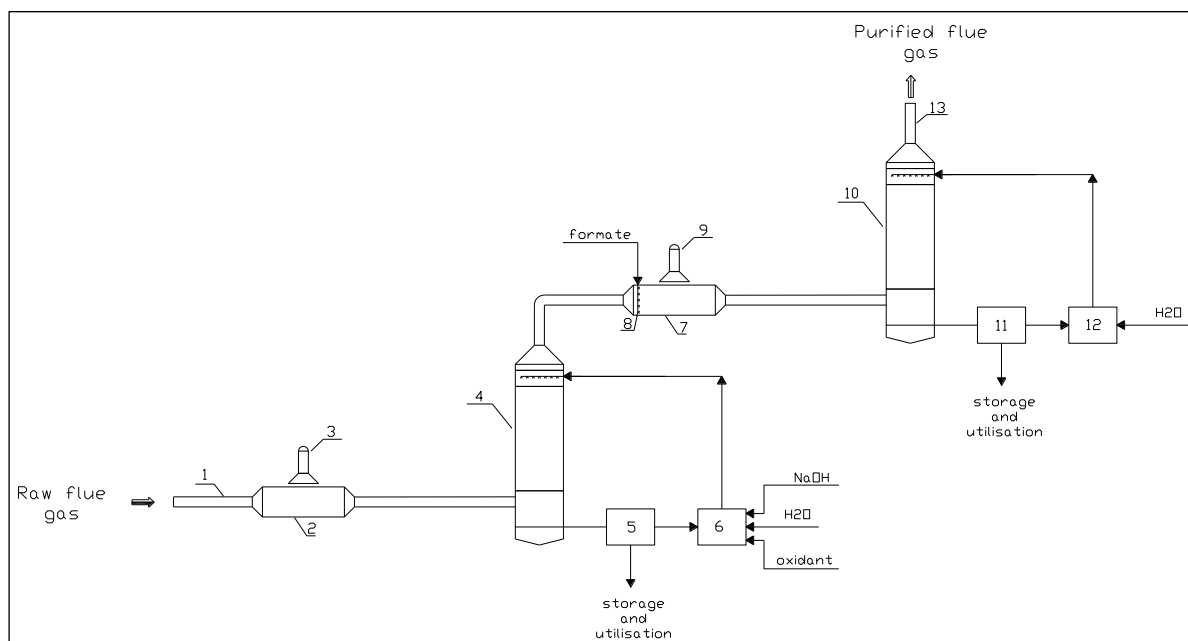


Fig. 4. Conceptual scheme of the electron beam induced carbon dioxide mitigation process: 1 – inlet channel, 2 – first stage reactor, 3 – accelerator, 4 – scrubber, 5 – absorbent solution purification system, 6 – absorption solution tank, 7 – second stage purification reactor, 8 – formate spraying nozzles, 9 – accelerator, 10 – scrubber, 11 – water purification system, 12 – water tank, 13 – outlet channel.

is directed to the purification system (5), which allows for the separation of the absorbed acidic pollutants. Part of the absorption solution stream, together with the separated impurities, is sent for disposal, and the purified solution is directed to the absorption solution tank (6), where water and reagents are supplemented, and then recirculated to the scrubber (4). After the acidic pollutants removal, the gas is directed to the second stage purification reactor (7), where an aqueous sodium formate solution is sprayed from the nozzles (8) located upstream of the second stage purification accelerator (9). As a result of the processes initiated by the electron beam, carbon dioxide is converted to oxalates, which, together with the gas, are directed to the second stage scrubber (10), where they are absorbed in water. Analogously to the first stage of purification, water containing absorbed pollutants is directed to the purification system (11), which allows for the separation of absorbed pollutants. Part of the water stream, together with the separated oxalates, is directed to disposal, and the remaining part of the water stream is directed to the tank (12), where the water losses are replenished, and then recirculated to the scrubber (10). The gas purified in this way is directed to the outlet channel (13).

