

Navigating within the Safe Operating Space with Carbon Capture On-Board

Valentina Negri, Margarita A. Charalambous, Juan D. Medrano-García, and Gonzalo Guillén-Gosálbez*

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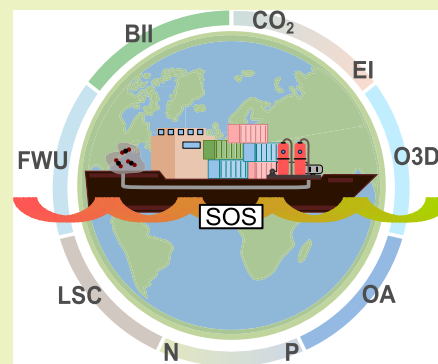
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ABSTRACT: Despite the global pandemic that recently affected human and cargo transportation, the emissions of the maritime sector are projected to keep growing steadily. The International Maritime Organization focused on boosting the fleets' efficiency to improve their environmental performance, while more sustainable fuels are currently under investigation. Here, we assess the economic, technical, and environmental feasibility of an interim solution for low-carbon shipping using state-of-the-art CO₂ capture technology, namely, chemical absorption, on-board cargo ships. We compute the carbon footprint of this alternative and perform an absolute sustainability study based on seven planetary boundaries. Our results show that the capture on-board scenario can achieve 94% efficiency on the net CO₂ emissions at 85 \$/tCO₂ while substantially reducing impacts on core planetary boundaries (relative to the business as usual) and outperforming a direct air capture scenario in global warming and all planetary boundaries, except for the nitrogen flow. Hence, capture on-board seems an appealing solution to decarbonize shipping in the short term while alternative carbon-free fuels and related infrastructure are developed and deployed.

KEYWORDS: container ship, lining industry, maritime emissions, CO₂ capture, direct air capture, global warming, planetary boundaries



INTRODUCTION

The reduction of the carbon intensity of rail, road, air, and sea transport modes must be set as a priority to cope with the forecasted increase in the global population and consequent freight business despite the remarkable decline of emissions resulting from the COVID-19 global pandemic.^{1–3} Considering that roughly 80% of the cargo is transported by sea, shipping is regarded as a very efficient and cost-effective way of moving goods.⁴ Nonetheless, since it is still a sector almost entirely powered by fossil fuels, it contributed to roughly 3% of global anthropogenic greenhouse gas (GHG) emissions in 2018.⁵

Given the relatively low share of emissions compared to other economic sectors, decarbonization of ships was never a priority and was not even explicitly mentioned in the Paris Agreement.⁶ However, maritime emissions are projected to increase due to population growth, while the average lifetime of vessels is 25–40 years,⁷ implying that today's actions will have long-lasting effects.⁴ Historically, attention has been paid to particulate matter (PM) and sulfur and nitrogen oxides (SO_x and NO_x) emissions, which motivated the International Maritime Organization (IMO) to introduce stricter policies to limit the effects of these components,⁸ and increase the energy efficiency of marine activities.^{9–11} Only recently, new initiatives and strategies have been proposed to tackle GHG emissions, with the European Union being at the forefront.¹²

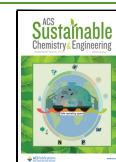
However, we are still far from reaching a scenario in line with a 50% GHG emissions reduction target in 2050.¹³

In addition to the IMO measures to increase ship efficiency, long-term sustainable solutions involve a substantial change in the current infrastructure and the manufacturing of new propulsion systems where low or zero-carbon fuels can be employed. Great interest has been expressed in liquefied natural gas (LNG), hydrogen (H₂), ammonia (NH₃), and methanol (MeOH),^{8,14–16} which can be produced from inputs such as sustainable biomass feedstock, solar energy, or renewable electricity.^{17,18} These alternative fuels, however, require compatible engines and large storage on board, given their lower volumetric energy density compared to heavy fuel oil (HFO).^{19–21} On the other hand, short-term solutions can be based on carbon dioxide (CO₂) capture, either at the source of emissions or from the atmosphere (*i.e.*, direct air capture, DAC²²), while the new infrastructure is developed. CO₂ capture, often coupled with geological storage (CCS), is a mature technology²³ and a very efficient way of reducing direct emissions in industry and power plants.²⁴ Different config-

