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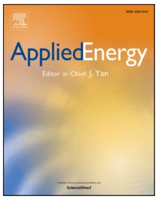

A review of large-scale CO_2 shipping and marine emissions management for carbon capture, utilisation and storage

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HIGHLIGHTS

- Assessed CO_2 shipping as a global decarbonisation strategy for future developments.
- Identified technical and safety challenges encountered during in CO_2 shipping chain.
- Evaluated the environmental impact of shipping emissions in the transport chain.
- Summarised emission control technologies as a key enabler in the CO_2 shipping chain.

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ABSTRACT

Carbon Capture, Utilisation and Storage (CCUS) can reduce greenhouse gas emissions for a range of technologies which capture CO_2 from a variety of sources and transport it to permanent storage locations such as depleted oil fields or saline aquifers or supply it for use. CO_2 transport is the intermediate step in the CCUS chain and can use pipeline systems or sea carriers depending on the geographical location and the size of the emitter. In this paper, CO_2 shipping is critically reviewed in order to explore its techno-economic feasibility in comparison to other transportation options. This review provides an overview of CO_2 shipping for CCUS and scrutinises its potential role for global CO_2 transport. It also provides insights into the technological advances in marine carrier CO_2 transportation for CCUS, including preparation for shipping, and in addition investigates existing experience and discusses relevant transport properties and optimum conditions. Thus far, liquefied CO_2 transportation by ship has been mainly used in the food and brewery industries for capacities varying between 800 m^3 and 1000 m^3. However, CCUS requires much greater capacities and only limited work is available on the large-scale transportation needs for the marine environment. Despite most literature suggesting conditions near the triple-point, in-depth analysis shows optimal transport conditions to be case sensitive and related to project variables. Ship-based transport of CO_2 is a better option to decarbonise dislocated emitters over long distances and for relatively smaller quantities in comparison to offshore pipeline, as pipelines require a continuous flow of compressed gas and have a high cost-dependency on distance. Finally, this work explores the potential environmental footprint of marine chains, with particular reference to the energy implications and emissions from ships and their management. A careful scrutiny of potential future developments highlights the fact, that despite some existing challenges, implementation of CO_2 shipping is crucial to support CCUS both in the UK and worldwide.

1. Introduction

Global CO_2 emissions from fossil fuel combustion in 2018, were estimated to be 37.1 Gt, which is a 2.7% increase over 2017 [1]. This is worrisome as a global average temperature rise of 1.5 °C will easily be exceeded if such increases continue. Deployment of renewable energy and energy efficiency are often considered by the general public as the priority for greenhouse gas (GHG) mitigations, however the potential of reducing emissions, via such routes, over the short term will not prevent serious impacts from climate change [2]. Carbon capture, utilisation and storage (CCUS) is considered to be a technical and economically viable method to lower GHG emissions. CCUS consists of a number of technologies which capture CO_2 from power generation and industrial sectors such as cement, iron and steel making [3]. These technologies vary

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from chemical absorption (Boundary Dam in Canada and PetraNova in the United States), physical separation (the Great Plains Synfuels Plant in North Dakota and the Terrell Natural Gas Processing Plant in Texas), membrane separation (Petrobas in Brazil, France's Air Liquide and Membrane Technology and Research Institute), calcium looping, chemical looping (CLEANKER pilot and pre-commercial scale project), direct separation (Low Emissions Intensity Lime and Cement pilot plant in Belgium) and oxy-fuel separation (Callide project in Australia and Heidelberg Cement's Colleferro plant in Italy) [4]. Most of the aforementioned technologies have been adopted globally in different sectors but their use is generally dependent on cost of installation, flue gas composition and properties, desired purity of the flue gas and integration with existing facility [4].

According to the IPCC Fifth Assessment Report, CCUS is essential to keep CO_2 concentrations in the atmosphere below 450 ppm by 2100. Current lack of implementation of CCUS will magnify the costs of future CCUS implementations by 138% or more [5,6]. Presently, there are sixty five commercial CCS facilities with twenty six in operation; in total these facilities can capture and store about 40 Mt of CO_2 per year [7]. A number of them are in advanced or early development ranging from pilot to demonstration scale projects. Some of the projects seek a commercial return from the captured carbon dioxide by either selling it for enhanced oil recovery (EOR) or by utilising it as a chemical feed stock [8,9].

The concentration of CO_2 in the atmosphere is currently about 411 ppm, and future increases will cause catastrophic climate change issues if storage and utilisation methods are not deployed [10]. The International Energy Agency (IEA) Blue Scenario Map which aims to halve global energy-related emissions by 2050, emphasises that CCUS could reduce emissions by 19% [11]. To date, the global use of CO_2 is estimated to be 230 Mt CO_2/year, mainly in the fertiliser, oil and gas and food and beverage industries [4]. New routes to carbon utilisation, including fuels, chemicals and building materials are currently being explored, with a high-level projection showing that potential use of CO_2 could reach 5 $GtCO_2$/year in the future [4]. However, in practice, it is unlikely that these estimates will be achievable in the near future, particularly given the economic costs of developing these products and technologies. Therefore, it is clear that the market demand for CO_2 in the forthcoming decades will still be significantly lower than that required for GHG emissions reduction. This necessitates disposal of captured CO_2 in geological formations or marine aquifers and, hence, the transport of captured CO_2 remain a critical aspect of CO_2 mitigation. Despite receiving less attention than other components of this chain, CO_2 transport poses both technical and operational challenges and must involve cooperation between multiple stakeholders and industries [12,13]. The transport options for captured CO_2 from power and industrial emitters includes pipelines, ships, railways and motor carriers. Pipeline systems are appropriate for transmitting large quantities of carbon dioxide over relatively short distances but are associated with high initial capital cost and limited versatility. Conversely, carbon dioxide shipping can discharge lower quantities over relatively longer distances given its low capital expenditure and high flexibility. Fig. 1 shows the whole chain of CO_2 shipping, which represents a promising alternative to pipelines for smaller and scattered sources [14].

Furthermore, there is a compelling commercial requirement to reduce emissions as climate impact is now a criterion that determines bank loans to shipping companies [15]. Lending and investing decisions will now be screened for environmental consequences, thus encouraging an industrial transition to cleaner energy technology. According to the third International Maritime Organisation (IMO) GHG study, maritime shipping represents approximately 3% of CO_2 emissions along with 13% and 15% of SO_x and NO_x emissions from anthropogenic sources, respectively [16,17]. Shipping emissions generation arises from fossil fuel consumption for on-board propulsion and electrical generation. Currently, dedicated on-board power plants using diesel engines are standard in marine applications [18].

The aquatic environment must also not be ignored, given that more than 70% of our planet is covered by water. Early marine activities were mostly for food harvesting and trading, but as a result of the industrial revolution, a vast increase in shipping has occurred. For instance, from 1992 to 2012, worldwide ship traffic increased by 300% [19]. These developments have led to oil spills, waste deposition, and noise pollution in the marine environment. Several techniques have been studied for controlling emissions on-board ships [20] but only limited studies have been done on reducing emissions using CCUS technologies. Onshore projects can use CCUS for power plants and other industrial processes, but these are not currently installed on-board ships [21–23]. CO_2 and SO_2 emissions are a major concern in any combustion process, especially when residual fuels are used. A world cap has been placed by the IMO on sulphur emissions from ships, which is effective as of 2020 [24]. The EU plans to reduce GHG emissions by at least 20% in 2020 in comparison to the 1990 levels [25]. A lack of up-to-date commercial applications of shipping with CCUS indicates that more R&D aimed at reducing operational costs of the chain is desirable, particularly due to the fact that carbon dioxide is perceived as a waste product rather than a valuable commodity. This paper reviews the current technological status and investigate the potential role of CO_2 shipping for the future of CCUS both in Europe and worldwide. In addition to exploring the literature on CCUS as it relates to shipping, the present work also focuses on the use of CCUS technologies to reduce CO_2 and SO_2 emissions, examining potential solvents that can serve for these dual purposes; thus, embracing the concept of a near zero-emission CO_2 shipping chain.

2. Comparison of CO_2 transport systems

Transport of CO_2 for sequestration requires the implementation of both a coordinated and efficient transportation network. As such pipelines are the most obvious solution, particularly where a constant flow from the CO_2 capture sites is required. Where economies of scale do not justify pipelines as the transportation method in a CCUS project, other possibilities include ships, railway and motor carriers. These are economically viable when emitters do not have direct access to a

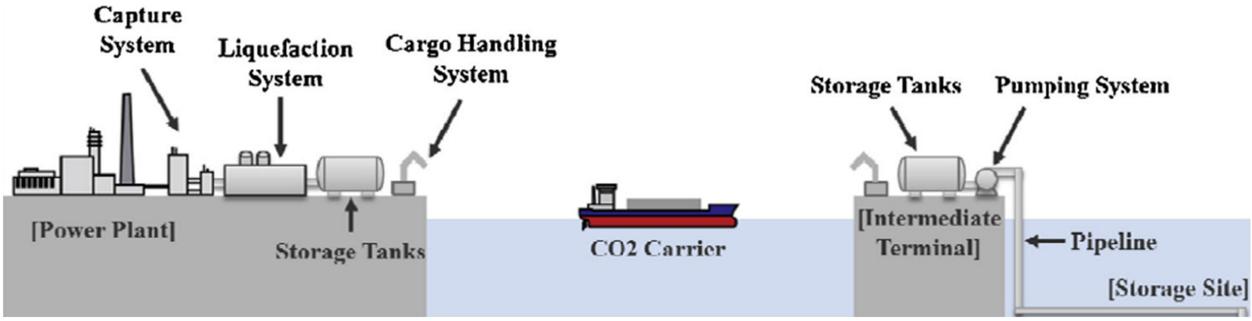


Fig. 1. Carbon dioxide shipping chain [14].

suitable pipeline or when the captured quantities are insufficient to justify pipeline construction. Access to adequate seaport facilities or proximity to the sea or railway system are some of the factors that impact decision makers. Pipeline and carrier transport of CO_2 are found to be comparable in cost for similar capacities when distances of 250 km or more are considered, as shown in Fig. 2 [26]. Despite being an early-stage study, this comparison has proved useful in identifying pipeline and water carriers as the main transportation solutions for CCUS.

The potential of railway CO_2 transport has been evaluated by Roussanaly et al. [27] who compared costs of conditioning and transport of pipeline and railway transport in relation to the distance for different project scenarios periods. Unlike the work of Svensson et al. [26], this study showed that, where there is an existing infrastructure in place, transport by means of railway system could represent a viable option to pipelines for long-range distances, mainly due to the lower financial risks. However, it should be noted, that in practise railway and motor carriers have seldom been considered for CCUS projects, and have limitations in route choice due to dangerous substance transport and potential disturbance to local populations as some of the key constraints [13,28–30].

A summary of CO_2 transportation solutions based on estimated transport capacities and conditions highlight the key issues associated with each system (see Table 1). Thus, Roussanaly et al. [31] performed a comprehensive multi-criteria analysis of pipeline and shipping as transport technologies for 10 Mt CO_2/year from an industrial cluster to identify the most appropriate transport solutions. Pipeline technology showed the best performance indicators with regard to operational costs and consumption of utilities, with shipping being more advantageous only in relation to the required capital expenditure. For this reason, shipping was deemed as a temporary solution for the first CCUS deployments in order to contain upfront costs and investment risk, before transitioning to pipeline infrastructure when larger capture quantities become available. The authors also put emphasis on the fact that pipelines show better performance compared to shipping with regards to fuel, electricity and water consumption in the chain, generating a transportation system with overall lower greenhouse gas emission footprint. The value of this study to decision makers stretches beyond economic considerations, by recognising the importance of life cycle assessment in selecting the best transport alternatives.

Knoope et al. [41] suggested that the flexibility of the shipping chain does not necessarily shift the investment decision from pipeline to ships, even when options such as abandoning the project, halting the capture process temporarily and switching to a different storage reservoir are considered. The reason is that components such as the liquefaction plant and intermediate storage represent 80% of the costs and are considered as fixed costs similar to pipelines.

The COCATE Project found that the cost of transporting 13.1 Mt CO_2/year over 450–600 km to an offshore storage site in the North Sea is marginally higher by onshore pipeline in comparison to ships, with the latter resulting in 5% lower costs [12]. Fimbres Weihs et al. [42] suggested that CO_2 shipment is economically advantageous over pipelines for distances higher than 700 km and quantities of the order of 6 Mt CO_2/year. The Zero Emission Platform [43] explored the cost of CO_2 transport in point-to-point connections for CCUS demonstration projects with typical transmission capacity of 2.5 Mt CO_2/year; the report found transport cost per ton of CO_2 to be 45% lower in offshore pipelines compared to shipping on the basis of a 180 km distance.

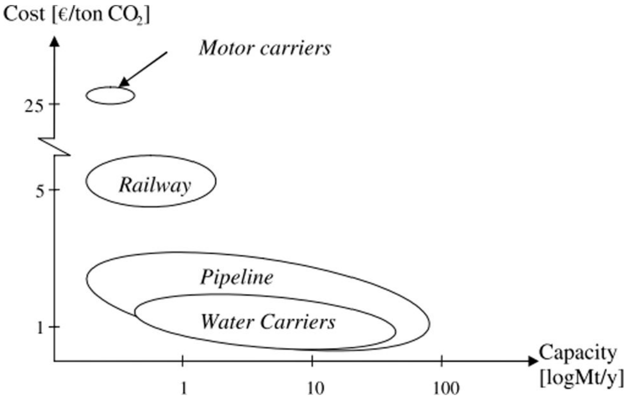


Fig. 2. Cost and capacity for transportation alternatives at 250 km [26].

The trend however reverses when transport distances of 500 – –1500 km are considered, where shipping cost per ton of CO_2 becomes 27–62% lower than that of offshore pipelines. The IEAGHG investigated the unit cost of pipeline and ship transport for different flow rates of 0.5–10 $MtCO_2$/year and a transport distance of 1000 km. Findings show shipping to be 64% less expensive in discharging 0.5 $MtCO_2$/year, with this economic gap progressively narrowing with increase of flow rates; here 2 $MtCO_2$/year sea vessel transport is only 10% cheaper than pipeline, and at 5 $MtCO_2$/year pipeline transport is 24% economically advantageous. Overall, larger disposal amounts generally shift breakeven distances towards larger distances for ship transport making this option advantageous [34,44]. Several more project variables such as geographical location, security, layout of port-terminals and seabed stability affect breakeven distances after which ships becomes more economic than pipelines.

Roussanaly et al. [45,46] performed detailed economic, technical and climate impact assessment comparisons between pipeline and shipping when considering transportation connecting both two onshore and two offshore areas. Unlike previous studies, these authors consider a range of distances and amounts. In line with other studies, they found that for a fixed throughput, a pipeline is preferred to discharge CO_2 over shorter distances. However, the study also emphasized that factors such as geographical location, regional fluctuations of pipelines costs, first-of-a-kind challenges and ownership arrangements can significantly affect the choice of transportation system. Conversely, project variables such as fluctuation of electricity and shipping fuel price do not appear to have a profound impact. However, complex transportation networks as opposed to single-system infrastructure are expected to show different trends and will require additional work to assess them.

Table 2 summarises the factors relevant to the practicality of pipelines and shipping systems in relation to economic aspects of the projects and Fig. 3 provides a graphical representation of the breakeven distances between ships and pipelines in the literature. Disagreements on trends for the cross-over point between pipelines and ships can also be attributed to the different economic methodology and assumptions. However, shipping compares favourably with offshore pipelines compared to onshore pipelines, due to the higher costs involved in putting offshore installations in place and the constraint on the drop of system pressure for offshore transport [46]. However, despite being more economically viable, onshore pipeline systems can better meet stringent health and safety operations due to the hazard of CO_2 exposure in inhabited areas [47]

In summary, the practicality of carrier transport is subject to a number of techno-economic and geographic considerations; it is generally agreed that pipelines are advantageous to transport larger amounts of CO_2 due to the high capital expenditure associated with onshore and offshore infrastructure in light of lower operational costs [34,38,45,50,51]; transport by ships has relatively higher operational costs and displays nonlinear dependency with distance, making it an attractive option to transport smaller volumes over longer distances [43,52,53]. Throughout this review, the role of carbon dioxide shipping in global CCUS transportation network will be investigated beyond simply considering the techno-economic aspects.

3. Overview of CO_2 shipping

The first serious investigation into liquid CO_2 shipping began in the early 2000s with studies by Mitsubishi Heavy Industries [48] and Doctor

Table 1
Carbon Dioxide transportation alternatives.