Practical realization of the electron beam induced carbon dioxide mitigation process will require certain solutions adequate for marine diesel flue gas composition and marine industry specificity. The typical composition of flue gas from marine diesel engines is presented in Table 2 [39].

As flue gas has very high temperature, initial cooling may be necessary. This process may be realized by spraying water into flue gas in flue gas ducts. Similarly in the case of flue gas irradiation, this process may be also realized in a separated part of flue gas ducts. However, as radiation occurs, the reaction unit must be separated with biological shields according to radiological protection standards. For the same reasons, application of self-shielded electron accelerators is recommended. Absorption process shall be realized with the use of packed, countercurrent absorbers. Absorption solution purification may be realized with application of membrane units. The condensed effluents containing absorbed acidic pollutants or oxalates shall be stored onboard and unloaded at harbor, regarding that sodium and potassium oxalates are commercial products and may be directed for further applications. The possible modification of the process may lead to formation of the sodium salt, present in ionic form, which may be discharged to the sea.

Table 2. Typical composition of flue gas from marine diesel engines [39].

Parameter	Value
Temperature [°C]	370
Main components [% vol.]:	
- nitrogen	75.8
- oxygen	13.0
- carbon dioxide	5.2
- water vapor	5.35
Gaseous pollutants [ppmv]:	
- nitrogen oxides	1500
- sulfur oxides	600
- carbon monoxide	60
- hydrocarbons	180
Particulates [mg/Nm ³]	120

As the electron beam induced carbon dioxide mitigation process is under development, more detailed solutions may be discussed after pilot scale phase of research.

5. CONCLUSIONS

The emission of carbon dioxide from shipping industry stands for 2.2% of global anthropogenic emission of this gas, however there are strong efforts for reduction of this emission. The 2023 International Maritime Organization Strategy on Reduction of GHG Emissions from Ships states that CO₂ emissions from international shipping shall be reduced by at least 40% by 2030, compared to 2008, and net-zero GHG emissions shall be reached by or around 2050.

At present, ships rely on fossil fuels for energy generation, where heavy fuel oils and marine diesel oil cover up to 96% of the fuel usage. Liquefied natural gas covers the remaining 4%. Therefore, it is very hard to meet the IMO greenhouse gases emission goals. The most common option discussed nowadays is fuel switching for low-carbon emission fuels, such as biodiesel, LNG, ammonia, methanol and others. However, the biofuels have certain drawbacks, such as high production costs in comparison to fossil fuels, not enough availability of fuel for shipping industry and lack of infrastructure and supply chains. On the other hand, LNG is a fossil fuel itself, therefore its application does not meet the IMO goals. Although application of biofuels is one of the possibilities of CO₂ emission mitigation, it may be regarded as an auxiliary method of CO₂ emission mitigation.

There are known several methods of CO₂ capture, such as absorption, adsorption, chemical looping combustion, membrane separation, hydrate-based separation and cryogenic separation; however, not every one of them may be applied in marine conditions. Among them there are four main technologies considered for carbon capture applications at shipping industry: chemical absorption, adsorption, membrane separation and cryogenic separation. Although there are carried out intensive research on application of these methods in marine industry, at present only few demonstrational attempts were achieved. Although the post-combustion carbon capture methods are regarded as a perspective solution of marine carbon dioxide emission, there is still a lot of issues to be solved.

Apart from the known CO₂ emission mitigation technologies, a new one – electron beam induced carbon dioxide mitigation process was proposed. The process is based on the reaction of oxalates creation from CO₂ under electron beam irradiation in the presence of formates. The technology involves a two-step process, where in the first step, acidic pollutants such as SO₂

and NO_x are removed in the hybrid electron beam flue gas treatment process, while in the second step, carbon dioxide is removed by irradiation in the presence of formates. The process is under development, however its application for marine conditions is possible.

This paper has been supported by the European Union – Horizon 2020 programme, project I.FAST (grant agreement No. 101004730) and by the Polish Ministry of Science and Higher Education (contract No. 5180/H2020/2021/2).