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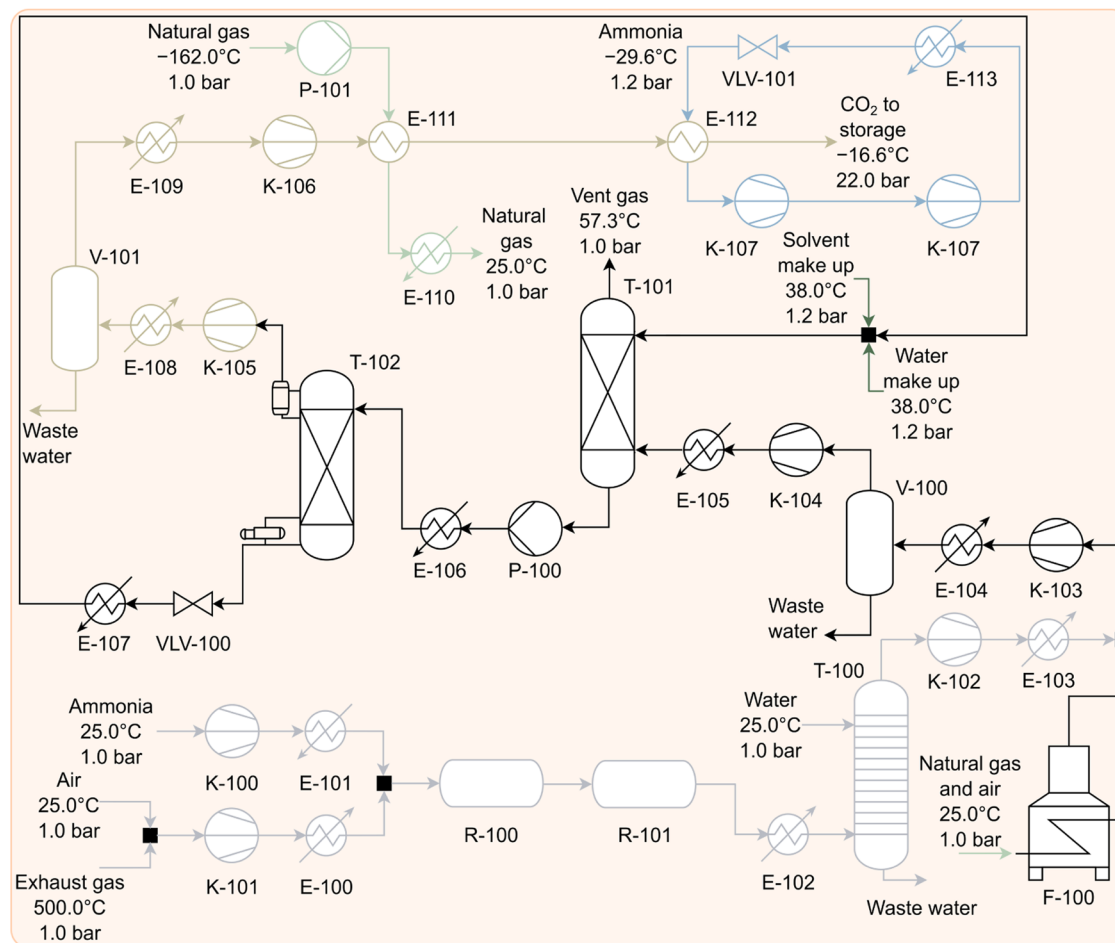


Figure 1. Process flowsheet of the retrofitted CO₂ capture plant. Three sections can be identified: pretreatment, carbon capture units, and refrigeration cycles for the storage of liquid CO₂ on-board.

urations can be adopted, namely post-, oxy-, and precombustion, using physical or chemical adsorbents and absorbents.²⁵ Although carbon capture on-board seems to represent a valid solution to tackle direct emissions in the short term and could be easily deployed on existing fleets, only a few studies were conducted on its technical and economic feasibility. Even more, only a small number of those focused on deep-sea transportation, e.g., container ships.^{26–30} The concept was first proposed by Det Norske Veritas and Process Systems Enterprise in 2013 and was recently reviewed by Al Baroudi and co-workers.³¹ Following this approach, the CO₂ captured from the exhaust gas must be stored on-board in liquid form until a port is reached, competing with the cargo for the available space and being potentially hazardous.³² Therefore, this solution requires little changes in the infrastructure of the ships, as they only require CO₂ storage tanks on-board and extra energy for the CO₂ capture system.

The relevant studies of CO₂ capture on-board mentioned above lack an absolute sustainability assessment and a comparison with alternative CO₂ capture technologies. Specifically, one of the main shortcomings of current life cycle assessment (LCA) studies is the lack of thresholds to interpret the results globally. Recent works started to apply the planetary boundaries (PBs^{33,34}), which define critical biophysical limits of the Earth, to the absolute sustainability assessment of industrial systems, including steel³⁵ and fuel³⁶ production, among others. However, these studies are scarce

and never evaluated the sustainability level of low-carbon technologies for shipping. In this work, we study cargo carriers, which contribute to a relevant share of the maritime sector emissions (approximately 37%³⁷). We carry out the first comprehensive techno-economic and global environmental analysis of a state-of-the-art carbon capture plant on-board cargo vessels to reduce direct emissions, and we report the results for global warming (GW) and a set of PBs metrics. Additionally, we perform a comparative assessment with DAC and evaluate which option is the most appealing in the short term, compared to the business as usual scenario (BAU), until carbon-neutral fuels might eventually become competitive. Such a technical solution available in the short term would require minor changes in the current fleet. Since some DAC facilities already exist, we compare them with the carbon capture on-board as another valuable alternative that provides emissions reduction, although the technological readiness level of DAC is considerably lower. Finally, we also review and evaluate the different alternative fuels that could break into the market in the future.