Transportation method	Conditions	Phase	Capacity	Remarks
Pipelines	4.8–20 MPa, 283–307 K [32–34]	Vapour, dense phase	~100 Mt CO_2/year [26] 6500 km of pipeline transport in operation [27]	• Higher capital costs, lower operating costs • Low-pressure pipeline system is 20% more expensive than dense phase transmission. • Well-established for EOR USE.
Ships	0.65–4.5 MPa, 221–283 K [35–38]	Liquid	>70 Mt CO_2/year [26]	• Higher operating costs, lower capital costs • Currently applied in food and brewery industry for smaller quantities and different conditions. • Enhanced sink-source matching
Motor carriers	1.7–2 MPa, 243–253 K [39,40]	Liquid	>1 Mt CO_2/year [26]	• 2–30 tonnes per batch • Not economical for large-scale CCUS projects • Boil-off gas emitted 10% of the load [39]
Railway	0.65–2.6 MPa, 223–253 K [27,39,40]	Liquid	>3 Mt CO_2/year [26]	• No large-scale systems in place • Loading/unloading and storage infrastructure required • Only feasible with existing rail line (Wong, 2005) • More advantageous over medium and long distances

et al [34]. Subsequently, the technological studies carried out on CO_2 shipping [8,36,37,54–56] have identified its potential and relevance for applications in CCUS and EOR applications. Table 3 provides a summary of the key literature published on CO_2 shipping for CCUS from the early stages up to date. Fig. 4 represents a graphical representation of the indicated shipping conditions in the literature.

The Netherlands and Norway, and in particular SINTEF and STATOIL [64], have started projects in Europe, while in the Far East – mostly Japan and Korea –a series of projects has meant that these countries have become key players in R&D on large-scale carbon dioxide shipment [48,57,65]. As of 2015, 60% of the literature relating to CO_2 shipping was published in Europe, whilst 35% of the literature came from the Far

Table 2
Breakeven distance comparison of shipping transportation with offshore and onshore pipeline options.

Source	Quantity	Methodology	Breakeven distance with shipping transport		Remarks
			Onshore pipeline	Offshore pipeline	
Mitsubishi Heavy Industries [48]	a. 6.2 Mt CO_2/year b. 30 Mt CO_2/year	Corporate economic model	a) 1,500 km	a. 700 km b. 1,500 km	Economies of scale can be considerable
Doctor et al. [34]	6 Mt CO_2/year	Cost estimation developed by authors	1,500 km	1,000 km	a. Higher amounts will favour long distances b. Full-scale considered
Decarre et al. [44]	a. 0.8 Mt CO_2/year b. 1.6 Mt CO_2/year c. 2.8 Mt CO_2/year d. 5.6 Mt CO_2/year	Economic model by French Environment and Energy Management Agency	a. 115 km b. 120 km c. 125 km d. 165 km	c. 300 km	a. Comprehensive economic model on full transport chain b. Vessel transportation is the most cost-intensive part of the chain .
ZEP [43]	10 Mt CO_2/year		700 km	500 km	
Fimbres Weihs et al. [42]	6 Mt CO_2/year	Integrated techno-economic model	1,150 km	a. Shallow pipeline: 900 km b. Deep pipeline: 750 km	a. Cost model was validated from wider literature b. Electricity and ship fuel are the main costs
Yoo et al. [49]	10 Mt CO_2/year	Techno-economic model developed by shipping company	500 km	300 km	
Vermeulen [36]	1–4 Mt CO_2/year		200 km	150 km	Based on CO_2 Liquid Logistics Shipping report by engineering consultancies and shipbuilders
Knoope et al. [41]	a. 1 Mt CO_2/year b. 2.5 Mt CO_2/year c. 10 Mt CO_2/year	Real Option Approach (ROA) based on standard Net Present Value (NPV)	N/A	a. 250 km b. <500 km c. <250 km	a. Assess the value of flexibility on investment decision of CCUS transport network b. Flexibility does not necessarily favour shipping systems
Element Energy et al. [38]	1 Mt CO_2/year	In-house techno-economic model based on 20-year lifetime project and 0% discount rate	250 km	N/A	Report commissioned by the UK's Business, Energy and Industrial Strategy Department
Roussanaly et al. [45,46]	a. 4 Mt CO_2/year b. 10 Mt CO_2/year	Scenario-range approach based on standard Net Present Value (NPV)	a. 410 km b. 580 km	a. 300 km b. 410 km	Impact and sensitivity of a range of project variables (utility costs, geographical location etc.) is considered into this work

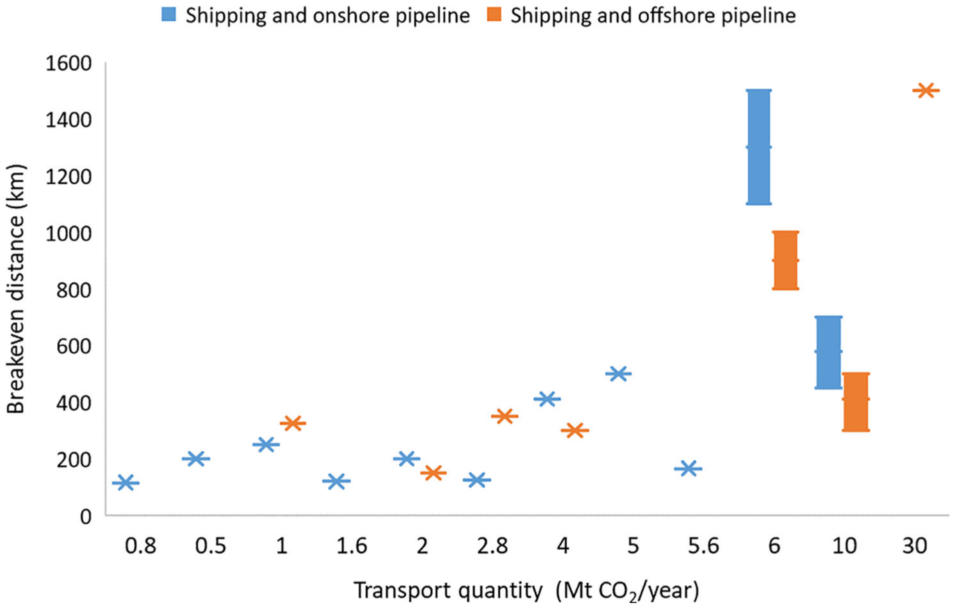


Fig. 3. Box and Whisker representation of breakeven distances between ships and pipelines in the literature.

East [54]. Carrier-based transport of CO_2 has however generated differing opinions by decision makers in recent years. As of 2012, ship-based transport of CO_2 was deemed by the then 'Department of Energy and Climate Change' in the UK to require short-term research and development in order to optimise transport [66]. However, more recently, the 'Role of CCUS in the below 2 degrees scenario' report [62] suggested that the near-future implementation of CCUS will require up to 600 marine vessels and create up to 10,000 jobs, with Norwegian firms being the most likely to benefit from such opportunities. Similarly, the British government found that CO_2 transport infrastructure, which includes shipping, is essential to support the deployment of CCUS in the UK [38].

A contrasting pattern is seen in North America, where the extensive network of pipelines and the presence of onshore EOR sites limit the focus of R&D on CO_2 shipping thus favouring pipeline implementation [34]. Shipping has been utilised in the last decade to transport relatively small quantities of food grade liquid CO_2 at 1.5–2 MPa and 243 K [8,36,38,56,61]. However, in order to become an option for transporting larger volumes, the literature suggests actual conditions should be as near to the triple point as possible (~0.7 MPa and 223 K) [36,38,41,51,56,67–70].

Shipping has the potential to introduce significant decarbonisation for a wider number of small industries due to its high flexibility in source-sink matching [13], and extend the benefits of CCUS to those countries where implementation of a pipeline-based transport network is essentially infeasible due to the propensity for natural calamities (e.g., earthquakes) such as Korea and Japan [37,59]. Moreover, CO_2 carriers are found to be particularly suitable due to the increased use of offshore sink sites, such as saline aquifers or depleted hydrocarbon sites [59].

In Norway, a significant number of sources are located on or near the coast and an already established maritime tradition has created a suitable environment for CO_2 shipping [56]; in the UK, the Department for Business, Energy and Industrial strategy is actively exploring the implementation of this technology in relation to sites isolated from CO_2 transport and storage infrastructure in the British North Sea [30].

In summary, with CCUS being perceived as a risk due to financial uncertainty, ship transport offers flexibility in terms of sources and destinations to implement capture, variations in the routes of CO_2 transported, the possibility to reutilise the ships and also short set-up times [50]. By contrast, the high capital investment of pipelines represents a sunk cost with few opportunities to reuse such infrastructure. Despite this, there are currently no demonstration projects that use shipping for the transport of CO_2 [61], although a full-scale CCUS demonstration project deploying carriers as carbon dioxide transport launched by Norway is expected to enter the realisation stage soon [71].

4. Existing experience

Large-scale CO_2 shipping can significantly benefit from knowledge developed by the more established LNG and LPG industries, especially regarding early-stage implementations. Despite the difference in pressure and temperature requirements, liquid carbon dioxide near the triple point has a comparable liquid/gas density ratio to LNG, making comparisons more appropriate (Table 4). Moreover, the design and operation strategy of CO_2 terminals can greatly benefit from LNG and LPG experience, especially in relation to process safety and liquid cargo handling procedures [72]. The design of tank arrangements on the carrier for low and medium pressure liquid CO_2 can largely be based on existing LPG ship designs due to their similar operating conditions [63]. The largest LNG ships have capacities of 120,000 m^3 up to 270,000 m^3 [48,56] which would potentially be relevant for large-scale carbon dioxide shipping projects. However, shipbuilding companies emphasise that retrofitting of LNG ships for liquid CO_2 purposes will involve significant efforts and challenges in the face of modest added value given that a ship's capital expenditure constituting only 14% of the project cost [38]. Conversely, the IEAGHG [63] reports that the conversion between cargo inventories is deemed practically feasible for single conversion only, thus providing an option to reduce risks to project feasibility. Some of the technical drawbacks are that only up to 60% of the tank capacity of LPG carriers can be utilised for CO_2 transport due to the difference in density between liquid CO_2 and LPG (550–700 kg/m^3 for LPG and 1050–1200 kg/m^3 for liquid CO_2) and the limit to the maximum storage pressures due to the fact that large LPG and ethylene carriers have maximum design pressures lower than 0.8 MPa. An exception is made for smaller LPG carriers, designed to operate between 1.1 and 1.9 MPa, that could potentially accommodate 2,000–3,000 tons of CO_2 at medium pressures. The report also provides a list of 26 potential LPG carriers with capacities ranging from 5,000 to 30,000 m^3 from several companies that could be repurposed for CO_2 transport [63]. The established experience in hydrocarbon carriers can also be beneficial in the design of equipment for onshore loading and offloading, with articulated loading arms developed in such industries also being deemed

Table 3
Summary of the literature on CO_2 shipping for CCUS.

Sources	Remarks
Mitsubishi Heavy Industries [48]	• Detailed report completed for IEAGHG R&D Programme based on a previous patent from Mitsubishi Heavy Industries • It explored feasibility of ship transport for CO_2 and sensitivity to several project variables by comparing costs with pipelines • Additional CO_2 emissions due to long distances and high energy requirements for liquefaction were found to be limiting factors
Svensson et al. [26]	• Comparison of costs of transporting CO_2 by pipeline, ships and railway within Europe • It was concluded that for offshore transport of large amounts of CO_2, both pipelines and ships will have a significant role in a pan-European transportation network • Lack of techno-economic analyses of stream liquefaction and conditioning
Hegerland et al. [9]	• Conference paper specifically focused on integration of CO_2 shipping for EOR • CO_2 shipping technology was deemed ready for implementation • Full-chain was found to be easily adaptable to allow handling quantities relevant to CCS and EOR
IPCC [34]	• Book chapter on CO_2 transport mainly based on the Mitsubishi Heavy Industries Report (2004) and corporate information from STATOIL • Techno-economic comparison between pipelines and ships with highlights of risks and process safety considerations • CO_2 shipping was found to be feasible and competitive with pipelines transport when small amounts or long distances are considered
Aspelund et al. [57]	• Technical peer-reviewed paper presenting the challenges encountered in large-scale CO_2 shipping to that date. • Concept of open- and close-cycle liquefaction is explained, and internal refrigeration system was deemed to be favourable, though no clear justification was provided • Energy and cost estimates highlighted that CO_2 liquefaction is the most-energy intensive part of the shipping chain • Considerable technical details area provided despite some limited assumptions (e.g. no clear transport distance)
ZEP [43]	• Technically detailed report based on real data; it compared costs of transport by pipelines and shipping by taking into account several project sensitivities. Despite covering several technical issues, its relatively simplistic assumptions may result in an underestimation of costs.
Vermeulen [36]	• Detailed report from Rotterdam CCS Network covering all aspects of CO_2 shipping including stream conditioning, ship design, loading and offloading • Comprehensive transport network (including pipelines) was considered • Uncertainties associated with selection of materials, carbon emissions and process safety are clearly highlighted • Provided information on absolute costs are subject to commercial sensitivity
Omata and Kajiyama [58]	• Detailed techno-economic analysis of feasibility of CO_2 shipping with direct injection from ship to sub-sea wellhead • Suitability of carrier transport in Eastern Asia was identified in relation to geographical factors • Unusual transport conditions are indicated though no clear justification was provided
Jung et al. [55]	• Publication on CO_2 transport scenarios and techno-economic analysis for offshore CCUS in South Korea • Transportation costs of shipping found to be higher than those of pipeline systems • Extensive optimisation of CO_2 transport networks was deemed incomplete yet essential to establish optimum CCUS transport alternatives suited for South Korea
Nam et al. [59]	• Analysis of an offshore, ship based CCUS system in South Korea combined with the transport of crude oil • Focuses on the optimal layout of the chain including location of the industrial units, appointment of the fleet, and the favourable cargo conditions for CO_2 transport • Unlike previous literature, optimum operating conditions are found to be case-sensitive and potentially not at the triple point
Yoo et al. [49]	• Work focused on the establishment of a CCUS infrastructure for future commercial projects showing the key role of shipping in discharging large amounts of carbon dioxide • Detailed technological and economic analysis is performed by exploring different disposal amounts, liquefaction cycles and ship carriers • Established that carbon dioxide shipping can play a key role in scenarios where short-distances and large-quantities are considered
Ozaki and Ohsumi; Ozaki et al. [37,60]	• Conference papers at GHGT-10 and GHGT-11 • Focuses on ship based offshore CCUS featuring shuttle ships and amongst the first studies to consider the concept of direct injection form ships • Shuttle transport is deemed more suitable than large CO_2 carriers in mitigating the risk of matching large-scale sink to large-scale sources • Indicated cargo conditions are considerably far from the triple point
Skagestad et al. [56]	• Technically detailed report on the status of CO_2 shipping, highlighted its role in discharging small volumes over longer distances • Challenges related to conditioning, loading, transport and offloading are highlighted but not found to be critical to the feasibility of carrier transport • Further and highly prioritised research is found to be required on injection of carbon dioxide to the storage site
Brownsort [54]	• Technical report by the Scottish Carbon Capture and Storage focusing on the implementation of CO_2 for Enhanced Oil Recovery with a shipping transportation system • Shipping found to be relevant to execute EOR projects in the North Sea • Detailed review of the available literature on carbon dioxide shipping emphasized the high-level of understanding of the chain despite limited projects running
Seo et al. [14]	• Study focusing on ship-based CCUS chain with different CO_2 liquefaction pressures to determine the optimal pressure • One of limited number of studies performing techno-economic analysis on different shipping conditions with sensitivity studies • Optimum transport pressure found to be 1.5 MPa regardless of disposal amount and distance
Ministry of Energy and Petroleum [35]	• Technical and economic study on the implementation of a CCUS chain in Norway, assigned by the Ministry of Petroleum and Energy and focusing on incentives and regulation framework • Different transport conditions – low-, medium- or high-pressure – are investigated along with their technical and safety considerations • Future demonstration projects availing themselves of CO_2 ships were considered.
De Kler et al. [61]	• Highly technical report commissioned by the Dutch National R&D programme for CCUS (CATO) on transportation and unloading of CO_2 by ship • Focus on North Sea storage sites by providing cost estimations with 50% margin with regards to different offloading options • Completion of studies focusing on realistic storage options in the North Sea is suggested
Neele et al. [8,50]	• Conference proceeding from GHGT-13 in Lausanne, Switzerland, here ship transport is found to be the most advantageous option to match sources with storage sites in the first phase of CCUS. • Costs associated with shipping projects are developed and validated with existing literature
ZEP [62]	• Broader report on the role of CCUS in a below 2 degrees' scenario, covering a range of case studies • Cooperation between industries and countries is deemed crucial with CCUS being considered responsibility of multiple stakeholders • Shipping is deemed to be fully implemented by 2050 by employing 600 vessels and 10,000 jobs; though no rationale is provided
Element Energy et al.[38]	• Study assigned by the UK's Department for Business, Energy and Industrial Strategy (BEIS) to explore the role of CO_2 shipping as part of CCUS strategies • A detailed summary of the existing literature is provided, and particularly in relation to economic assumptions; aspects relating to emissions from ships are also explored

(*continued on next page*)

Table 3 (*continued*)

Sources	Remarks
	• Overall outline of international opportunities and current barriers highlight that carrier-based transport can well be a key part of the UK decarbonisation. • Detailed techno-economic models are produced for a range of project sensitivities.
Element Energy [30]	• Report commissioned by BEIS to identify dispersed emitters in the UK and the challenges they exhibit to deployment of CCS infrastructure • For the majority of the cluster groups – including South Wales and clusters close to big ports – a combination of pipelines and shipping represent the most advantageous transportation option
IEAGHG [63]	• Infrastructural limitations of some ports to accommodate CO_2 ships, lack of experience in sea vessel transport and viable business models represent the main drawbacks to implementation • The report demonstrated that long-distance, low-volume (<2 $MtCO_2$/year) transport of CO_2 by shipping vessels from different cluster emitters represents a viable decarbonisation option • Based on a shipping distance of 1,000 km, minimal cost advantage or penalty is found in relation to increasing/decreasing the ship size from the standard 10,000 tons CO_2 capacity • Direct injection is found to be the most cost-effective offloading solution with transfer to floating storage injection unit being the least cost-effective option

suitable for CO_2 carriers [63].