6. LITERATURE

- [1]. Gray, N., McDonagh, S., O'Shea, R., Smyth, B., & Murphy, J.D. (2021). Decarbonising ships, planes and trucks: An analysis of suitable low-carbon fuels for the maritime, aviation and haulage sectors. *Adv. Appl. Energy*, 1, 100008. <https://doi.org/10.1016/j.adapen.2021.100008>.
- [2]. Aakko-Saksa, P.T., Lehtoranta, K., Kuittinen, N., Järvinen, A., Jalkanen, J.-P., Johnson, K., Jung, H., Ntziachristos, L., Gagné, S., Takahashi, C., Karjalainen, P., Rönkkö, T., & Timonen, H. (2023). Reduction in greenhouse gas and other emissions from ship engines: Current trends and future options. *Prog. Energy Combust. Sci.*, 94, 101055. <https://doi.org/10.1016/j.pecs.2022.101055>.
- [3]. Wright I. (2019). *World Map of Shipping Traffic Density*. Retrieved August 27, 2024, from <https://moverdb.com/shipping-traffic-density/>.
- [4]. International Maritime Organization. (2021). *Fourth IMO greenhouse gas study 2020*. London: International Maritime Organization.
- [5]. Ritchie, H., Rosado, P., & Roser, M. (2024). *CO₂ and Greenhouse Gas Emissions*. Retrieved August 5, 2024, from <https://ourworldindata.org/co2-and-greenhouse-gas-emissions>.
- [6]. International Energy Agency. (2023). *CO₂ emissions in 2022*. Paris: International Energy Agency. <https://www.iea.org/reports/co2-emissions-in-2022>.
- [7]. Prentice, I.C. (lead author). (2001). The Carbon Cycle and Atmospheric Carbon Dioxide. In J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, X. Dai, K. Maskell, & D.A. Johnson (Eds.), *Climate Change 2001: The Scientific Basis*. New York: Cambridge University Press. <https://www.ipcc.ch/site/assets/uploads/2018/02/TAR-03.pdf>.
- [8]. International Energy Agency. (2023). *Global CO₂ emissions by sector, 2019-2022*. Retrieved August 5, 2024, from <https://www.iea.org/data-and-statistics/charts/global-co2-emissions-by-sector-2019-2022>.
- [9]. Ritchie, H. (2020). *Cars, planes, trains: where do CO₂ emissions from transport come from?* Retrieved August 5, 2024, from <https://ourworldindata.org/co2-emissions-from-transport>.
- [10]. Climate and Clean Air Coalition. (2020). *Black carbon*. Retrieved August 5, 2024, from <https://www.ccacoalition.org/short-lived-climate-pollutants/black-carbon>.
- [11]. International Maritime Organization. (2018). *UN body adopts climate change strategy for shipping*. Retrieved August 5, 2024, from <https://www.imo.org/en/MediaCentre/PressBriefings/Pages/06GHGinitialstrategy.aspx>.
- [12]. International Maritime Organization. (2023). *IMO Strategy on reduction of GHG emissions from ships*. Retrieved August 5, 2024, from <https://www.imo.org/en/OurWork/Environment/Pages/IMO-Strategy-on-reduction-of-GHG-emissions-from-ships.aspx>.
- [13]. Khan, U., Ogbaga, C.C., Omolabake Abiodun, O.-A., Adeleke, A.A., Ikubanni, P.P., Okoye, P.U., & Okolie, J.A. (2023). Assessing absorption-based CO₂ capture: Research progress and techno-economic assessment overview. *Carbon Capture Sci. Technol.*, 8, 100125. <https://doi.org/10.1016/j.ccst.2023.100125>.
- [14]. Leung, D.Y.C., Caramanna, G., & Maroto-Valer, M.M. (2014). An overview of current status of carbon dioxide capture and storage technologies. *Renew. Sustain. Energy Rev.*, 39, 426-443. <http://dx.doi.org/10.1016/j.rser.2014.07.093>.