METHODS

Reference Ship. We consider a reference ship that belongs to the liner shipping industry, therefore traveling fixed routes and distances,³⁸ with the following characteristics. We assume a cargo ship of an average size of 8500 twenty-foot equivalent units (TEU)³⁹ powered by HFO in a conventional combustion engine. The

emissions are calculated based on the rated speed of the ship³⁸ and the type of fuel (here HFO).⁴⁰ Here, we assume that the engine was characterized and optimized at 26.5 knots, just above normal cruising speed.³⁹ Consequently, we consider a journey from the port of departure to the destination that lasts one week. As a reference for the reader, we report that the current route of the vessel GUDRUN MAERSK took four and half days from Tanjung Pelepas, Malaysia, to Yantai port, China, sailing at a speed of 18.5 knots, based on port calls data.⁴¹ The exhaust gas composition analyzed in our case study is reported in Table S1 of the Supporting Information (SI). We take into account CO₂, oxygen (O₂), nitrogen (N₂), water vapor, SO_x, and NO_x, although combustion emissions can include more than 400 different compounds.³¹

Process Modeling and Scenarios Definition. Our study includes a detailed process modeling where we consider three necessary consecutive steps: exhaust gas cleaning, CO₂ capture, and CO₂ liquefaction, which are interconnected in the energy analysis. The process is designed based on available data in the literature and further adapted to the final design of our case study by means of sensitivity analyses, as described in the SI. The process simulation is carried out in Aspen HYSYS v11.

The exhaust cleaning section includes the technology that is currently already on-board of ships for the reduction of SO_x and NO_x. This section has been included in our simulation to the best of our knowledge to perform the heat integration of the full process.

HFO is the most common and inexpensive fuel used in heavy maritime transport, and it comes with the downside of containing up to 4% sulfur in its chemical composition,⁴⁰ which leads to the production of SO_x during its combustion. Additionally, due to the high temperatures achieved in the engine, NO_x are also formed along with PM. To comply with current emission regulations, a cleaning system designed to remove PM, NO_x, and, depending on the fuel, SO_x, is mandatory in the current generation of ships. These pretreatment units are very similar, if not the same, as those found in standard coal power plants,⁴² and consist mainly of a trap for PM, a selective catalytic reactor for NO_x, and a scrubber for SO_x removal. In our study, we perform the pretreatment stage using the SNOX technology, which manages to remove 100% of PM, 96% of NO_x, and 94% of SO_x.⁴³ We refer to Figure 1 for the process flow diagram, while we report in the SI the simulation details such as temperatures of the streams and the reactions modeled.

The exhaust stream is first mixed with air that provides the O₂ necessary for the following steps. Then, the mixture enters the denitrification reactor (DeNO_x) with NH₃, where NO_x and SO_x are converted into N₂ and sulfur trioxide (SO₃), respectively. Additionally, any unreacted NH₃ is also oxidized into N₂. The resulting mixture is cooled down to 200.0 °C at the temperature of the wet scrubber, and it is put into contact with water, thus forming sulfuric acid (H₂SO₄). We consider that H₂SO₄ is not stored due to safety and weight issues; hence, this process is operated in an open loop. Therefore, the H₂SO₄ stream is mixed with seawater, which alkalinity neutralizes the acid effectively³⁸ and is discharged into the ocean.

In our design, the scrubber installed on-board for SO_x reduction is also necessary to avoid a fast degradation of the solvent used in the CO₂ capture process.³² We design a conventional⁴⁴ carbon capture plant that can be installed on-board by retrofitting the current ship architecture without significant changes. Compared to the commercially available alternatives, such as solid adsorbents or membranes, the advantages of this technology are the high technology readiness level and associated know-how that lead to a straightforward installation and high efficiency,⁴⁵ at the expense of a considerable space reduction on-board due to the large-scale system required. At this point, the exhaust gas that contains mainly CO₂ as an impurity is first sent to a flash to separate the wastewater and then enters the absorption column on the bottom tray. An aqueous solution of monoethanolamine (MEA) 30 wt % gets in contact with the gas from the top, and it leaves at the bottom of the absorber as a CO₂-rich solution. The CO₂-lean gas (CO₂ less than 1 mol %) is vented to the atmosphere from the top. The solvent solution is circulating in a closed loop: from the absorber, it is sent to a second column where

the CO₂ is desorbed by means of heat provided by the reboiler with a heat consumption rate of 5.9 MJ/kg CO₂. The gaseous stream containing 90 mol % of CO₂ leaves from the top to go to the refrigeration section. The MEA lean solution is recycled back to the absorber, with the addition of fresh solvent and water to keep it at the desired concentration due to losses in the system. The heat required by the reboiler, *i.e.*, medium-pressure steam, is provided by a natural gas (NG) furnace installed on-board. The flue gas from the furnace is mixed with the exhaust stream from the engine and sent together to the absorber to capture the net CO₂ of the system. The CO₂-rich stream that leaves the stripper at 74.0 °C is stored on-board and transported until destination as refrigerated liquid, following common commercial practices.⁴⁶ We design a first refrigeration system that makes use of the NG required in the furnace. The amount of NG, however, is not sufficient to bring the CO₂ stream to the desired conditions. A refrigeration cycle with NH₃ adapted from the literature^{47,48} is implemented in a closed loop to provide further cooling from -13.8 °C to the final temperature. The CO₂ stream is then stored in commercially available tanks at 22.0 bar and -16.6 °C⁴⁹ until the ship reaches the port, where the CO₂ is unloaded and transported to suitable storage sites. We report the operating conditions of the equipment, such as the number of plates, pressure, design specifications, and the commercial tanks used in the SI.