There are 3 types of tanks suitable for the transport of liquid gases [34,51];

- pressure type, manufactured to limit boiling of the content under ambient conditions;
- low-temperature type which are suitable for large-scale transport and designed to operate at low temperatures; and
- Semi-refrigerated type which combines both the pressure and low-temperature type, and is pressurised and cooled.

Currently, semi-refrigerated type C tanks are identified as the only applicable solution due to the trade-off between pressure and temperature requirements; and the largest existing pressurised refrigerated gas transport ship has a capacity of 30,000 m^3 [48]. Six LPG/ethylene semi-refrigerated carriers of 8–10,000 m^3, owned by IM Skaugen, have been approved for transport of carbon dioxide in bulk quantities [38]. Furthermore, TGE Marine has focused on building 30,000 m^3 ships implementing Type C tanks and has operated a 7,500 m^3 carrier [28]. Doctor et al. [34] stated that carrier vessels for carbon dioxide transport with a size of 22,000 m^3, capable of transporting up to 24,000 t, are feasible and do not pose significant new technical challenges. Accordingly, large ships of 40,000 m^3 and 100,000 m^3 with pressurised on-board tanks have been proposed [60,73]. In summary, it appears that the existing shipbuilding experience derived from LNG and LPG can greatly assist in the construction of large CO_2 carriers and that no major technical challenges have been identified. Designs can integrate a variety of concepts such as close packing of vertical tanks and X-bow design – insulation and double-walled cargo options [65]. Potential arrangements of the carrier have been extensively explored in the literature with the aim of finding the optimum solutions [34–36]; a potential carrier arrangement is shown in Fig. 5. It is found that vessels for transportation of CO_2 at low pressure would have designs similar to those of LPG boats [35,36], and could avail themselves of cylindrical tanks. These ships will transport carbon dioxide at the highest density, requiring the smallest vessels size. Transport of carbon dioxide at medium pressures however permit designs typical of carriers currently used in the commercial transport of CO_2 for the food and brewery industries; conversely, high-pressure solutions would require small cylindrical bottles similar to those used in pipe transport of natural gas. In such a case, a ship would typically require 700–900 cylinders, thus creating challenges in terms of available space [35]. Neele et al. [50] suggested that the shipping design should consider the required wellhead conditions at the storage site rather than the conditions of the stream during capture, thus recommending medium- or high-pressure conditions. Implementation of a Dynamic Positioning system (DPS) is suggested to track the location of the carrier at the offshore site [38,64]. Existing and scheduled CO_2 carrier projects are summarised in Table 5.

It is worth noting that CO_2 shipment has been exploited for over 30 years on a significantly smaller scale in the brewery and food industries at conditions of 1.4–1.7 MPa and 238–243 K. However, the cumulative transport across Europe amounts to 3 Mt CO_2/year [54]; such quantities are significantly lower than those intended for CCUS- projects [38]. Three projects have selected ship transport: two are located in Korea and are known as Korea–CCUS 1 and Korea–CCUS 2. The third project was implemented in China, the Dongguan Taiyangzhou IGCC with CCUS Project that switched from pipeline to ships in 2003 [29,40]. The first ship built with the purpose of transporting CO_2 is the ‘Coral Carbonic’ with a 1,250 m^3 capacity, which translates to a cargo capacity of 600 t; design transport limits are 1.9 MPa and 233 K; finally four additional CO_2 carriers (1,250 m^3) are currently being built [43] by Yara Gerda in projects with cumulative disposal capacity of 400,000 t CO_2/year, approximately half the amount of a CCUS demonstration project. Larvik shipping operates three food-grade CO_2 shipping carriers – two of which have a capacity of 900 t and one of 1,200 t – from the Yara fertiliser plant in Larvik to various destinations in Europe at 243 K and 2 MPa. However, all of the above-mentioned quantities and, therefore, specifications are not suitable to transport large-scale CCUS-related CO_2 cargoes, due to lower pressures required in larger vessels [60].

5. Role of shipping in global CO_2 transport

Industrial and power emitters are seldom found in close proximity to geological storage sites and relocation in order to reduce transportation distances is usually unrealistic. Therefore, designing an optimum transport network that integrates pipelines and ships can lead to a flexible and sustainable infrastructure and facilitate the implementation of CCUS worldwide [8,13,36,51,55,67,76]. The European Commission’s GATEWAY report found that CCUS technology could have been applied to the power generation and industrial sectors for several years, though no full chain has in fact yet been established in Europe due to the uncertainties in the financial framework of CCUS [77]. Svensson et al. [26] indicated that coordinated pan-European transport networks can contribute to reducing transportation costs to as low as \$2.3/t when a long-term infrastructure capable of handling 40–300 Mt CO_2 per year is considered.

From a wider prospective, the Global CCS Institute [78] highlighted that global underground storage resources are certainly sufficient to meet the Paris climate targets. As shown in Fig. 6, countries such as the US, Canada, China, Brazil and Australia all have significant onshore storage capacity and will probably not require significant implementation of carrier-based transport as part of their CCUS strategies, thus favouring a pipeline-based approach. Conversely, scenarios such as Europe, where storage sites are dislocated in the North Sea, or Japan where CO_2 emitters are mainly concentrated in proximity to the coast, suggest that carrier-based transport can facilitate sink-source matching and enhance flexibility of a transport network. In 2011, Morbee et al. [79] suggested that carrier transport of carbon dioxide will not likely be

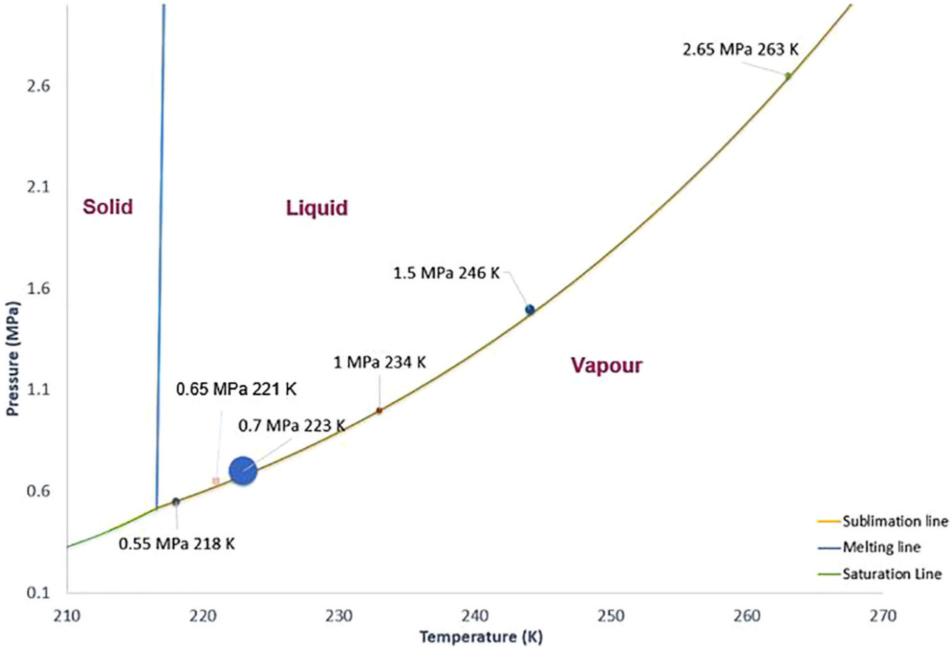


Fig. 4. Graphical representation of proposed shipping conditions in the literature on the CO_2 phase diagram. Size of the bubble represents the proportional representation of shipping conditions in the literature.

Table 4
Typical conditions and properties across the shipping chain [29].

Properties	Units	Typical LNG	Typical CO_2 buffer storage and transport by ship	Typical CO_2 buffer storage and transport by road	Typical CO_2 transport by pipelines	Typical CO_2 injection and storage (sequestration)
Fluid	–	Liquid	Semi-refrigerated liquid	Semi-refrigerated liquid	Semi-refrigerated fluid (dense phase)	Supercritical fluid (dense phase)
Density	kg/m^3	450	1163	1078	838	702
Density ratio (liquid/gas)	–	600	568	545	424	355
Pressure	MPa (gauge)	0.005	0.65	2	7.3–15	10
Temperature	K	113	221	243	293	308

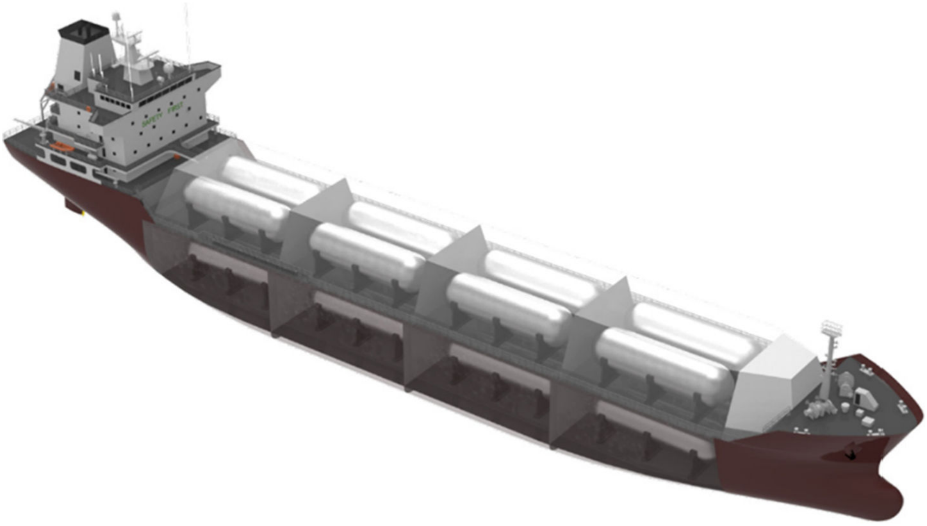


Fig. 5. Conceptual design of CO_2 carrier [14].

implemented during early-stage CCUS projects due the inadequate maturity of shipping technology; and as such only four large-scale integrated projects between Europe and Asia proposed CO_2 shipping as the selected transportation method [13]. However, significant technological progress has been made since this work was published, indicating that large-scale CO_2 shipping can and will be a key part of global

Table 5
Existing and scheduled CO_2 carrier projects.

Developer	Application	Location	System	Status	Remarks	Source
IM Skaugen	Unspecified	Unspecified	6 × 8,000–10,000 m^3 semi-refrigerated ships	Approved for transport of CO_2 (2010)	2–3 Mt CO_2/year; 480 km	[74]
Anthony Veder – Coral Carbonic	Food and beverage	Port-to-port – Northern Europe	1,250 m^3 – 600 t cargo capacity	In operation	1.8 MPa, 233 K; LNG/CO_2 dual purpose	[54]
Yara	Food and beverage	Port-to-port – unspecified	4 × 1,250 m^3	In operation	Disposal capacity 0.4 Mt CO_2/year	[13]
Larvik Shipping	Food and beverage	Port-to-port – Europe	2 × 900 tons capacity ships; 1 × 1,200 tons capacity ship	In operation	2 MPa, 243 K,	[54]
Yara & Larvik Shipping	Food and beverage	Port-to-port – Europe	1–4 × 1,850 m^3 ships; 1.776 – 7,104 tons capacity	Planned	1.6 MPa, 248 K	[64]
Yara Embla and Yara Froya	Food and beverage	Port-to-port – Europe	1,800 tons capacity	Reconditioned	Reconditioned LPG tanker, 1.5 MPa, 243 K	[54]
Praxair/ Larvik Shipping	Food and beverage	Port-to-port – Europe	1,200–1,800 tons capacity	Reconditioned	Reconditioned from cargo carriage, 1.6–2.1 MPa, 243 K	[38]
Vermeulen	CCUS (storage)	Offshore storage sites, NL	6 × 3,833 m^3 tanks; 26,450 tons	Proposed	0.7 MPa, 223 K	[36]
Yoo et al.	CCUS (storage)	Unspecified offshore storage	6 × 5,000 m^3 tanks; 34,500 tons	Proposed	0.7 MPa, 223 K	[49]
Brevik	CCUS (storage)	Offshore storage sites, Norway	2,315 – 9,787 tons	Proposed	1.4 – 1.9 MPa; 0.2 – 0.8 Mt CO_2/year	[38]
Polarkonsult, Praxair, Larvik Shipping			2,400 – 9,400 tons capacity ships	Proposed	1.4 – 2 MPa, 233 – 243 K	[75]
Nippon Gases Europe AS	Food and beverage	Port-to-port – unspecified	3 × ships with 1,770 tons capacity	In operation	2 MPa, 243 K	[63]
Nippon Gases Europe AS	Food and beverage	Port-to-port – unspecified	1,200 tons capacity ship	In operation	2.1 MPa, 243 K	[63]

decarbonisation strategies [62].

Potential storage assets in the North Sea can be deployed by implementing shipping in the early stage and potentially on a longer term (2030–2040) for CCUS across Europe (Table 6). Ships can extend the feasibility of CCUS to smaller emitters where implementation of a pipeline is economically infeasible, and they can exploit relatively smaller storage sites without incurring high sunk costs. Several potential shipping routes to decarbonise the Netherland's emitters clusters have been explored in the 2013 GCCSI report [80] with the intention of diversifying CCUS transportations solutions and reducing costs. Demonstration projects such as in the Port of Antwerp with relatively low emissions (<1 Mt CO_2/year) were found to favour shipping for distances of approximately 400 km, with offshore pipeline being preferred when higher amounts of 5 Mt CO_2/year are considered [80].