- [15]. Kanniche, M., Gros-Bonnivard, R., Jaud, P., Valle-Marcos, J., Amann, J.-M., & Bouallou, C. (2010). Pre-combustion, post-combustion and oxy-combustion in thermal power plant for CO₂ capture. *Appl. Therm. Eng.*, 30, 53-62.
- [16]. Ochedi, F.O., Yu, J., Yu, H., Liu, Y., & Hussain, A. (2021). Carbon dioxide capture using liquid absorption methods: a review. *Environ. Chem. Lett.*, 19, 77-109. <https://doi.org/10.1007/s10311-020-01093-8>.
- [17]. Sai Bhargava Reddy, M., Ponnamm, D., Sadasivuni, K.K., Kumar, B., & Abdullah, A.M. (2021). Carbon dioxide adsorption based on porous materials. *RCS Adv.*, 11, 12658. DOI: 10.1039/d0ra10902a.
- [18]. Czakiert, T., Krzywanski, J., Zylka, A., & Nowak, W. (2022). Chemical looping combustion: A brief overview. *Energies*, 15(4), 1563. <https://doi.org/10.3390/en15041563>.
- [19]. Lyngfelt, A. (2020). Chemical looping combustion: Status and development challenges. *Energy Fuels*, 34, 9077-9093. <https://doi.org/10.1021/acs.energyfuels.0c01454>.
- [20]. Chmielewski, A.G., Urbaniak, A., Palige, J., Roubinek, O., Wawryniuk, K., & Dobrowolski, A. (2019). Membrane installation for biogas enrichment – Field tests and system simulation. *Chem. Process Eng.*, 40(2), 235-260. <https://doi.org/10.24425/cpe.2019.126116>.
- [21]. Harasimowicz, M., Orluk, P., Zakrzewska-Trznadel, G., & Chmielewski, A.G. (2007). Application of polyimide membranes for biogas purification and enrichment. *J. Hazard. Mater.*, 144(3), 698-702. <https://doi.org/10.1016/j.jhazmat.2007.01.098>.
- [22]. Gkotsis, P., Peleka, E., & Zouboulis, A. (2023). Membrane-based technologies for post-combustion CO₂ capture from flue gases: recent progress in commonly employed membrane materials. *Membranes*, 13, 898. <https://doi.org/10.3390/membranes13120898>.
- [23]. Khan, M., Warriar, P., Peters, C., & Koh, C. (2022). Hydrate-based separation for industrial gas mixtures. *Energies*, 15, 966. <https://doi.org/10.3390/en15030966>.
- [24]. He, J., Liu, Y., Ma, Z., Deng, S., Zhao, R., & Zhao, L. (2017). A literature research on the performance evaluation of hydrate-based CO₂ capture and separation process. *Energy Procedia*, 105, 4090-4097. doi: 10.1016/j.egypro.2017.03.867.
- [25]. Dashti, H., & Lou, X. (2018). Gas Hydrate-Based CO₂ Separation Process: Quantitative Assessment of the Effectiveness of Various Chemical Additives Involved in the Process. In Z. Sun, C. Wang, D. Post Guillen, N.R. Neelameggham, L. Zhang, J.A. Howarter, T. Wang, E. Olivetti, M. Zhang, D. Verhulst, X. Guan, A. Anderson, S. Ikhmayies, Y.R. Smith, A. Pandey, S. Pisupati, & H. Lu (Eds.), *Energy Technology 2018. Carbon Dioxide Management and Other Technologies*. Cham: Springer. The Minerals, Metals & Materials Series. https://doi.org/10.1007/978-3-319-72362-4_1.
- [26]. Songolzadeh, M., & Soleimani, M. (2014). Carbon dioxide separation from flue gases: A technological review emphasizing reduction in greenhouse gas emissions. *Sci. World J.*, 2014, 828131. <http://dx.doi.org/10.1155/2014/828131>.
- [27]. Balcombe, P., Brierley, J., Lewis, C., Skatvedt, L., Speirs, J., Hawkes, A., & Staffell, I. (2019). How to decarbonise international shipping: Options for fuels, technologies and policies. *Energy Convers. Manag.*, 182, 72-88. <https://doi.org/10.1016/j.enconman.2018.12.080>.
- [28]. Mallouppas G., Yfantis E.A., Ioannou, C., Paradeisiotis, A., & Ktoris, A. (2023). Application of biogas and biomethane as maritime fuels: A review of research, technology development, innovation proposals, and market potentials. *Energies*, 16, 2066. <https://doi.org/10.3390/en16042066>.
- [29]. Chmielewski, A.G., Urbaniak, A., & Wawryniuk, K. (2013). Membrane enrichment of biogas from two-stage pilot plant using agricultural waste as a substrate. *Biomass Bioenergy*, 58, 219-228. <https://doi.org/10.1016/j.biombioe.2013.08.010>.
- [30]. Oh, J., Kim, D., Roussanaly, S., Anantharaman, R., & Lim, Y. (2024). Optimal capacity design of amine-based onboard CO₂ capture systems under variable marine engine loads. *Chem. Eng. J.*, 483, 149136. <https://doi.org/10.1016/j.cej.2024.149136>.
- [31]. Tavakoli, S., Gamlem, G.M., Kim, D., Roussanaly, S., Anantharaman, R., Yum, K.K., & Valland, A. (2024). Exploring the technical feasibility of carbon capture onboard ships. *J. Clean. Prod.*, 452, 142032. <https://doi.org/10.1016/j.jclepro.2024.142032>.
- [32]. Oil and Gas Climate Initiative. (2021). *Is carbon capture on ships feasible? A report from the oil and gas climate initiative*. Stena Bulk.