In our analysis, we consider three scenarios sketched in Figure 2. We compare a retrofitted carbon capture plant on-board of container

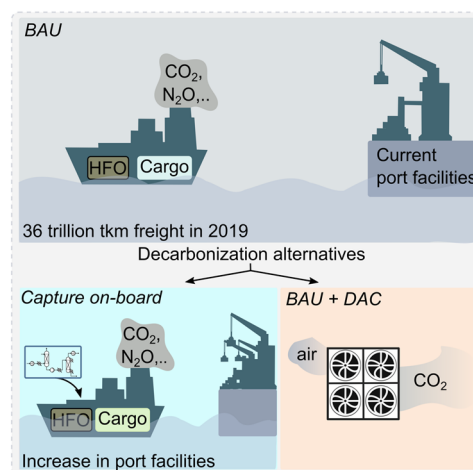


Figure 2. Scenarios considered in the study. BAU is represented at the top as the current scenario, where the shipping industry operates without introducing any measure to mitigate direct emissions. The capture on-board and BAU + DAC scenarios are represented in the bottom left and right, respectively. In these scenarios, the net CO₂ captured is the same. The increase in the port facilities in the capture on-board scenario corresponds to the displacement of the cargo and consequent increase in ships.

ships (capture on-board scenario) with the BAU, *i.e.*, the current fleet of container ships (BAU scenario). Lastly, the capture on-board is assessed against an alternative carbon capture technology. We consider that DAC facilities powered by heating with NG and electricity are installed to capture the CO₂ emissions from the BAU, with a 90% efficiency²² (BAU + DAC scenario). We impose that DAC achieves the same net CO₂ removal as in the CO₂ capture plant on-board to provide a fair comparison, meaning that the CO₂ from the exhaust and the furnace captured by the plant on-board is equal to the CO₂ from the air and the NG heating captured by DAC. Further details about the activities considered in the BAU and the DAC plant are provided below and in the SI.

Feasibility and Economic Assessment. The first step to assess the feasibility of the retrofitted carbon capture plant before carrying out the economic and environmental analysis is to ensure that the

equipment can be placed on-board. In their recent work, Stolz and co-workers based this assessment on the maximum permissible draft,¹⁷ while in our study, we assume that the retrofitted plant displaces the current cargo to maintain the same total weight on the ship corresponding to 8500 TEU. We estimate the volume and the weight of the capture plant, consisting of the absorber, stripper, furnace, pumps and compressors, flash units, and heat exchangers, including NH₃, LNG, MEA, and CO₂ storage tanks, based on the design of each equipment. The weight considers only the extra units needed for the CO₂ capture (*i.e.*, the scrubber for the SO_x and NO_x reduction is already present on-board of current vessels and, therefore, it is not accounted for). Then, we translate this information into equivalent TEU based on the standard dimensions of the latter⁵⁰ to obtain the cargo displacement on a volume basis. On the other hand, we compare the weight of the plant with the maximum cargo allowed on-board, which comes from the vessel dead weight tonnage subtracting the fuel, to calculate the cargo displacement on a mass basis. Since we impose that the final weight of the ship must be the same, the cargo that is displaced must be transported by additional ships with the same retrofitted CO₂ capture plant design. We calculate the increase in the number of ships traveling the same route and the consequent increase in the port facilities to accommodate the bigger fleet in the year. More information about the calculation of the cargo displacement is reported in the SI.

Given the large scale of the plant retrofitted on-board, the economic assessment is carried out based on the correlations and installation factors available in Towler and Sinnott.⁵¹ We consider a shaft generator on-board that supplies the electricity to the additional components, *i.e.*, pumps and compressors, and a marine seawater desalination system that provides high-quality fresh water. Both technologies are already commercially available, *e.g.*, from Wärtsilä.⁵²

The calculations and a figure illustrating the technical feasibility of the system under study are reported in the SI, together with the assumptions for the cost calculation.

Environmental Assessment. The environmental analysis is carried out according to the LCA methodology, following the ISO 14040/44 standards.^{53,54} The goal is to assess the absolute environmental sustainability of the current cargo demand for container ships considering the environmental benefits of implementing CO₂ capture on-board or sequestering the same amount of CO₂ with DAC. The functional unit (FU) corresponds to the global annual tonne-kilometer (tkm) demand for container ships, estimated at 36 trillion tkm in 2019 by the International Energy Agency.³⁷ We adopt a well-to-propulsion scope following an attributional approach, using average market data to model the system's inventory while introducing appropriate changes to the existing product system. Therefore, the system boundaries include all of the upstream activities, *i.e.*, HFO production, utilities required for the capture on-board, and fuel combustion emissions in the engine. In the system boundaries of the scenarios assessed, we also consider the container ship manufacture and maintenance and the port facilities. A complete list of the activities used in the modeling of the environmental assessment is provided in the SI.