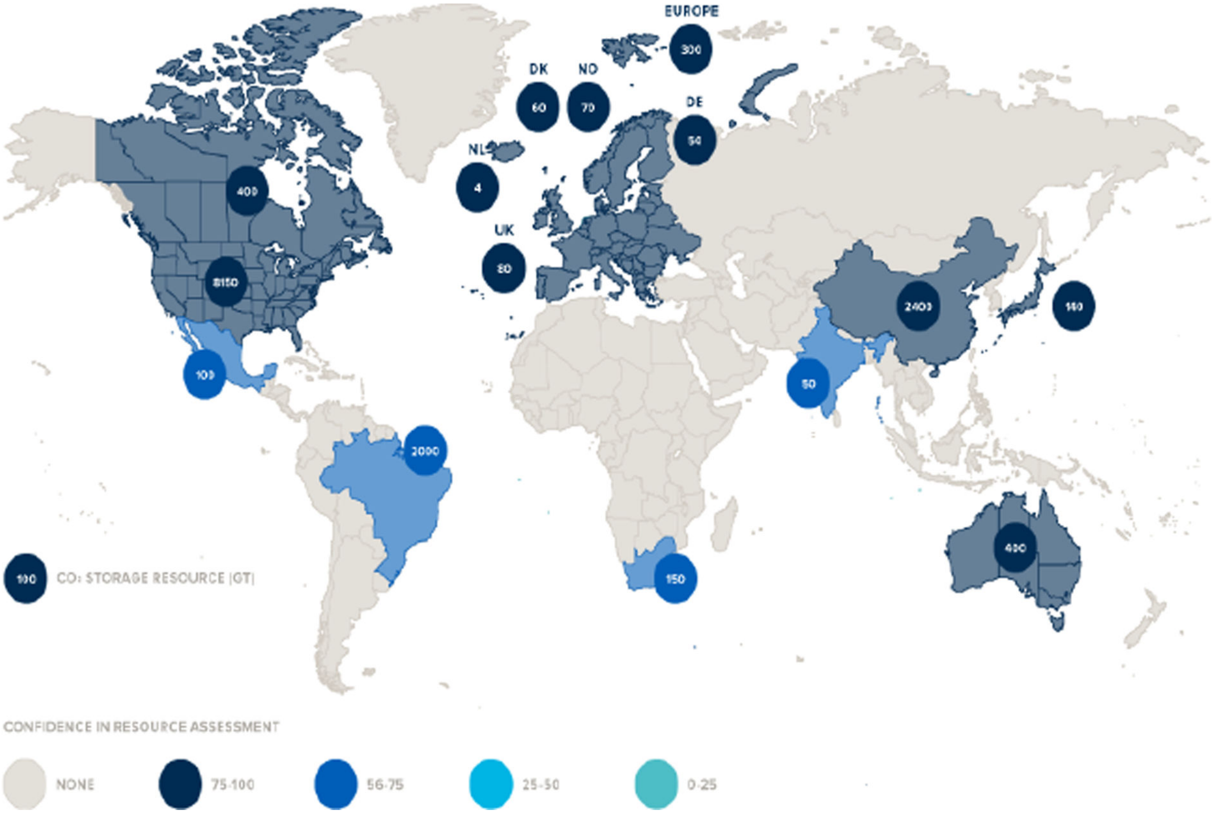


Fig. 6. Global storage resource potential [78].

Conversely, when longer transport distances of 1,000 km were considered for the same discharge amounts in the Skagerrak-Kattegat region in Scandinavia, transport by ship was only deemed to be a transitional approach until a full-scale pipeline system was implemented, despite dislocated distribution of emitters favouring a flexible shipping solution [81].

During the ramp-up phase of the project, as more clusters become decarbonised, a combination of ship and pipeline transport was deemed advantageous. Kjärstad et al. [82] however suggests that due to the modest size and geographical coastal dislocation of Norwegian emitters, shipping will be viable to integrate additional cluster combinations around the region as well. Interestingly, poor injectivity in reservoirs in the Baltic Sea can make transportation of emissions captured from Finnish sources more economically viable than injection into unsuitable storage sites, despite additional distances of 800–1,300 km being required to reach the aquifers in the Skagerrak region of the North Sea. As a general consideration, CO_2 pipelines can connect the major sources or collection hubs to the storage site, while discharges from minor sources are more suitable for transportation by ship to a hub. Recently, a demonstration project has been developed and pursued by the Norwegian government with the intention of making themselves one of the early movers in CCUS. The ‘Northern Lights’ project [83] – currently undergoing feasibility scrutiny, is forecasted to capture 800,000 tons of CO_2 per year from three Norwegian emitters situated on the east coast – including a cement plant and an ammonia plant – and ship them to a collection hub in the west coast of the country prior to permanent storage in the North Sea. Participating entities include Gassco, Total, Equinor, Larvik Shipping AS and Knutsen OA. The shipping options has been selected in order to facilitate ramp-up to higher transport amounts from multiple sources and hence allow expansion and involvement of neighbouring countries by importing up to 4 Mt CO_2/year from other European countries. This approach can facilitate the implementation CCUS projects from an early stage.

In the UK, the Acorn CO_2 SAPLING project has synergies with the Norwegian Northern Lights project; and aims to establish a strategic transportation infrastructure capable of delivering over 12 Mt CO_2/year from emitters in the North Sea for permanent storage in the Central North Sea, and provide a model for similar hubs in Europe and elsewhere [84]. As illustrated in Fig. 7, large shipping vessels can be accommodated within Peterhead Port and import 6 Mt CO_2/year from neighbouring European countries. The Acorn project is currently expected to reach its final investment decision in 2020/21.

The recent report by Element Energy et al. [38] highlighted the potential of carrier transport to connect the ports in the UK with other emerging CCUS projects from Norway and The Netherlands, and relevant industrial sites that exhibit modest storage potential, for countries such as France and Germany. Within the UK, shipping can allow transport of emissions from South Wales CCUS clusters to Hamilton storage site as well as decarbonisation from several clusters on the east coast – Teesside, Humber, Thames and Grangemouth – thus collecting up to 5 Mt CO_2/year to supply the St. Fergus offshore pipeline and storage at Captain Aquifer in the North Sea [38]. A further study on the deployment of CCS at dispersed industrial sites in the UK [30], could serve as the first step to the establishment of a European transportation network.

The Far East will also likely exploit shipping as part of its decarbonisation efforts. In Japan and South Korea, where CO_2 emitters are concentrated at coastal locations and an offshore pipeline network is not in place due to minimal activities of oil and gas industries and the high probability of earthquakes, implementation of a pipeline network would be impractical according to Ozaki and Ohsumi and Nam et al. [59,60]. Moreover, the presence of offshore storage capacity located in proximity of Japan’s coast (Fig. 6) suggests that CO_2 shipping is a suitable solution to mitigate the sink-source matching conditions and facilitate implementation of CCUS in East Asia. Specifically, the concept of short range shuttle ships transporting relatively low amounts of CO_2 at high-pressures is identified by Ozaki et al. [37] as the best approach for Japan due to the limited capacity of individual storage sites. Conversely, Jung et al. [55] suggests that a CO_2 transportation approach based on pipelines will be more economical than a ship-based approach for CCUS in Korea when amounts of 1–6 Mt CO_2/year are considered. These authors however emphasized that future efforts are needed to shape the CCUS vision and provide costing data on both demonstration and commercial stages, with carrier transport expected to become considerably more economically competitive in future.

Chiyoda Corporation [58] and Kokubun et al. [85] investigated the applicability of gas carriers to transport liquid CO_2 on coastal locations of Japan and found that discharging a few million tons of carbon dioxide per year over 200 km and 400–800 km is feasible and necessities the implementation of three 3,000 m^3 ships. Direct injection from ship to offshore storage site was explored in order to eliminate offshore storage platforms, and particularly in relation for the high propensity for earthquakes and tsunamis; however, further work is required to make this option techno-economically feasible.

In summary, in a realistic scenario where no prior infrastructure is in place, the preferred transport solutions between shipping and pipeline will be subject to considerations of transport distances, and the

Table 6
Potential CCUS Transport Networks implementing shipping transport [38,55,80].

Storage	Type/Capacity	Offshore transport	CO_2 sources	Remarks
P18/P15 (NL)	Dep. Gas Field ~79 Mt CO_2	Pipeline	Rotterdam	Selected by the ROAD and Green Hydrogen projects in The Netherlands
Q1 (Netherland)	Aquifer ~200 Mt CO_2	Pipeline Shipping	Rotterdam Eemshaven	Suitable for the Dutch Continental Shelf
Dan Oilfield EOR (D)	Dep. Oil Field	Shipping	Rotterdam Eemshaven	Selected for the Green Hydrogen project in The Netherlands
Q1 (Netherlands)	Aquifer ~200 Mt CO_2	Pipeline Shipping	Rotterdam FS Eemshaven Antwerp	Suitable for the Dutch Continental Shelf
South North Sea Aquifer (UK)	Aquifer [>2000 Mt CO_2]	Pipeline Shipping	Rotterdam FS Antwerp	Potential sink site for CCUS projects in the UK
Captain Aquifer (UK)	Aquifer [>360 Mt CO_2]	Shipping Pipeline	Rotterdam FS Antwerp Eemshaven FS	Potential CO_2 storage site for Scotland in the North Sea.
Captain Aquifer (UK)	Aquifer [>360 Mt CO_2]	Pipeline, Shipping	St Fergus, Teesside clusters	Potential future transport scenario for the UK
Bunter Aquifer (UK)	Aquifer	Pipeline	St Fergus	Potential future transport scenario for the UK
Utsira Sandstone (Norway)	Aquifer [>Gt]	Shipping	Eemshaven FS	CO_2 storage site in place for Sleipner project in the North Sea
Ulleung Basin, Korea	5.1 Gt CO_2	Pipeline, Shipping	Hadong and Boryeong Power Plant,	Transport strategy implies offshore pipelines or shipping [55]

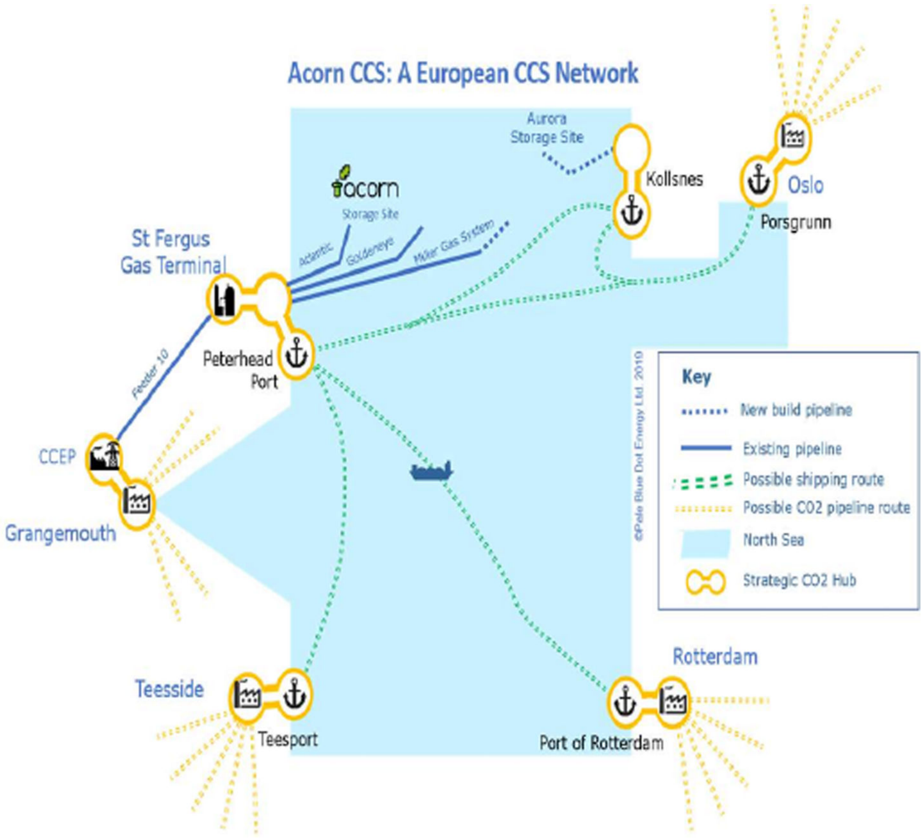


Fig. 7. Representation of the CO_2 SAPLING project of common interest (PCI) ambition and transnational connectivity [84].

quantities and location of emitters. Geographical and environmental factors are key and can significantly influence the selection and design of transportation networks. Lower discharge amounts and early CCUS implementations favour shipping solutions due to low capital investment, with a transition to offshore pipelines indicated when demonstration projects develop and must handle significant capture amounts; there is an exception to such scenarios where emitters are dislocated and a pipeline installation is, therefore, impractical, whereas carrier transport can provide the required flexibility. Unfortunately, the literature is not in agreement in assessing the role of shipping in future CCUS projects; some work suggests it is only a temporary solution [80], while more recently, several studies suggest that it will have a crucial part in long-term CCUS infrastructure [38,62]. The development of complex transportation systems that can interconnect a substantial number of emitters in any given region should involve multiple stakeholders and industries cooperating in the region [12,13]. As such cross-border transport of carbon dioxide emissions can successfully avail itself of the flexible shipping option and potentially create a market for countries whose storage capacity are significantly higher than their expected emissions. Currently, some crucial impediments to the implementation of CO_2 shipping exist. The first one is the London Protocol – a regulating agreement which forbids cross-border transport of CO_2 as part of its scope to prevent the export of “waste to other countries for dumping” within Convention on the Prevention of Marine Pollution by Dumping of Wastes [38]. Another significant limitation is represented by the EU ETS Directive, which precluded CO_2 shipping from being part of the greenhouse gas emission trading scheme thus preventing it from availing itself of financial incentives for CCUS [63]. While the former is currently under amendment through a resolution in October 2019, that effectively enables rectifying Contracting Parties to temporarily adopt cross-country transport within CCUS applications until enough ratifications for this permanent amendment of the Protocol become effective, the latter remains a major barrier. The IEAGHG [63] recommends active participation of parties in addressing such regulatory limitations, including a revision of the ETS Directive to extend to CO_2 shipping and acceleration of the amendment of the London Protocol by promoting an increasing number of Contracting Parties to sign in the near future.

6. Properties relevant to carbon dioxide shipping

A detailed understanding of thermo-physical properties of CO_2 is essential to enable efficient, safe and cost-effective operations in the transport chain, including CO_2 shipping. Table 7 summarises physical and thermodynamic properties relevant to CO_2 shipping systems.

6.1. Density

Density is a major factor influencing utilisation of available cargo capacity and, therefore, transportation schedule and shipping chain costs; it also affects the voyage and vessel stability during sea transport [95]. From an operational point of view, a high-density state, i.e., near triple-point conditions, is desirable to maximise the utilisation of cargo capacity. Therefore, a thorough understanding of the density of carbon dioxide related to shipping conditions is essential. The Energy Institute [73] and Al-Siyabi [86] note that change in pressure (0.5–5 MPa) has a moderate effect on density when sub-zero temperatures of 228–243 K are considered (Fig. 8). The presence of soluble impurities however, has a major impact on density; non-condensable contaminants reduce the density of the carbon dioxide mixture [87], thus decreasing the storage capacity and increasing the injection pressure required. The standard molar volume of most impurities is higher than that of CO_2 resulting in impurities occupying a higher volume even though their percentage concentrations are low. Seo et al. [14] reported the density of liquefied CO_2 is inversely proportional to the storage pressure, ranging from 1159 kg/m^3 at 0.6 MPa and 221 K to as low as 649 kg/m^3 at 6.5 MPa and 298 K. The authors investigated the cargo tank volume required to discharge

Table 7
Physical and thermodynamic properties and their relevance to CO_2 shipping.

Property	Relevance	Remarks	Impurities	Sources
Density	Vessel dimensioning, compressor and pump design, carrier stability	Highest near the triple point	N_2, Ar, H_2S	[86–88]
Solubility of water	Risk of corrosion and hydrate formation	Limited experimental data covering shipping conditions	CH_4, N_2, NO_2, SO_2, O_2	[89–91]
Viscosity	Estimation of pressure drop in the system Design of process equipment	Liquid viscosity data is limited to CO_2-H_2O systems	H_2O	[88]
Phase Equilibria	Water solubility Phase boundaries Liquid loading/unloading Temperature-pressure characteristics	Minimal presence of impurities can alter phase equilibria significantly	H_2, SO_2, N_2	[92–94]

the same amount of CO_2 to be 78% higher at the low-density state of 6.5 MPa compared to the high-density condition of 0.6 MPa. This will result in a significantly higher number of storage and cargo tanks required, which will in turn increase the required capital investment of any given project. Additionally, and beyond simple density considerations on storage capacity, the maximum size of a single storage vessel decreases with increase of pressure due to limitations in wall thickness; this consideration poses a further cost penalty the storage capacity for high-pressure, low-density states.

Studies and experimental work on the supercritical phase, and evaluations for the liquid phase near the triple point are relatively scarce [87]. Moreover, only a few studies focus on the densities of binary mixtures [88] such as the CO_2–H_2S system [96–98]. Some work focuses on the presence of SO_2 and O_2 but only for a limited concentration range [88]. There is also a dearth of experimental findings on CO_2-H_2O mixtures at temperatures below 273 K and for binary mixtures of other impurities like as CO, NO, NO_2 N_2O_4 and NH_3 [93]. When considering real composition scenarios encountered in CCUS, Engel and Kather [95] found that liquid densities of pure, post-combustion, pre-combustion and oxy-fuel composition scenarios are similar at conditions typical of CO_2 shipping (218–225 K and bubble-point pressure).

6.2. Solubility of water

Free water is an unwanted impurity capable of producing operational and technical challenges such as corrosion and hydrate formation. Therefore, numerous models to determine the solubility of water in carbon dioxide have been made and several validations of those models have been reviewed by Austegard et al. [89]. Empirical results are generally limited to the gas phase or conditions related to pipeline transport [99] with limited data available in low-temperature, liquid phase; unfortunately the available empirical data does not necessarily focus on CCUS projects [89,100]. As highlighted in Fig. 9, the solubility tends to increase with pressure and, more strongly with higher temperatures [89,99]. The solubility of pure H_2O in low-temperature, liquid carbon dioxide decreases from 1000 ppm at 283 K to 180 ppm at 233 K. Liquid CO_2 exhibits higher water-carrying capacity than gas-phase CO_2 and, hence, water solubility in CO_2 increases significantly during the transition from gaseous to liquid state [101].