- [33]. Sweeney, B.N.C. (2020). *RECAST - A system to decarbonise long-distance shipping*. Retrieved August 5, 2024, from <https://calix.global/wp-content/uploads/2020/09/INEC2020-RECAST-a-system-to-decarbonise-shipping-V04c.pdf>.
- [34]. Basfar, A.A., Fageeha, O.I., Kunnummal, N., Chmielewski, A.G., Licki, J., Pawelec, A., Zimek, Z., & Warych, J. (2010). A review on electron beam flue gas treatment (EBFGT) as a multicomponent air pollution control technology. *Nukleonika*, 55(3), 271-277.
- [35]. Torims, T., Chmielewski, A., Kravalis, K., Mattausch, G., Pawelec, A., Pikurs, G., Ruse, A., Vretenar, M., & Zimek, Z. (2021). Development of a hybrid electron accelerator system for the treatment of marine diesel exhaust gases. In *Proceedings of the 11th International Particle Accelerator Conference, 10-15 May 2020, Caen, France* (THVIR14). Geneva, Switzerland: JACoW Publishing.
- [36]. Pawelec A., Chmielewski A.G., Sun, Y., Bułka, S., Torims, T., Pikurs, G., & Mattausch, G. (2021). Plasma technology to remove NO_x from off-gases. *Nukleonika*, 66, 227-231.
- [37]. Bobrowski, K. (2017). Radiation chemistry of liquid systems. In Y. Sun and A.G. Chmielewski (Eds.), *Applications of ionizing radiation in materials processing* (pp. 81-116). Warszawa: Institute of Nuclear Chemistry and Technology. <http://www.ichtj.waw.pl/ichtj/publ/monogr/sun2017/sun-chapter4.pdf>.
- [38]. Hu, C., Al Gharib, S., Wang, Y., Gan, P., Li, Q., Denisov, S.A., Le Caer, S., Belloni, J., Ma, J., & Mostafavi, M. (2021). Radiolytic approach for efficient, selective and catalyst free CO₂ conversion at room temperature. *ChemPhysChem*, 22, 1900-1906. <https://doi.org/10.1002/cphc.202100378>.
- [39]. MAN B&W Diesel A/S. (2004). *Emission control, MAN B&W Two-stroke Diesel Engines*. Copenhagen, Denmark: MAN B&W Diesel A/S.