The life cycle inventory (LCI) phase is implemented in SimaPro v.9.2.0.2 using the Ecoinvent v3.5 database, combining data of the foreground and background systems. The former includes information on the mass and energy flows from the process simulation that was developed. In the BAU + DAC scenario, the data are retrieved from the work by Keith et al.,²² which is based on an existing commercial plant. The process is scaled to match the amount of CO₂ captured in the capture on-board scenario. The inventory of the BAU scenario is defined to meet the specifications of the reference ship used in the study based on activities available in the Ecoinvent database.⁵⁵

During the life cycle impact assessment, we quantify the absolute environmental sustainability performance of the proposed decarbonization solutions and the BAU using seven PBs metrics. The PBs define limits of allowable human perturbation that, if surpassed, could threaten the Earth's stability; therefore, they delimit the safe operating space (SOS) in which humanity can operate. To quantify the impacts on the PBs, we use the characterization factors proposed by Ryberg et

al.⁵⁶ and Galán-Martín et al.⁵⁷ that can convert the LCI elementary flows into impacts on seven PBs. Additionally, we calculate the GW impact of the scenarios considered using the IPCC 2013 GWP 100a method.

In the life cycle interpretation phase, we analyze the relative impacts with respect to the full SOS (%). We clarify that an impact above 100% indicates the transgression of the corresponding PB. We note that by using the full SOS, we avoid allocating a share of the PBs to the container ships industry. Consequently, during the result interpretation phase, each scenario should be carefully evaluated and regarded as sustainable only if the SOS occupied leaves sufficient space for additional economic activities, which all together should operate within the PBs.

RESULTS AND DISCUSSION

Technical and Economic Results. The retrofitted CO₂ capture plant on-board scenario is technically feasible and economically competitive compared to other carbon capture options, such as DAC or less mature technologies omitted in this analysis, *e.g.*, solid adsorbents.⁵⁸ The design described in Figure 1 has a net efficiency of 94%, *i.e.*, considering the CO₂ from the exhaust gas and the furnace. The total cost of the additional equipment required on-board is 85 \$₂₀₁₉/tCO₂, annualized considering 7446 h per year based on an annual utilization factor of 0.85⁵⁹ and a 30-year lifetime of the units on the vessel, hence in agreement with literature results for conventional post-combustion capture applications at power plants.⁶⁰ The equipment needed to achieve 94% capture of the net CO₂ emissions takes 7% of the cargo on a mass basis and 4% in volume for a week-long trip. The number of ships that fulfill the global tkm in 2019 featuring the new design proposed is calculated based on the nominal capacity of 8500 TEU. The increase in the number of vessels to transport the cargo displaced by the retrofitted plant on-board corresponds to 3% of the current fleet in that year (weight and volume displacement of the cargo based on an average trip of a week). However, we estimate that for longer traveling times, such as 4 weeks, the displacement could be up to 25 and 12% of the cargo in mass and volume, respectively, which would be economically unattractive.

The CO₂ sequestered is stored on-board in liquid form in commercial tanks until the ship reaches the port, where it is unloaded and transported to suitable storage sites, *e.g.*, saline aquifers, via pipeline. We note that the transport of liquid CO₂ is a major safety concern due to its instability at the triple-phase point.³⁰ However, at ambient pressure, gaseous CO₂ requires large space available on-board, which would make this option infeasible even for a week trip.

In the alternative scenario where CO₂ is captured using DAC, the energy requirement and the total cost are estimated from the literature. This technology currently leads to a capture cost of 300 \$/tCO₂ for high-temperature liquid sorbents⁶¹ and 600 \$/tCO₂ for low-temperature solid sorbents,⁶² with an estimated CO₂ levelized cost of 94 to 232 \$/tCO₂²² for scaled-up systems; hence, the lower bound (optimistic estimate) is already 10% more expensive than our solution. However, even given the economic competitiveness of the capture on-board scenario, the capital investment should be supported by international policies and government incentives to build the network infrastructure for injecting the CO₂ underground.