In streams which also contain impurities such as CH_4, N_2 or O_2, the solubility of water in CO_2 is further reduced [89,103,104]. Minimal amounts of NO_2 and SO_2 (500 ppm) are found to reduce water solubility significantly more, in comparison to the other impurities mentioned above. By contrast, H_2S at concentrations as low as 200 ppm can result in increased water solubility [99].

Finally, in order to investigate the interaction between impurities in realistic capture scenarios, a study by Pereira et al. [105] covering a composition of 89.83% CO_2, 5.05% N_2, 3.07% O_2 and 2.05% Ar, (typical of oxy-fuel capture scenarios) found that at 15 MPa the presence of these impurities results in the solubility of water being reduced by 20% in comparison to a pure CO_2 stream at the same conditions. However, it should be noted that the published data relating to the absolute effects of impurities on realistic capture compositions remains very limited, especially with regards to liquid, cryogenic scenarios [91].

In summary, more empirical results and better thermodynamic models are required to cover cryogenic shipping conditions typical of shipping transport for realistic complex composition scenarios as opposed to simple binary and tertiary mixtures. Results available in the gaseous and supercritical phase can provide an indication of the effect of certain impurities on solubility of water, although they are not directly relevant to shipping and are therefore unreliable for planning real operations.

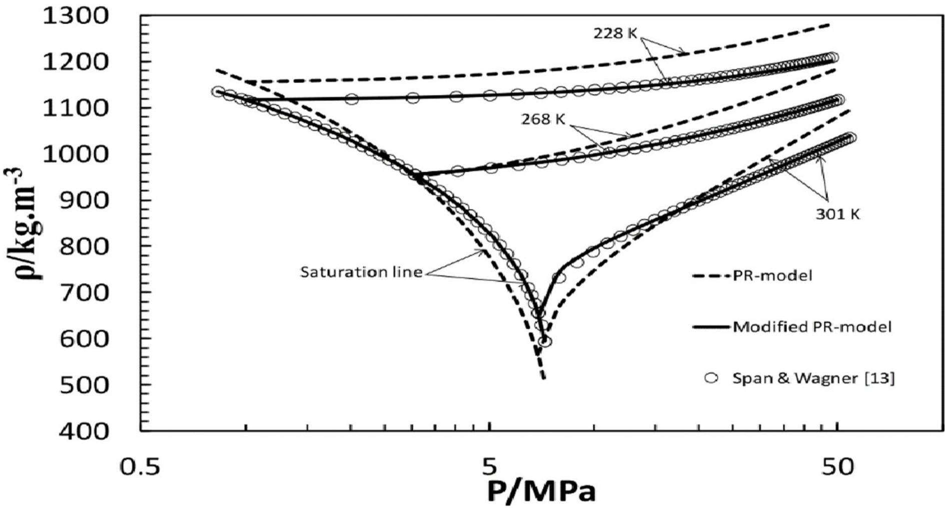


Fig. 8. Liquid and saturation liquid densities of carbon dioxide [86].

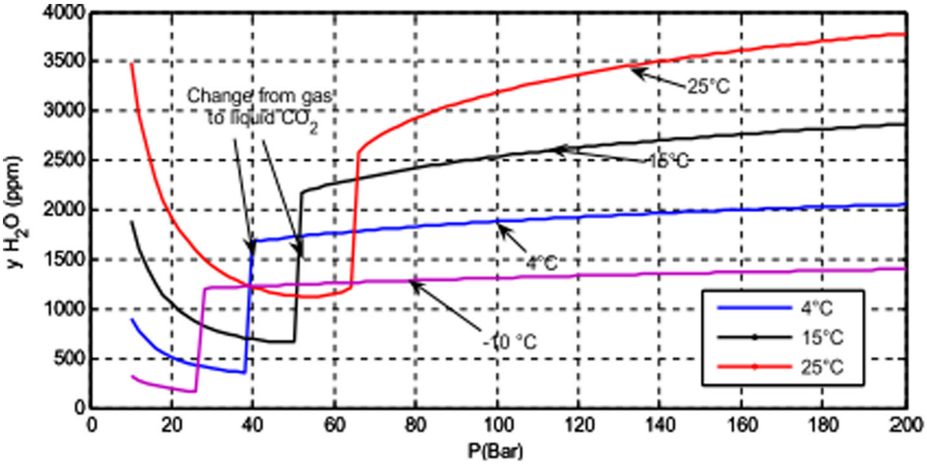


Fig. 9. Solubility of water in pure carbon dioxide [102].

6.3. Phase equilibria

Extensive understanding of pressure–temperature-composition mechanisms is essential to develop appropriate conditioning, transport and storage procedures as CO_2 will need to be processed in liquid forms at all times throughout the chain. Overall, there is a lack of vapour-liquid equilibrium (VLE) data relevant to shipping conditions for binary systems such as CO_2–COS, CO_2–NO, or CO_2–amines, CO_2–SO_2 and, even more remarkably for tertiary systems, as highlighted by Munkejord et al. [88] in Table 8.

Upon liquefaction, the supplied CO_2 will be stored and transported as a liquid. The presence of relatively small amounts of impurities can significantly alter pressure–temperature phase equilibria and two-phase regions at conditions relevant to carbon dioxide shipping as showed in Fig. 10.

Even a minimal presence of H_2 and N_2 (<0.5 mol%) can increase vapour pressure by 30% thus making carrier transport infeasible due to the elevated bubble-point pressures at cryogenic temperatures as summarised in Table 9; such impurities, and particularly N_2, also widen the two-phase envelope in the stream, thus increasing the risk of operational issues throughout the chain.

In contrast, the presence of SO_2 is found to reduce the bubble pressure, although other process safety considerations exist in relation to the presence of SO_2 in the mixture. Chapoy et al. [90] developed commercial software predictions for 98 mol% CO_2 and 2 mol% H_2 mixtures at 253 K and 263 K, which showed bubble-point pressures of 6.12 MPa and 6.24 MPa, respectively. These values are moderately higher than pure CO_2 scenarios. When considering real CCUS capture compositions, Wetenhall et al. [91] (Table 10) and Engel and Kather [95] assessed bubble-point curves and phase envelopes for the worst-case impurity scenarios; and despite some discrepancies between the two studies, their work was in line with the trend for binary and tertiary systems, it appears that marine transport of such streams would not be feasible under most capture options due to the high liquefaction pressures exhibited even at cryogenic temperatures. Purification of such streams thus becomes necessary to implement carrier transport. Conversely, compression power does not appear to be highly affected by impurities.

6.4. Stream composition and presence of impurities

Despite the lack of significant technical limitations to achieving high-purity CO_2 streams captured from industrial plants, the composition of discharge streams is mainly dictated by process safety and techno-economic considerations throughout the CCUS chain. A thorough understanding of the impact of contaminants is of critical importance in the shipping chain for several reasons. From a process safety prospective, minimal amounts of H_2 S or SO_2 greatly increases the risk associated with the transport of the stream due to their toxicity. Their presence therefore implies rigorous scrutiny of regulations during real operations, particularly in scenarios involving loss of containment and leaks [106]. Understanding the impact of impurities on constituents is also crucial to preserve the integrity of vessels and components; for instance the performance and degradation of metallic and non-metallic materials alike [107] at conditions typical of shipping projects is particularly important, with H_2S generating a risk of embrittlement and SO_x, NO_x and O_2 enhancing corrosion hazards [106].

Impurities also affect the vapour-liquid and phase equilibria of CO_2, with non-condensable contaminates such as N_2 or O_2 in particular increasing the saturation pressure of liquid CO_2 thus impacting on the selection of potential conditions of shipping projects and liquefaction processes. Additionally, the density for different composition scenarios is greatly affected by the presence of impurities, and this aspect needs to be considered to ensure the stability of the sea vessel during voyage and to evaluate the cargo capacity of the ship for economic reasons [91].

Table 8
VLE data for CCUS-relevant systems at shipping conditions [88].

System	Sources	Points	Temperature (K)	Pressure (MPa)	CO_2 concentration (mol%)
CO_2–N_2	34	>700	208–303	0.6–21.4	0.15–0.99
CO_2–O_2	8	>292	218–298	0.9–14.7	0.15–0.99
CO_2–Ar	4	~200	233–299	1.5–14	0.25–0.99
CO_2–H_2S	8	>270	248–365	1–8.9	0.01–0.97
CO_2–CO	3	106	223–293	0.8–14.2	0.2–0.99
CO_2–H_2	8	>400	218–303	0.9–172	0.07–0.99
CO_2–N_2–O_2	3	80	218–273	5.1–13	0–0.93
CO_2–CO–H_2	1	36	233–283	2–20	0.17–0.98
CO_2–CH_4–N_2	2	>100	220–293	6–10	0.27–0.99
CO_2–CH_4–H_2S	1	16	222–239	2.1–4.8	0.024–0.78
CO_2–CH_4–H_2O	5	>132	243–423	0.1–100	0.001–0.83

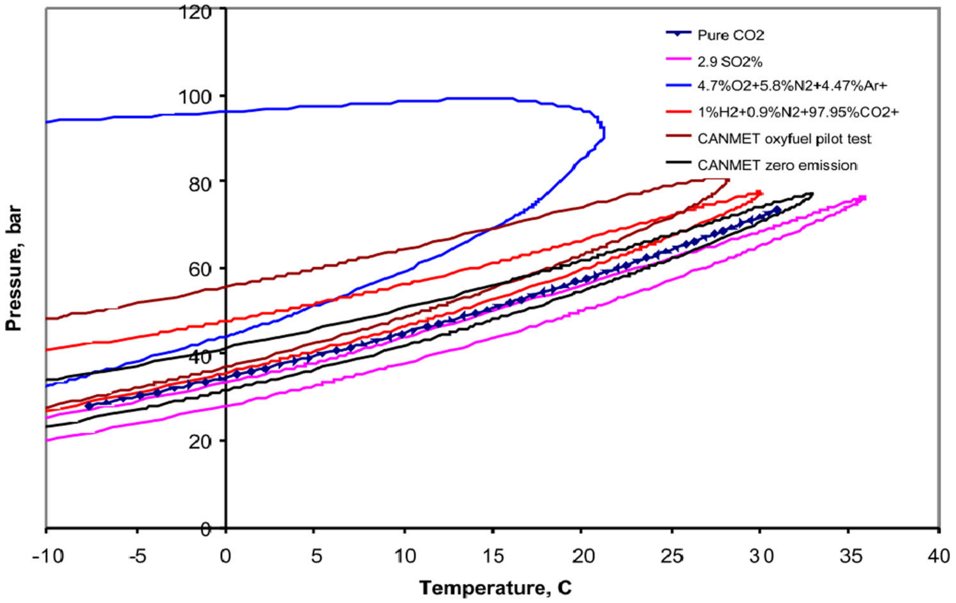


Fig. 10. Calculated phase boundaries for mixtures of carbon dioxide [87].

Table 9
Effect of impurities on equilibrium pressure of carbon dioxide at 223 K [36].

Mixture	Vapour pressure	Mixture	Vapour pressure
100% CO_2	0.67 MPa	CO_2 mixture – 0.05 mol% O_2	0.69 MPa
CO_2 mixture – 0.05 mol% N_2	0.7 MPa	CO_2 mixture – 0.05 mol% H_2	1.03 MPa
CO_2 mixture – 0.1 mol% N_2	0.73 MPa	CO_2 mixture – 0.05 mol% CO	0.7 MPa
CO_2 mixture – 0.5 mol% N_2	0.97 MPa	CO_2 mixture – 0.05 mol% Ar	0.68 MPa

Lack of operational data implies rather conservative limitations in relation to the presence of impurities [36,53,94]. Potential reactivity between impurities and construction material results in an enhanced risk of corrosion and formations of acids in the presence of free water [106]. A number of projects, including ENCAP, DYNAMIS, IMPACT, CO_2QUEST and CO_2Mix have helped establish appropriate CO_2 quality recommendations in order to guarantee the durability and integrity of the transport infrastructure [93,102,108,109]. Their focus was largely focused on the effect of contaminants on transportation by pipelines thus these studies are somewhat lacking in data relevant to CO_2 shipping systems. However, capture compositions and impurity content ranges have been investigated in the literature and details are provided in Table 11.

The tolerance to the presence of impurities can vary in relation to the expected transport and storage conditions, as well as destination of the stream (EOR or storage). Findings from the DYNAMIS project [102] are summarised in Table 12 and compared to investigations from the United States National Energy Technology Laboratory (NETL) [110]; however, NETL's specifications are more stringent. Conservative allowances in both projects are attributed to the lack of experimental results assessing the effects of oxygen underground [102]. Moreover, there is a significant shortage of empirical findings covering the effect of impurities such as O_2, Ar, SO_2, CO, H_2 despite their relevance to CCUS [94]. High concentrations of H_2S and SO_x can react to form elemental sulphur, which may result in blockages at temperatures above 673 K; this consideration is particularly relevant to the liquefaction process, where compressor discharge can approach such temperatures [36]. Finally, there is a dearth of data directly applicable to shipping conditions, as thermophysical properties of carbon dioxide under liquid, cryogenic conditions are expected to differ significantly from those typical of pipelines under gaseous or supercritical state.

7. Selection of transport conditions and economic aspects

7.1. Choice of shipping conditions

The literature generally indicates 0.7 MPa and 223 K is the preferred

Table 10
Summary of bubble-point curves and electrical consumption of four-stage compressions from 0.18 MPa to 11 MPa for several capture scenarios [91].

	vol% content								Power consumption (MW)
	CO_2	O_2	N_2	Ar	H_2	CO	H_2S	CH_4	
Pure	100								48
Adsorption 1	90	1	9						51.25
Adsorption 2	95		5						49.67
Oxyfuel 1	90	6	3	1					50.78
Oxyfuel 2	96.5	0.5	2.5	0.5					49.07
Pre-combustion	98				2				49.34
CO_2 membrane 1	93		7						50.33
CO_2 membrane 2	97	3							48.81
Calcium looping	95	1	2	2					49.33
H_2 membrane	96		1		1	0.5	1.5		49.33
Methane	98							2	48.82
Blast furnace	96		0.5			3.5			49.33

Table 11
Impurity range scenarios. Adapted from Munkejord et al. [88].

Impurity	Content range (mol%)
CO_2	75–99
N_2	0.02–10
O_2	0.04–5
Ar	0.005–3.5
SO_2	$<10^{-3}$–1.5
H_2S/COS	0.01–1.5
NO_X	$<$0.002–0.3
CO	$<10^{-3}$–0.3
H_2	0.06–4
CH_4	0.7–4
H_2O	0.005–6.5
Amines	$<10^{-3}$–0.01
NH_3	$<10^{-3}$–3

condition for CO_2 shipping for CCUS, though this choice is often simply attributed to the high-density state and lower capital cost of the vessels near the triple point rather than a comprehensive techno-economic analysis of the transport chain [8,36,54,56,57]. It is expected that operations near the triple point will require additional measures to mitigate the risk of freezing during operations, thus resulting in more stringent safety protocols and higher costs [64]. Table 13 summarises shipping conditions highlighted in several projects. As can be seen, conditions near the triple point, often indicated in the literature, tend to be based on generic assumptions and corporate preference. Some work actively investigate case-specific scenarios [14,35,59] and suggests that optimal shipping conditions can move away from the triple point when complex transportation infrastructure is considered.

As summarised in Table 14, the Norwegian Ministry of Petroleum assesses vessel transportation of CO_2 at three different conditions; although all the solutions are reported to be technologically feasible, however different considerations must be carefully evaluated. Low-pressure conditions, although associated with higher propensity for dry-ice formation due to the proximity to the triple point, enhances cargo efficiency due to its high-density state. Conversely, a high-pressure state implies lower energy-intensive processes but results in more challenging and costly tank design and unfavourable cargo efficiency. Finally, medium-pressure conditions around 1.5–2 MPa in pressure represent a mature concept that is already extensively applied for transporting CO_2 for the food and brewery industries but poses several techno-economic disadvantages such as complicated tank design which may not be economically viable for large CCUS projects.

Some of the literature that has highlighted the selection of appropriate conditions in the shipping chain as part of the wider transportation infrastructure is case-sensitive and related to numerous project variables; according to this approach, selection of appropriate

Table 12
Quality recommendations from the DYNAMIS project and NETL allowance [102,110].

Component	Concentration	Limitation
H_2O	500 ppm	Lower than solubility range of H_2O in CO_2
H_2S	100–200 ppm	Health and Safety evaluation
CO	1200–2000 ppm	Health and Safety evaluation
O_2	Aquifer $<$ 4 vol% E.O.R. 100–1,000 ppm	Due to absence of experimental findings on effect of oxygen underground
CH_4	Aquifer $<$ 4 vol% E.O.R. $<$ 2 vol%	Based on previous project
N_2	$<$4 vol%	Based on previous project
Ar	$<$4 vol%	Based on previous project
H_2	$<$4 vol%	Limits the energy requirement in the chain
SOx	100 ppm	Health and Safety evaluation
NOx	100–200 ppm	Health and Safety evaluation
CO_2	$>$95.5%	

Table 13
Summary of conditions indicated for CO_2 shipping projects.

Source	Conditions	Remarks
Skagestad et al. [56,81]	0.7–0.8 MPa, 223 K	Deemed optimum for CCUS-related quantities
Hagerland et al. [9]	Close to 0.52 MPa, 217 K	To reduce investment costs of tanks and ship
Engel and Kather [111]	0.7–0.8 MPa, 223 K	Low pressure is desirable on an economic point of view
Seo et al. [14]	1.5 MPa, 246 K	Based on the full shipping chain's energetic and economic analysis for pressures 0.6–6.5 MPa
Nam et al. [59]	1 MPa, 234 K	Based on system configuration and economic analysis of a realistic CO_2 transport chain in Korea
Mitsubishi Heavy Industries [48]	0.7 MPa, 223 K	Deemed advantageous for large scale projects due to enhanced density and relatively lower pressure.
Wong [39]	0.7–0.8 MPa, 223 K	Lower pressure results in vessels with lower cost
Worley Parsons [29]	0.75 MPa, 223 K	Density is enhanced under liquid conditions
Omata [58], Ozaki et al. [37]	2.65–2.8 MPa, 263 K	Adaptable to small ship-shuttle concept; reduced liquefaction cost; no heat treating on tank is required this temperature
Yoo et al. [49]	0.7–0.8 MPa, 223 K	Enhanced cargo capacity for large vessels
Zahid et al. [72]	0.7 MPa, 223 K	Higher pressures – 0.8 MPa and 0.9 MPa – are considered; their liquefaction capital investment is lower, but storage and ship investment are higher. Overall capital expenditure is higher in both cases
Scottish Development International and Scottish Enterprise [112]	0.7–0.9 MPa, 218 K	Similar cargo condition to semi-refrigerated LPG carriers currently in operation
Aspelund et al. [57,70]	0.55 MPa, 218 K	Enhanced density at such conditions
Ministry of Petroleum and Energy et al. [35]	i. 0.7–0.8 MPa, 223 K ii. 1.5 MPa, 248 K iii. 4.5 MPa, 283 K	i. High density, LPG experience ii. Technically ready to be implemented iii. Lowest energy demand
Kang et al. [113]	0.7 MPa, 223 K	Lower costs associated with low-temperature carrier
Jakobsen et al [114]	0.65 MPa, 223 K	Relevant to large-scale projects
Engel and Kather [95]	0.68 MPa, 223 K	Pipeline-shipping system; lower pressure results in lower capital expenditure for the vessels
Vermeulen [36]	0.7 MPa, 223 K	Based on economic analysis
Koers and Looji [67]	0.7 MPa, 223 K	No remarks made
ZEP [43]	0.7 MPa, 223 K	Based on enhanced density and lower pressures for large projects
Roussanaly et al. [31,68]	0.65 MPa, 223 K	Appropriate for large CCUS projects
Knoope et al. [41]	0.7 MPa, 223 K	Conditions near the triple point
Yoo et al. [115]	0.7 MPa, 223 K	Enhanced density at these conditions
Neele et al. [50]	0.7–0.9 MPa, 218 K	Appropriate for large volumes
Svensson et al. [51]	0.7 MPa, 223 K	Enhanced density; low pressure
Brownsort et al. [54]	0.65 MPa, 221 K	Shipping is more cost-effective at lower pressures
Element Energy et al.[38]	I. 0.7 MPa, 223 K II. 1.5 MPa, 248 K III. 4.5 MPa, 283 K	Different conditions are indicated but transport near the triple point is deemed most appropriate as per wider literature conclusions

conditions should not be based simply on corporate experience and assumptions [14,59]. As such, Seo et al. [14] explored a different approach and developed a comprehensive comparison of different carbon dioxide shipping conditions. These authors considered seven pressure conditions – 0.6 MPa, 1.5 MPa, 2.5 MPa, 3.5 MPa, 4.5 MPa, 5.5 MPa and 6.5 MPa for conditioning, preparation and shipping components of the chain and found life-cycle costs (LCC) of the overall chain to be the lowest at 1.5 MPa and 245 K, which contrasts with the majority of the literature on CCUS shipping summarised in Table 13.

In order to consolidate their findings, sensitivity analyses that took into account discharge amounts, distances, uncertainties of CAPEX estimations and electricity costs were made to evaluate the impact of such variables on LCC of the chain [14]. Despite the fact that a lack of reliable data at such an early stage of shipping implementation can affect the reliability of findings, this study [14] is a useful starting point for decision-makers in the field. Furthermore, a techno-economic analysis of the overall CO_2 shipping chain for CCUS projects in South Korea investigated the discharge of 6 Mt CO_2/year using southeast Asian offshore oil wells as storage locations; here Nam et al. [59] found that the most favourable cargo transport condition in a scenario that integrated shipping with pipeline to be 1 MPa and 234 K. This study represents a rare and valuable investigation of plant location and fleet assignment for specific CCUS clusters and projects and it clearly highlights the fact that development of a viable transportation network for CCUS is case-sensitive and dependent on various factors. As such, selection of optimum shipping conditions must carefully consider long-term decarbonisation strategies. Limited studies are available on case-specific approaches and planning of shipping projects for the future of CCUS [36,38,59,60]. More work is required to explore ad-hoc techno-economic optimisation of wider CCUS clusters and transportation networks both in Europe and Asia, as these findings will strongly affect the conditions at which shipping projects will operate. Nonetheless, several economic assumptions made in the literature are still associated with a high level of potential inaccuracy due to lack of commercial applications [35], thus strengthening the need for CO_2 shipping demonstration projects worldwide. Beyond mere economic considerations, optimal transportation conditions can also vary in relation to climate and geographical location; the phenomenon of boil-off gas generation within the cargo tank during voyage, due to heat leak from the atmosphere [72,116], is expected to be more significant in the warmer regions of the planet. Therefore, it is suggested that shipping projects covering such routes should explore the implementation of higher liquefaction pressures and temperatures to reduce the extent of heat ingress from the atmosphere and thus limit the pressurisation of the tank during transport.

7.2. *Economic and financial aspects of CO_2 shipping*

The determination of costs of carrier transport projects is complex and subject to several financial and logistical factors. Economic considerations for transport systems are not known in detail due to lack of implementation of CCUS projects. Economies of scale are anticipated to be key in reducing the costs of carrier-based transport [34], as larger ships are found to be relatively cheaper to construct than smaller ones. Costs related to shipping projects have been extensively assessed in the relevant literature – as summarised in Table 15 and graphically represented in Fig. 11 – covering a range of geographical locations, distances, and disposal amounts [36,45,56–58]. The literature consistently indicates that carbon dioxide shipping will require significantly lower capital expenditure in comparison to pipeline transportation [34,36,43,51]. Accordingly, Aspelund et al. [57] and Element Energy et al [38] found that in a scenario where up to 3 Mt CO_2/year is to be transported over 600–1,500 km, ship and liquefaction alone can constitute 73–83% of the specific costs of the chain, with operational expenditure contributing to 54% of the total costs. Specific operating and capital costs involved in the shipping chain are therefore found to be strongly dependent on project variables including discharge amount and distance. The Mitsibushi Heavy Industry report [48], Fimbres Weihs et al. [42] and Ozaki et al. [37] suggest that when long shipping distances are considered, costs relating to conditioning, storage and harbour fees are relatively low in comparison to the added economic value of sea transportation over pipelines thus making shipping more viable for long routes. unlike pipeline transport, shipping costs for CO_2 exhibit a non-linear dependency with transport distances [14,43] and for this reason, Knoope et al. [41] suggested that carrier transport is economically advantageous over pipeline for greater distances and lower amounts of carbon dioxide; while at constant, high-capture throughput, higher transportation distances are required to justify the choice of vessel transport over pipelines.

The choice of appropriate shipping conditions is essential to minimise expenditures and create a cost-effective transportation system; unfortunately, no consensus is available in the literature due to the high sensitivity to project variables such as transport distance, quantity and size of emitters and storage sites. Ozaki et al. [37] found that for Japan's situation, where emitters are dislocated and near the coast and storage sites are of medium capacity, the concept of shuttle carriers including a direct injection system is more economically viable than large-scale ships. Optimal conditions are found to be 2.65 MPa and 263 K due to the reduced energy requirement for both onshore liquefaction and offshore heating near the injection site. An additional consideration from these authors is that at temperatures above 263 K no heat treatment procedure after welding is required, thus facilitating the cargo tank design. Conversely, transportation routes in Europe would imply large carriers operated in conjunction with collection hubs that interconnect major clusters to port terminals at lower pressures, as indicated by several preliminary studies [36,50]. A comparative study based in South Korea indicated that optimum global shipping pressure should be 1.5 MPa [14] for distances of 300–700 km, with LCC increasing with conditioning pressure. This gap widens when the considered amounts increase from 1 to 3 Mt CO_2/year. This analysis covers all parts of the chain, starting from stream conditioning to the pumping system.

Cumulative costs are related to the shipping schedule and can be reduced by selecting the appropriate ship size for each distance and disposal amount. Low disposal amounts favour smaller ships, while

Table 14
General assessment of alternative transport conditions for carbon dioxide shipping [35].

Condition	Low-pressure (0.7–0.8 MPa, 223 K)	Medium-pressure (1.5 MPa, 248 K)	High-pressure (4.5 MPa, 283 K)
Advantages	– High density. – Established know-how on LPG experience. – Scalable tank size and ships	Commercially mature concept in the food and brewery industries	– Low conditioning costs – Most appropriate condition for direct-injection from ship.
Challenges	– Proximity to solid phase – High conditioning costs – Complex insulation	– Relatively high volume of steel in the tank – Technically challenging tank structure	– Complex design of tanks – Low TRL – Low density – Risk for cold boiling liquid expanding vapour explosion (BLEVE)

Table 15
Summary and cost comparison of CO_2 shipping projects.

Source	Year	Shipping system	Conditions	Transport capacity	Location	Storage	Transport Cost	Capital Expenditure	Distance
Mitsubishi Heavy industries [48]	2004	50,000 tons ship (5 tanks)	0.7 MPa, 223 K	7 $MtCO_2$/year	Japan	Saline formation or gas field	a. $10/t CO_2 b. $44/t CO_2	M$ 150	a. 200 km b. 1,200 km
Aspelund et al. [57]	2006	20,000 m^3 ship	0.65 MPa, 221 K	2 $MtCO_2$/year	Northern Europe	Depleted oil field	$20–30/t CO_2	N/A	North Sea distances
ZEP [43]	2010	40,000 m^3 ship	0.7 MPa, 223 K	2.5 $MtCO_2$/year	North Sea	Saline formation	a. $15/t CO_2 b. $17/t CO_2 c. $18/t CO_2 d. $22/t CO_2	a. M$ 153 b. M$ 174 c. M$ 193 d. M$ 237	a. 180 km b. 500 km c. 750 km d. 1,500 km
Kokubun et al. [85]	2011	a. 2 × 1,500 m^3 tankers shuttle carrier b. 4 × 1,500 m^3 tankers shuttle carrier	2.65 MPa, 263 K	1 $MtCO_2$/year	Japan	Sub-seabed geological formation	a. $106/t CO_2 b. $167/t CO_2	a. M$ 91 b. M$ 142	a. 200 km b. 400–800 km
Skagestad et al. [56]	2014	13,000 m^3 ship	0.7 MPa, 223 K	0.8 $MtCO_2$/year	Norway	Johansen formation – saline aquifer	$23/t CO_2	M$ 81	670 km
De Kler et al. [61]	2016	a. 2 × 50,000 tons ships b. 3 × 30,000 tons ships	0.7 – 0.9 MPa, 218 K	a. 4.7 $MtCO_2$/year b. 2.6 $MtCO_2$/year	North West Europe	Saline formation	a. $15/t CO_2 b. $31/t CO_2	a. M$ 358 b. M$ 394	a. 400 km b. 1,200 km
Jacobsen et al. [114]	2017	a. 25,000 tons ship b. 35,000 tons ship c. 45,000 tons ship	0.65 MPa, 223 K	0.93 $MtCO_2$/year	Norway	Depleted gas field or saline formation	$53/t CO_2	M$ 44 (ship)M$ 52 (ship)M$ 60 (ship)	300 – 730 km
Neele et al. [50]	2017	a. 5 × 10,000 tons ships b. 4 × 30,000 tons ships c. 6 × 10,000 tons ships d. 4 × 30,000 tons ships	0.7 MPa, 218 K	a. 4.2 $MtCO_2$/year b. 2.1 $MtCO_2$/year c. 4.7 $MtCO_2$/year d. 2.6 $MtCO_2$/year	North Sea	Depleted gas field or saline formation	a. $12/t CO_2 b. $38/t CO_2 c. $16/t CO_2 d. $34/t CO_2	a. M$ 348 b. M$ 461 c. M$ 393 d. M$ 465	a. 400 km b. 1,200 km c. 400 km d. 1,200 km
Element Energy et al. [38]	2018	10,000 tonsship	0.65 MPa, 223 K	1 $MtCO_2$/year	North Sea	Depleted gas field or saline formation	$12/t CO_2	N/A	600 km
IEAGHG [63]	2020	3 × 10,000 tons ship	0.8 MPa, 223 K	a. 1.8 $MtCO_2$/year b. 5 $MtCO_2$/year c. 10 $MtCO_2$/year	North Sea	Medium depth offshore site	a. $34/t CO_2 b. $30/t CO_2 c. $29/t CO_2	M$ 124 (ships + onshore buffer)	1,000 km

higher amounts imply the selection of larger ships at constant transport distance. Moreover, smaller ships are indicated for shorter distances and larger ships are required for longer distances when constant amounts are considered [115]; overall costs decrease significantly when the ship size increases, though this trend is expected to reach a limit [48]. By contrast, the IEAGHG [63] report emphasises that little economic advantages or penalties arise from the implementation of ships with capacities larger than 10,000 tons , when transportation routes in Europe and distances of 1,000 km are considered, highlighting the fact that optimal ship size is strongly related to flowrates. In line with this analysis, Roussanaly et al. [68] found that choice of different ship size lead to similar costs for transportation of 13.1 Mt CO_2/year over 480 km from Le Havre to Rotterdam. Higher utilisation rate for medium size ships however makes them marginally more economically advantageous than small vessels. Beyond mere economic considerations, it is found that larger ships will generally spend a higher proportion of the project time offloading rather than transporting the captured carbon dioxide, particularly due to the fact that maximum unloading rates in case of direct injection from the vessel are limited by the capacity of the reservoir [63]. This consideration will also affect the shipping schedule and discharge capacity. Moreover, larger sea vessels are more likely to encounter constraints at the receiving port, and can potentially require modifications of existing infrastructure. These factors are therefore expected to have a significant impact on selection of ship size in CCUS

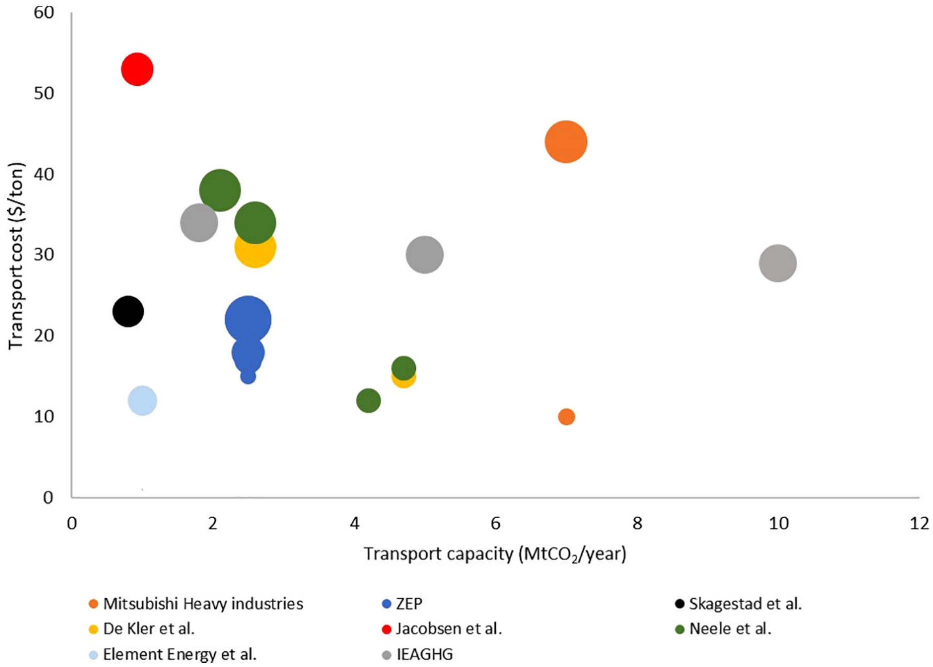


Fig. 11. Graphical representation of cost comparison in CO_2 shipping projects with respect to transport capacity; bubble areas are the relative representation of the transport distance.

projects, meaning that bigger ships are not necessarily expected to dominate in all circumstances, despite the economic benefits.