Our solution relies on the geological sequestration of CO₂, whose elements, namely, capture, transportation, and injection technologies, are mature and commercially available for

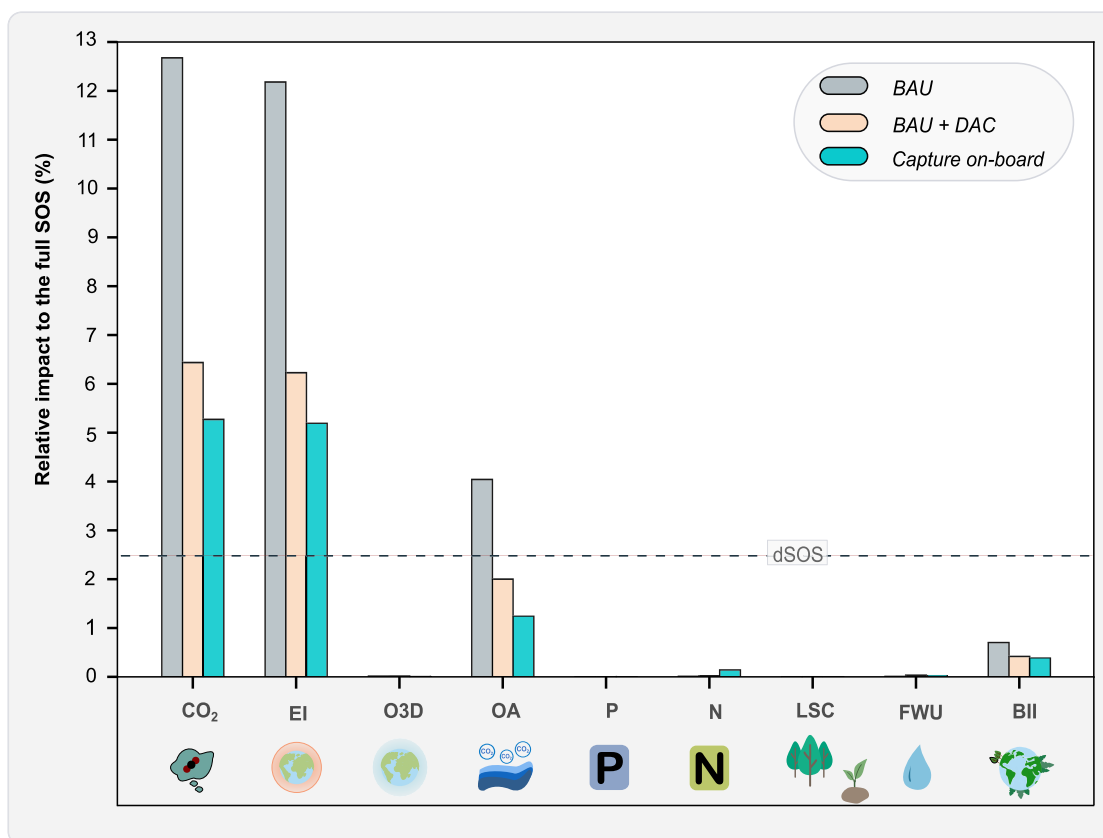


Figure 3. Scenarios performance on the PB control variables. The impacts on the PBs most strongly connected to GHG emissions, namely, CO₂ atmospheric concentration (CO₂), energy imbalance (EI), ocean acidification (OA), and biosphere integrity (BII) are the most significant in all scenarios. dSOS represents the downscaled safe operating space based on the contribution of the shipping sector to the global gross value added.

decades.⁵⁸ CCS projects are slowly spreading and increasing worldwide, with 27 operational projects for a total of 36.6 MtCO₂ stored per year as of 2021. CCS is part of various countries' strategy to fight global warming, benefiting from shared infrastructure (pipeline, storage wells),⁶³ and positively impacting international climate policies. While lessons about cost projections and storage safety have been learned, legal and regulatory frameworks have still to be put in place to remove social and political barriers, especially for complex projects.⁶⁴ Although the scenario proposed is a temporary solution to mitigate direct emissions, the capital investment realized to retrofit the carbon capture plant on-board and the required infrastructure could be used in the future for circular low-carbon fuels, such as MeOH.

Planetary Boundaries. We assess the performance of the capture on-board scenario compared to the BAU and BAU + DAC on the SOS of the seven PBs considered. The results are displayed in Figure 3. Our analysis shows that the global demand for container ships occupies up to 13% of the full SOS. The most significant impacts occur in the GHG-related PBs (atmospheric CO₂ concentration (CO₂), energy imbalance (EI), ocean acidification (OA), and biosphere integrity (BII)). Indeed, 13% of the CO₂, 12% of EI, 4% of OA, and 1% of BII are consumed by the current container ships sector to fulfill the global tkm demand. The impact on the remaining PBs is negligible (<1%). However, we stress that the full SOS should accommodate all economic sectors that together should not surpass the given limits to operate sustainably. For example, the current chemical sector already takes up 25% of the CO₂

SOS,⁵⁷ which adds to the 13% of the cargo shipping industry, contributing to 38% of the global SOS for the CO₂ control variable. Alternatively, part of the SOS could be allocated to the container ships following downscaling principles.^{65,66} For example, this share could be defined based on the sector gross value added (GVA), considering that the overall ocean economy contributed to conservatively 3% of the global GVA in 2010.⁶⁷ Based on the sector GVA, the SOS space allocated to cargo ships would be greatly reduced and hence transgressed.