Given the current uncertainties over CCUS, minimisation of financial demand and investment risks is essential. Overall, implementation strategy can significantly reduce capital expenditure and uncertainties related to the future CO_2 projects. As CCUS-related infrastructure would be deployed gradually, CO_2 shipping can prove to be particularly advantageous in the early stage, prior to the deployment of pipeline networks [68]. For small-scale, short-duration (10 years) projects, the effect of potential sunk costs is found to be significantly lower for shipping in comparison to pipelines. This is because the lack of high up-front CAPEX required to implement carrier-based CO_2 transport, coupled with short lead time represent an advantage over offshore pipeline, particularly due to the fact that feasibility of construction of the latter relies on constant volumes throughput during the entire project life [36,76,117]. Although large scale carbon dioxide shipping is deemed technologically feasible, demonstrational projects are still required to generate confidence in the economic investment, demonstrating validity of cost estimation made in the literature and the effect of the economy of scale on reduction of project costs [30]. Under this framework, the full-scale CCUS project in Norway aims to generate a pan-European storage infrastructure and provide this economic demonstration. The Norwegian project will start-off by collecting emissions from two sites, progressively ramping to 1.5 $MtCO_2$/year capacity in Phase 1 to up to 5 $MtCO_2$/year in Phase 2 [63].

Potential cost reduction by re-utilisation of existing infrastructure is found to be negligible for carrier transportation in comparison to pipeline [38], due to the fact that the capital expenditure of the ship only representing 14% of total costs; conversely Aspelund et al. [57] found that cost of the ship accounts for 30% of the specific costs when 3 Mt CO_2/year are to be transported over 1,500 km thus, thus adding value to the concept of ship re-utilisation. The IEAGHG [63] emphasizes that the repurposing process of LPG and ethylene ships between different gases – although only feasible for a single conversion – is an attractive option to reduce capital expenditure of the projects thus de-risking investments of early stage CO_2 shipping projects.

The flexibility of the shipping option for collection from several European CCUS clusters such as Norway, the Netherlands and, potentially, France and Germany to serve several storage sites is particularly beneficial in creating a dynamic architectural system and consequently increasing transport capacity in while maintaining relatively low capital investments. As such, there is potential for the UK to import CO_2 emissions from other European countries in the future by availing itself of a flexible and efficient transport and storage infrastructure and, thus, create a new market to contribute to the economic growth of the United Kingdom. As previously noted, there are several CCUS clusters in Norway and the Netherlands, but also in France and Germany that can be connected to British North Sea storage sites via shipping. Nonetheless, there is a lack of a suitable framework of business models in relation to CO_2 shipping for CCUS, due to the fact that existing LPG and LNG financial arrangements are not found to be adaptable to carbon dioxide shipping [30]. Despite this, the IEAGHG proposes that standard conceptual models – namely voyage charter, time charter and bareboat charter – that specify contractual arrangements for the specific cargo to be discharged between given ports and ships – could be deemed relevant for CO_2 transport. On this basis, the exclusion of ship transportation from the EU framework of emissions trading of the ETS directive – as discussed earlier in this work – effectively makes any CCUS value chain looking to implement sea vessel as transportation option unable to access relevant financial incentives that could otherwise generate an advantageous business model for the commercialisation of this technology, and implementation of CCUS as a whole. This in turn has the repercussion of creating an environment of unpredictability for stake holders willing to make CO_2 shipping part of their value chain, although this burden should not be perceived as absolute and can be reviewed by the ETS Directive under the initiative of EU member states [63].

8. Components of the CO_2 shipping chain

In the shipping chain, carbon dioxide is liquefied upon arriving from the capture plant in the form of pressurised or non-pressurised gas [38]. It is then stored in appropriate tanks prior to being loaded onto the ship by means of a cargo handling system; the carrier then completes its journey by reaching the final storage destination or port terminal (Fig. 12). In the case of shipping to a port, the carbon dioxide is unloaded to intermediate storage tanks before being pumped and heated to conditions suitable for pipeline transmission to its final destination. Transport to offshore storage is also an option for shipping projects, whereby the two unloading alternatives are direct injection from ship or onto a platform with storage. In the case of direct injection, the fluid is pumped and conditioned on board the ship and transmitted to the injection well of an offshore storage site. The second offshore unloading option is to transfer the CO_2 in liquid form to an offshore platform, where it is stored prior to injection to the storage site. Accurate planning of the shipping chain, from liquefaction to offshore unloading, is essential to enhance the commercial feasibility of CO_2 shipping projects [59,60] as inaccurate schedules will inevitably result in project delays. Such delays can thus lead to requirement of more ships to discharge a fixed amount of carbon dioxide, hence inevitably producing higher costs. Throughout this section, technical insights of the shipping chain's operations provided in the literature are summarised and critically reviewed with the aim of elucidating the key challenges and level of consistency of the literature.

8.1. Conditioning

8.1.1. Dehydration

Dehydrating the carbon dioxide stream is a necessary step to preserve integrity of the system, including the loading of pipelines and vessels in order to reduce the potential for corrosion, hydrate formation and freezing. Unfortunately, there is no uniform consensus in terms of quantifying the acceptable moisture level, albeit that the ultimate objective is the minimisation or elimination of free water. As previously noted, the solubility of water varies in relation to the stream conditions and presence of impurities and, therefore, a detailed understanding of phase behaviour specific to CO_2 shipping conditions is essential. The maximum allowable water content in the system is often regarded to be 10–50 ppmv or, otherwise less than 60% of the dew point, in order to avoid operational issues when handling liquid, cryogenic carbon dioxide [36,53,118]. However, the DYNAMIS project [102] conclusions suggest that these specification are too rigid. Also, technical challenges are still being addressed to achieve full-scale implementations of dehydration plants for such low moisture contents. As shown in Fig. 13, several dehydration methods are available depending on required stream specifications; but data disclosed by vendors are limited due to commercial sensitivity, hence, technical and economic information available in the literature is also limited and associated with some degree of uncertainty. Some solutions, such as refrigerant drier and compression and cooling, do not achieve the required moisture levels required for CO_2 shipping, but they can be implemented as a preliminary step to reduce the duty required from the main dehydration unit, thus leading to less costly dehydration processes.

In some circumstances, the presence of some impurities is unacceptable due to their potential for system damage or impairment of the stringent dehydration requirements associated with their presence; in such cases, their removal in an alternative process becomes a requirement, as summarised in Table 16. Impurities such as amines, glycols, SO_x and NO_X can be significant for both the triethylene glycol (TEG) system and molecular sieve dehydration, but their impacts are still not well-understood and further research is required to assess their impact on these processes.

Absorption by TEG followed by desorption is an established gas dehydration method that can achieve 30–150 ppmv moisture levels in CO_2 systems depending on intensity of the process and glycol concentrations [80,118]; however, when very low water content (~1 ppmv) is required, the use of solid adsorbents is the most appropriate choice [119]. A comparison between the two technologies highlighted that capital expenditure and energy consumption of molecular sieve are 20% and 80% higher than TEG respectively [36]. One of the current limitations remains the lack of empirical validations on the effect of impurities on solubility of water at liquid cryogenic conditions [80].

8.1.2. Liquefaction

Appropriate conditioning of CO_2 is required to conveniently transport it in liquid form via cargo vessels, hence, several studies have focused on liquefaction of carbon dioxide streams for transportation by ship [53,120–123]. According to Aspelund et al. [57] liquefaction takes 77% of the energetic requirement of the transmission chain, or 10% of the total consumption for the entire CCUS chain according to Lee et al. [124]; here the duties and costs of compressors dominate energy requirements and capital expenditure of the process, respectively. This is 11–14% more energy than comparable purification and pipeline conditioning [125]. As shown in Fig. 14, liquefaction can be achieved using either open- or closed-cycle refrigeration processes, the choice depending on temperature/availability of cooling water and refrigerants [122,125]. Open-cycles, also known as internal refrigeration systems, involve the compression of the stream to a pressure higher than the intended conditions prior to single or multi-stage expansion to achieve the desired condition; the first authors to explore such liquefaction solutions applied to carbon dioxide are Aspelund et al. [53], although further extensive optimisation studies were subsequently performed by Lee et al. [124] .

Closed-cycles, or external refrigeration systems, involve the compression of the stream to the liquefaction pressure and refrigeration using external coolants such as ammonia, propane, R134a, or

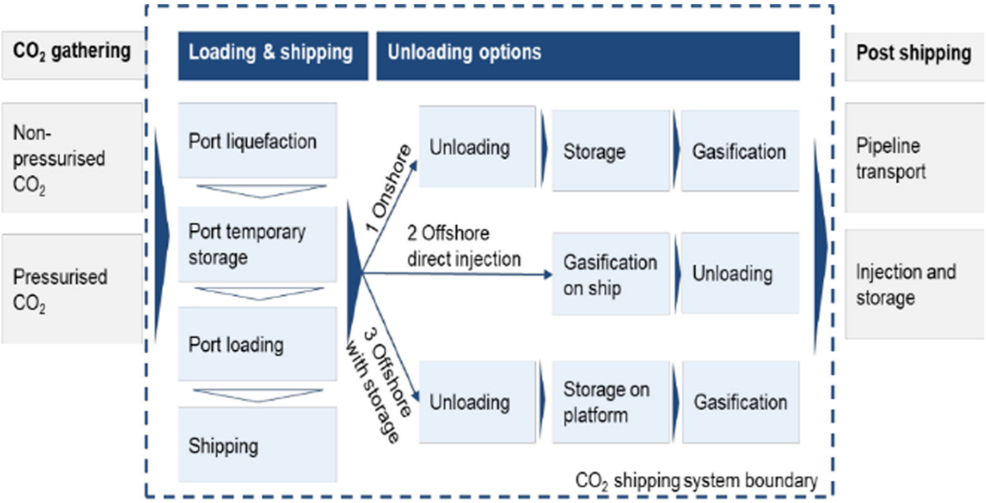


Fig. 12. Components of the CO_2 shipping chain [38].

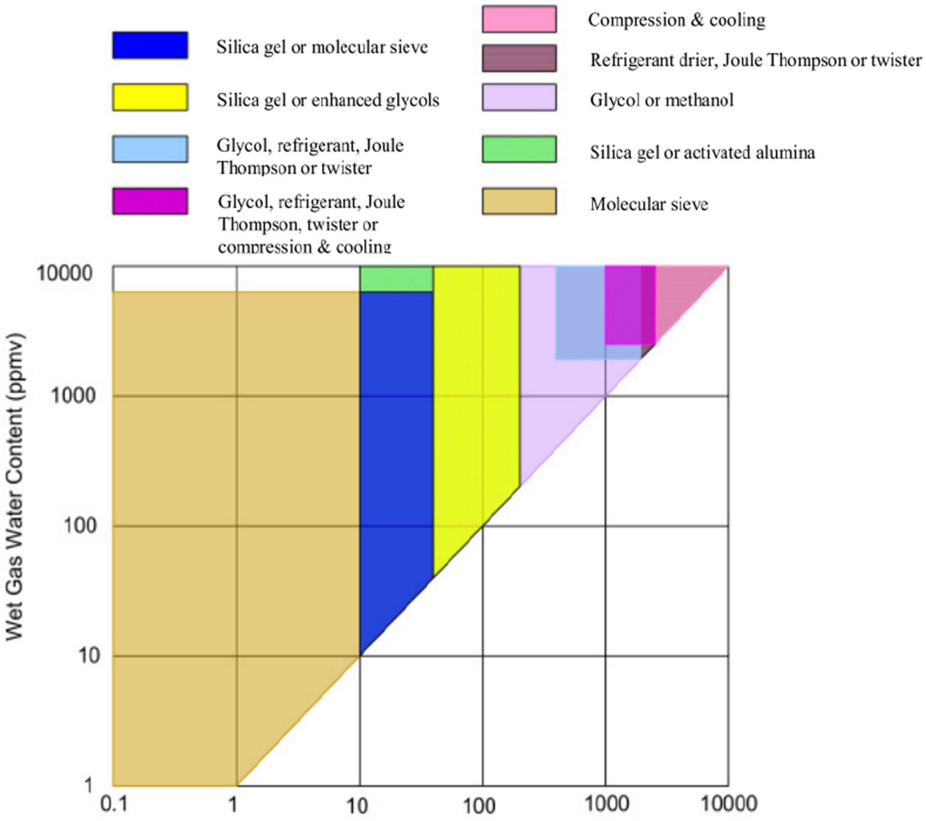


Fig. 13. Comparison of different dehydration technologies [118].

combinations of these. Seo et al. [14] suggests propane and ethane as refrigerant for closed systems at 0.6 MPa, propane at 1.5–3.5 MPa and ammonia when the target liquefaction pressure is 4.5–6.5 MPa Generally, there appears to be little effort to compare liquefaction systems and most work focuses on a single process based on local cooling service availability or corporate experience, although some detailed comparative evaluations are available [120]. Some work actively investigate the effect of delivery pressure and presence of impurities on liquefaction costs and the selection of appropriate processes [123,126], though further study is required to integrate findings related to the liquefaction cycles within the wider chain.

As shown in Table 17, most of the literature recommends conditions near the triple point for shipping of liquid CO_2, owing to the lower storage costs and enhanced density [36,43,53,57]. However, Nam et al. [59] and Seo et al. [14] found liquefaction to be most energy efficient at 6 MPa and 295 K, although the optimum's chain conditions differ when a pipeline infrastructure is also considered. This consideration indicates that choice of appropriate liquefaction must not be based simply on energetic and economic performance of the process, but also consider the wider chain and project variables. Overall, energy requirement of the liquefaction process can vary significantly in relation to disposal amount, desired conditions and type of process.

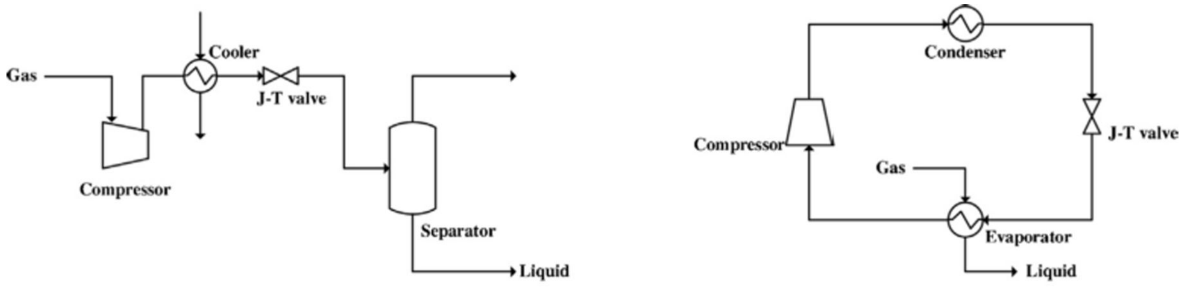
The work of Aspelund and Jordal [53] and Alabdulkarem et al. [122] suggested that internal CO_2 systems are preferred when large amounts of CO_2 are considered, due to stringent expenditure related to the implementation of heat exchangers and external refrigerants. In addition, external refrigeration processes are deemed to be economically advantageous only when low pressures are considered (0.6 MPa), as higher pressures (1.5 MPa, 2.5 MPa, 3.5 MPa, 4.5 MPa, 5.5 MPa and 6.5 MPa) facilitate implementation of internal refrigeration systems instead [120]. LCCs of both open and closed systems provide a comparable trend in relation to liquefaction pressures. As far as internal liquefaction systems are considered, variation of intercooling seawater temperature due to seasonal and locational variations can have a remarkable effect on plant layout and energy consumption; for a seawater temperature range of 278–303 K the total compressor power can vary from 90 to 140 kWh/t CO_2; temperatures of the seawater also appears to affect the layout of the liquefaction plant [127]. On the other hand, the impact of seawater conditions on external refrigeration systems is modest. Zahid et al. [72] suggests that operational costs of closed-cycle liquefaction processes increase with higher liquefied pressures, unlike Seo et al. [14] who concluded that liquefaction power decreases with higher pressures when conditions of 0.6–6.5 MPa and corresponding saturation temperatures are considered. The trend is attributed to the fact that the resulting reduction in refrigeration power at higher pressures is more significant than the increase of compression power, making 6.5 MPa and 298 K the optimal liquefaction condition in terms of energy intensity. The authors however found 4.5 MPa and 283 K to be the most cost effective liquefaction condition in terms of life-cycle cost due to the fact that compression to 5.5–6.5 MPa requires equipment that demands higher capital expenditure [14]. Overall, and despite the profound impact of the liquefaction process on the chain's economic aspect, it was found that optimal project conditions with regards to costing to be 1.5 MPa and 245 K [14], demonstrating that optimisation of liquefaction processes is not necessarily the key aspect within the full-chain. Both Engel and Kather [95] and Øi et al. [121] found that energy efficiency in the external refrigeration system can be improved by adding a series of refrigeration stages at variable temperatures; and propene, ammonia-propane and ammonia are found to be the most energy optimal refrigerants in the 1-stage, 2-stage and 3-stage closed cycles, respectively [95]. The effect of the working fluid is also important in the 1-stage closed-cycle system but less important in both the 2-stage and 3-stage cycles. In a subsequent study, these authors moreover identified measures of process optimisation by energy recovery from the stream – including liquid expanders and phase separators instead of conventional cascade heat exchangers – and found that energy intensity of the

Table 16
Effect of contaminants on TEG and molecular sieve systems [118].