Our analysis proves that the decarbonization options assessed can decrease the current pressure exerted by container ships on the Earth-system processes. More specifically, the capture on-board scenario proposed performs better than the BAU and BAU + DAC in all of the GHG-related PBs. Notably, a decrease of 58% can be achieved in the CO₂ concentration and OA, 57% in EI and 48% in BII PBs compared to the BAU. On the contrary, an 18-fold increase in the impacts is observed in the nitrogen flows (N) PB. Nonetheless, the impacts on the latter PBs remain negligible compared to the GHG-related ones. Finally, the BAU + DAC scenario can decrease the impacts by 49% in all of the GHG-related PBs compared to the BAU, except BII, which is decreased by 41%. However, the impacts in N and freshwater use (FWU) PBs increase by two and almost five times, respectively, although they are still rather low compared to the impact on the carbon-related PBs. The remaining acronyms in Figure 3 are as follows: stratospheric ozone depletion (O₃D), phosphorus flow (P), and land system change (LSC).

Global Warming. We report in Figure 4 the impacts of the three scenarios on GW ($\text{kg CO}_2\text{-eq}$), considering the activities

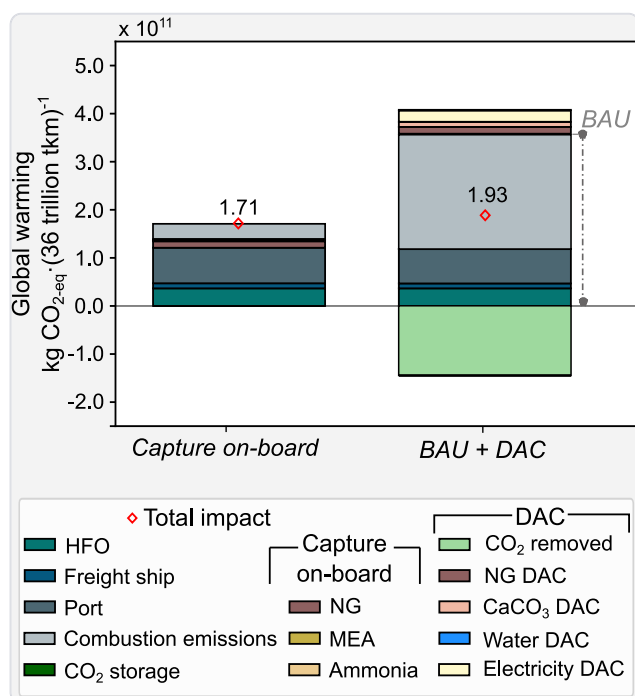


Figure 4. Global warming potential of the three scenarios considered. The capture on-board scenario performs best in global warming, outperforming the BAU and BAU + DAC scenarios by 52 and 11%, respectively.

common to both scenarios (“HFO,” “freight ship,” “port,” “combustion emissions,” “CO₂ storage”), those specific to the capture on-board scenario (“NG,” “MEA” and “NH₃ added on-board”), and finally the ones in the BAU + DAC scenario (“CO₂ removed,” “NG DAC”), calcium carbonate (“CaCO₃ DAC”), “water DAC,” and “electricity DAC”). CO₂ storage refers to CO₂ transportation and injection underground.

We find that Capture on-board performs better overall ($1.71 \times 10^{11} \text{ kg CO}_2\text{-eq}$) compared to the BAU ($3.53 \times 10^{11} \text{ kg CO}_2\text{-eq}$) and BAU + DAC ($1.93 \times 10^{11} \text{ kg CO}_2\text{-eq}$) scenarios, leading to a reduction in GW by 52 and 11%, respectively. We note that in the BAU, the impact from the combustion emissions corresponds to 66% of the total, followed by the port facilities (20%) consuming electricity for their operation and, finally, the HFO fuel (10%). The capture on-board scenario tackles the largest contributor of the impacts, achieving an 86% reduction in the combustion emissions contribution compared to the BAU. However, implementing the capture on-board scenario requires an increased construction and operation of the port facilities, which takes up 43% of the impacts, while the HFO contributes 21%. The BAU + DAC scenario requires electricity and natural gas as utilities to operate the DAC unit causing a 3-fold impact on GW compared to the energy inputs of the capture on-board scenario. Notably, capturing the emissions at the point source is less energy-intensive than from the air.

From Figure 4, it is evident that the impact of the port facilities is very high in all scenarios. Therefore, for further decarbonization efforts, renewable electricity should be

considered to satisfy the energy demand at the port facilities, and zero or low-carbon fuels should be considered for the propulsion of the vessel, as discussed next.

Alternative Fuels in the Long-Term Solution. The carbon capture scenario proposed could enable the maritime sector to meet the 50% GHG emissions reduction target in 2050 until more sustainable fuels are deployed and does not intend to be a long-term solution relying on fossil resources, *i.e.*, HFO. Among the fuels of interest currently under investigation in future fleets are liquid ones such as NH₃, MeOH, bio-based alternatives, and gaseous ones such as H₂ and (bio)NG. The production routes include CO₂ utilization, reformed NG with CCS, and renewable electricity (electro-fuels).¹⁸ Stolz and co-workers also considered the direct use of electricity in bulk cargo ships with Li-ion batteries, given their rapidly increasing energy density.¹⁷ Despite a thorough techno-economic analysis of different options being carried out by these authors, alternative fuels should be analyzed from a life cycle perspective.⁶⁸

In particular, drop-in biofuels such as bio-MeOH, bio-dimethyl ether, or bio-oil have been assessed with prospective LCA^{69,70} to consider technological improvements, electricity mix changes, and other socio-economic factors usually set constant in LCA assessments. In the works of Mukherjee et al. and Watanabe and coauthors, sustainable feedstock such as waste biomass or manure and forest residues was investigated in different processes, *e.g.*, gasification, anaerobic digestion, hydrothermal liquefaction, or pyrolysis.^{69,70}

According to the literature, all aforementioned alternative fuels will face technical challenges due to their characteristics, *e.g.*, toxicity, corrosiveness, low energy density leading to large storage on-board, and chemical composition, making them not suitable as a drop-in at the moment.^{68,71,72} Additionally, the switch to low- or zero-carbon fuels is hampered by the economic competitiveness of HFO and marine gas oil⁷⁰ and their current high share in the market (86%⁷³), and it will unlikely happen without a solid regulatory framework.¹⁸ Furthermore, the maritime industry will compete for these fuels with other transportation sectors, namely, land-based transport and aviation.⁷⁰ Although it is challenging to identify a clear winner among the many suitable candidates, NH₃ and MeOH may dominate the 2050 mix¹⁸ if the infrastructure in place today is updated, although bio-based fuels might be preferred in the long run because they can be directly used in the current engines.

From the discussion above, it seems unrealistic to think that a complete replacement of the current fuels will happen instantly, and interim solutions such as the one proposed in our work will be pivotal. Additionally, carbon capture technologies are mature, and the implementation on-board will not require considerable changes in the existing infrastructure, especially for ship owners. Moreover, we may implement CO₂ capture on-board today and switch from HFO to biomass-derived fuels in the future with the advancement of engines. In that case, we could even achieve negative emissions in the next generation of container fleets.

CONCLUSIONS

The application of carbon capture by chemical absorption using monoethanolamine solvents to cargo ship exhaust was analyzed from a technical, economic, and environmental perspective. The scenario was assessed compared to the business as usual and the direct air capture technology. Our

analysis proves that carbon capture on-board is a technically feasible and economically attractive solution to reduce the direct emissions from the cargo shipping industry at 85 \$₂₀₁₉/tCO₂. The plant retrofitted on-board displaces 7 and 4% of the freight on a mass and volume basis, respectively, which can be transported by additional ships with the same design. The solution proposed was assessed considering seven planetary boundaries. The results show that capture on-board does not transgress the full safe operating space while halving the current pressure exerted by the business as usual on three core planetary boundaries. It also outperforms direct air capture, decreasing the carbon footprint of the current scenario by 52%.

Overall, the solution proposed can be implemented in the short term with minor modifications to the current fleet until engines running on alternative fuels will be developed and will operate on newbuilds. In the long-term solution, low or zero-carbon fuels such as biofuels or electrofuels should be employed where using electric power is challenging, e.g., for long-distance transportation. Moreover, a carbon-negative scenario could also be achieved by retrofitting carbon capture on-board and deploying biomass-based fuels.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.2c04627>.

Process parameters, process design and cost assumptions, and environmental assessment inventories (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Gonzalo Guillén-Gosalbez – Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich, Switzerland; orcid.org/0000-0001-6074-8473; Email: gonzalo.guillen.gosalbez@chem.ethz.ch

Authors

Valentina Negri – Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich, Switzerland; orcid.org/0000-0003-4292-0924

Margarita A. Charalambous – Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich, Switzerland; orcid.org/0000-0001-6097-0592

Juan D. Medrano-García – Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich, Switzerland; orcid.org/0000-0001-5422-1683

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acssuschemeng.2c04627>

Notes

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■ ACRONYMS

BAU	business as usual
DAC	direct air capture
DeNO _x	de-nitrification reactor
FU	functional unit
GHG	greenhouse gas
GVA	gross value added
GW	global warming
IMO	International Maritime Organization
LCA	life cycle assessment
LCI	life cycle inventory
PBs	planetary boundaries
PM	particulate matter
SOS	safe operating space
TEU	twenty-foot equivalent units
tkm	tonne-kilometer

Chemicals

CO ₂	carbon dioxide
H ₂	hydrogen
H ₂ SO ₄	sulfuric acid
HFO	heavy fuel oil
LNG	liquefied natural gas
MEA	monoethanolamine
MeOH	methanol
N ₂	nitrogen
NG	natural gas
NH ₃	ammonia
NO _x	nitrogen oxides
O ₂	oxygen
SO ₃	sulfur trioxide
SO _x	sulfur oxides

Planetary Boundaries Categories

BII	biosphere integrity
CO ₂	climate change-atmospheric CO ₂ concentration
EI	climate change—energy imbalance
FWU	freshwater use
LSC	land system change
N	nitrogen flows
O3D	stratospheric ozone depletion
OA	ocean acidification
P	phosphorus flow

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