Impurity	Effect on TEG system	Max. limit	Effect on molecular sieve	Max. limit
H_2O	Formation of liquid droplets can weaken absorption capacity	N/A	Degradation of the sieve or reaction with the binder; damage to the system	N/A
Inert gases (N_2, Ar, H_2, CH_4)	No impact	N/A	No impact reported	No limit
O_2	Oxidative degradation of TEG	N/A	If hydrocarbon present: coke formation, pore blockage; if sulphur present: blockages	15–50 ppm
H_2S	N/A	3000 ppm	Degradation of the sieve, corrosion caused by the generation of free sulphur	Up to 1000 ppmv none if oxygen is present
NO_X, SO_X	N/A	N/A	Damage to sieve system and life-span	N/A
HCl	Lower pH causes corrosion	200–300 ppm, Chlorides pH 6–9	De-alumination of zeolite framework, causing dust formation	1 ppmv
CO	N/A	N/A	No impact	No limit
COS	N/A	N/A	Corrosion	N/A
Amines	Foaming	N/A	Dust and damage to the system	N/A
Aldehydes	Change in pH, corrosion, foaming	N/A	Polymerisation and generation of toxic materials	200 ppmv
Methanol	Column flooding	N/A	Hydrogen formation	513 K maximum stream temperature
NH_3	N/A	N/A	Damage to sieve system	5–10 ppmv
Glycols	N/A	N/A	Premature damage to the system	N/A
NaCl	Corrosion	N/A	Blockages and damage to materials	N/A

processes can be reduced by 30–40% [111]. Although such studies are relevant in providing an overview of the energy consumption of different liquefaction cycles, they do not take into account cost analyses and the effect of the discharge amount on choice of the appropriate cycle. Increasing the inlet pressure to the liquefaction system reduces energy requirements and costs for both types of liquefaction systems, although the impact is more significant for internal cooling systems and, in general, with higher pressures; an inlet pressure of 1 MPa results in five times the total cost in comparison with an inlet pressure of 10 MPa [48,57,95].

The location of the liquefaction plant has been extensively investigated in order to establish the ideal location of the infrastructure to minimise transmission costs. Nam et al. [59] developed a modelling tool with the aim of maximising efficiency of the chain, which shows that when an industrial or power emission cluster is considered, it is convenient to establish a liquefaction plant in the high emitting regions and connect it to low emitting regions via pipelines, thus promoting a transportation infrastructure. As previously noted, contaminants directly impact the phase boundaries of CO_2-rich streams and, hence, the choice of liquefaction conditions and processes. Most realistic capture scenarios are found to require high purification to facilitate the CO_2 being transported as liquid. Wetenhall et al. [91] summarised the power required to compress twelve realistic capture scenarios, from 0.18 MPa to 11 MPa to assess the effect of impurities; they found the additional power requirements to be 1.5% to 7% higher than the pure CO_2 reference state, with adsorption capture (90 vol% CO_2, 1 vol% O_2 and 9 vol% N_2) being the most intensive and CO_2 membrane (97 vol% CO_2, 3 vol% O_2) the least demanding. This analysis is particularly relevant to open-cycle liquefaction systems where streams are compressed above the critical point prior to expansion. The pure CO_2 stream requires the lowest electrical consumption whilst the absorption and oxy-fuel scenarios, containing nitrogen and oxygen, respectively, are the most power intensive [53]. Overall, the extra power required does not exceed 7% for the worst-case scenarios. This work found, for example, that energy consumption of an oxy-fuel scenario is 10% higher than for a pre-combustion capture scenario. Such energy assessment does not address the consumption related to refrigeration of carbon dioxide and regeneration of coolant and it is, therefore, incomplete in relation to systems that imply external refrigerants. By contrast, Deng et al. [123] investigate three realistic composition scenarios encountered in captured streams from the industry and power sectors and emphasised that the presence of contaminants can result in higher liquefaction costs of up to 34% compared to pure CO_2 scenarios when external refrigeration systems implying ammonia are considered. The highest cost was encountered in a pre-combustion Rectisol stream from coal fired power plants, which contain methanol, hydrogen, carbon monoxide and hydrogen sulphide as well as nitrogen and water [123]. On the other hand, a modest increase in liquefaction cost was found in the post-combustion stream from a cement plant which mainly contains water and a minimal amount of nitrogen. Delivery pressures below 3 MPa appeared to be greatly affected by the presence of different impurities. It was moreover noted that purity constraint of the liquefied stream, mainly due to process safety considerations, can impact the cost of the process. This work provides a good outline of the conditioning and liquefaction requirements of several emitters by targeting a range of potential storage conditions; however, it lacks a comparative analysis of different liquefaction processes relative to the different delivery pressures and composition scenarios [123]. Engel and Kather [95] noted that the



Open process

Closed process

Fig. 14. Open- and closed-cycle liquefaction systems [120].

Table 17
Summary of carbon dioxide liquefaction projects.

Type of system and refrigerant	Inlet stream condition	Liquefaction conditions	Inlet composition (mass%)	Quantity	Energy consumption	End use	Remarks	Author
Open cycle, CO_2 as refrigerant	0.1–2 MPa	0.6–0.7 MPa, 221 K	97.62% CO_2 2.38% H_2O	Unspecified	144–378 kJ/kg depending on inlet pressure	EOR, storage	0.2–0.5 mol% volatiles 50 ppm water dehydration	Aspelund and Jordal ([53])
Open cycle, CO_2 as refrigerant – multi-stage expansion – optimised	0.1 MPa, 298 K	0.65 MPa, 221 K	97.62% CO_2 2.38% H_2O	2.8 Mt CO_2/year	353–356 kJ/kg	Offshore storage	90% of a 600 MW coal plant \$9.95–10.51/tCO_2 4-stage compression and 3-stage expansion 2 multi-stream heat exchangers	Lee et al. [124]
Open cycle, CO_2 as refrigerant	0.1 MPa	0.8 MPa, 228 K	89.98% CO_2 9.99% H_2O 0.016% N_2	0.7 Mt CO_2/year	327–366 kJ/kg with optimisation	Storage		Alabdulkarem et al. [122]
External refrigeration using different coolants a. NH_3 b. NH_3-CO_2 c. C_3H_8-NH_3 d. C_3H_8-CO_2 e. R134a-NH_3	0.1 MPa	0.8 MPa, 228 K	89.98% CO_2 9.99% H_2O 0.016% N_2	0.7 Mt CO_2/year	a. 387 kJ/kg b. 409 kJ/kg c. 371 kJ/kg d. 432 kJ/kg e. 377 kJ/kg	Storage		Alabdulkarem et al. [122]
External refrigeration process with multi-stage compression and expansion	a. 0.13 MPa, 313 K b. 10.3 MPa 293 K	a. 0.7 MPa, 223 K b. 0.7 MPa, 227 K	a. 97.55% CO_2 2.39% H_2O 0.05% N_2 b. 99.93% CO_2 0.07% N_2	7.3 Mt CO_2/year	a. 442 kJ/kg b. 52 kJ/kg	Storage	R22 utilised as coolant. Molecular sieve dehydration system included	Mitsubishi Heavy Industries [48]
a. Single-stage ammonia refrigeration cycle b. Two-stage ammonia refrigeration cycle c. Simple internal refrigeration process d. Multi-stage internal refrigeration process	0.2 MPa, 293 K	0.7 MPa, 223 K	97.62% CO_2 2.38% H_2O	1.1 Mt CO_2/year	a. 299 kJ/kg b. 296 kJ/kg c. 515 kJ/kg d. 313 kJ/kg	Storage	CAPEX 25.2–30.9 M\$ depending on the process	Øi et al. [121]
External refrigeration processes	0.18 MPa, 313 K	a. 0.6 MPa, 221 K b. 1.5 MPa, 245 K c. 2.5 MPa, 262 K d. 3.5 MPa, 274 K e. 4.5 MPa, 283 K f. 5.5 MPa, 291 K g. 6.5 MPa, 299 K	98.26% CO_2 1.72% H_2O 0.012% N_2	1 Mt CO_2/year	a. 473 kJ/kg b. 378 kJ/kg c. 331 kJ/kg d. 331 kJ/kg e. 315 kJ/kg f. 331 kJ/kg	Offshore storage		Seo et al. [14]
a. Linde Hampson b. Linde dual-pressure system c. Precooled Linde-Hampson system d. Closed liquefaction system	0.1 MPa, 308 K	1.5 MPa, 245 K	100% CO_2	1 Mt CO_2/year	a. 485.9 kJ/kg b. 472.5 kJ/kg c. 381.9 kJ/kg d. 2,376 kJ/kg	Storage site	Seawater temperature 303 K, Compressor adiabatic efficiency 75% CAPEX 34–43 M\$ depending on the process	Seo et al. [120]

energy requirement of an external refrigeration system with high-pressure pipeline as inlet stream also increases with the presence of impurities, with the oxy-fuel scenario being the most significant. This trend is maintained even where more refrigeration stages are added to the process.

8.2. Storage

Upon liquefaction, liquid carbon dioxide must be intermediately stored at its bubble point before being loaded onto batch shipping; inside the tank, both liquid and gaseous phases coexist at the same pressure and temperature. Storage tanks can be filled to a maximum loading level of 72–98% depending on the selected pressure, thus intentionally leaving part of the volume for the gaseous phase to prevent operational issues caused by heat ingress, and rapid transient pressure spikes which may result in catastrophic vessel failure [64]. The design of appropriate intermediate storage is key to facilitate an efficient shipping schedule and optimally discharge continuous liquid CO_2 flow from the liquefaction plant [36,48]. Table 18 summarises the existing literature on intermediate storage tanks in relation to several projects. The intermediate storage tanks are required to comply with the relevant regulations such as BS5500 PD code [44]. Lower-pressure conditions require more energetic processes in the land liquefaction plant, though they favour storage due to enhanced density of liquid CO_2 near the triple point and reduced thickness of the vessel. Seo et al. [14] found that the overall costs of storage tanks increased linearly with storage pressure, in contrast to Nam et al. [59] as highlighted in Fig. 15.

The literature suggests that the appropriate intermediate storage to cargo ship vessel size ratio should be in the order of 1.5–2 to enhance the flexibility of operations in the chain [8,9,57] with the exception of ZEP [43] which indicates a ratio of 1:1 to be sufficient. Intermediate CO_2 storage cylindrical vertical tanks capable of holding 3,000 t of carbon dioxide are currently utilised in commercial-grade projects by Yara Praxair [128]. Different design options such as cylindrical, bi-lobate or spherical semi-pressurised tanks have also been investigated in the literature, as they are currently applicable to other industrial applications [36,57,122,129]. Spherical tanks are reported by manufacturers to have marginally lower cumulative installation costs despite construction being more challenging; moreover, suitable construction materials include carbon steel, aluminium 1050 or 304L/316L stainless steel [129]. The maximum size and wall thickness of cylindrical storage tanks differ depending on the selected pressure; larger ships generally require lower wall thicknesses due to lower dynamic pressure resulting from the smaller ship acceleration. According to Decarre et al. [44] the optimal storage tank solution for projects discharging 0.8–5.6 Mt CO_2/year is a tank of cylindrical shape, made of 9% Ni steel, with a 10 mm thickness and a volume of 4,500 m^3; Lee et al. [129] favour 20,000 m^3 spherical carbon steel tanks instead. Conversely, Seo et al. [130] analysis is based on LCC, including the economic implication of unavailability of temporary storage, to determine optimum volume of tanks. LCC was found to be closely related to the storage capacity, and this resulted to be most economically viable when carrier capacity and intermediate storage capacity are equal. Factors such as size and number of carriers, CO_2 trade cost and distance did not appear to affect the optimal storage volume significantly. However, a limitation of this study lies in the fact that it offers primarily an economic approach to determine optimum parameters of a complex CO_2-handling terminal. The impact of inappropriate storage unavailability, was calculated considering carbon credits in this study, however this can lead to mass CO_2 emissions in a real scenario, potentially harmful to both the environment and any humans present. Experience in other industries indicates, a more comprehensive and realistic approach must take into account environmental issues and process safety in addition to focussing just on costs [131]. Seo et al. [14] assert that selection of materials for storage vessels is mainly dependant on liquefaction pressure and corresponding liquid temperature; the authors suggest the choice of A517 steel – with a low-temperature rating of 228 K – when operating pressures are comprised between 1.5 and 6.5 MPa, conversely suggesting the choice of A547-grade and specifying that the choice of materials used in temporary storage and cargo tanks is the same.

Interestingly, Vermeulen [36] and Kokubun et al. [85] regard the choice and design of tanks to be case sensitive and significantly dependent on the expected increase of pressure of the cargo due to heat leaks. Storage and the unloading system are estimated to represent 12%

Table 18
Summary of intermediate storage variables indicated in the literature.

Source	Type of storage tanks	Size or capacity	Material	Conditions	Discharge amount	Distance	Remarks
Decarre et al. [44]	Cylindrical or bi-lobate	14x 4,500 m^3	3.5%, 5% and 9% Ni Stainless steel 304L and 316L Aluminium 1050	1.5 MPa, 243 K	2.5 Mt CO_2/ year	1,000 km	• M$8 or 8% of total project cost • Choice of material is dependent on temperature. • Design to comply with BS5500 PD code. • Account for increased pressure due to boil-off gas production. • 10 mm thick casing
Haugen et al. [128]	Cylindrical	3,000 t	Steel	1.5 MPa, 245 K	670 kt CO_2/ year	NA	Design of storage facility is flexible with regards to geographical location and discharge amount
Aspelund et al. [57]	Semi-pressurised cylindrical tanks	10 × 3,000 m^3	Steel	0.65 MPa, 221 K	1 Mt CO_2/ year	1,500 km	Semi-pressurised vessels are indicated Cumulative storage capacity to be 150% the ship capacity
Vermeulen [36]	Bullet type tanks	3-10 ×10,000 m^3	P335NL2	0.7 MPa, 223 K	1.5 Mt CO_2/ year 2.7 Mt CO_2/ year 4.7 Mt CO_2/ year 6 Mt CO_2/ year	220–400 km	Final sizing of storage design is dependent on liquefied amount
Seo et al. [14]	Cylindrical	90 - 5,000 m^3 depending on pressure	A517 Steel	0.6 MPa, 221 K 1.5 MPa, 246 K 2.5 MPa, 261 K 3.5 MPa, 273 K 4.5 MPa, 283 K 5.5 MPa, 292 K 6.5 MPa, 298 K	1 Mt CO_2year	300–700 km	Costs of the tanks increase with liquefaction pressure.
Kokubun and Ozaki [85]	Cylindrical bilobe	2 × 1,500 m^3	Carbon Steel	2.65 MPa, 263 K	1 Mt CO_2/ year	200–800 km	Design of storage tanks is based on LPG experience.
Mitsubishi Heavy Industries [48]	Spherical tanks	20,000 m^3 each	High tensile steel	1–10 MPa	7.3 Mt CO_2/ year	200–12,000 km	

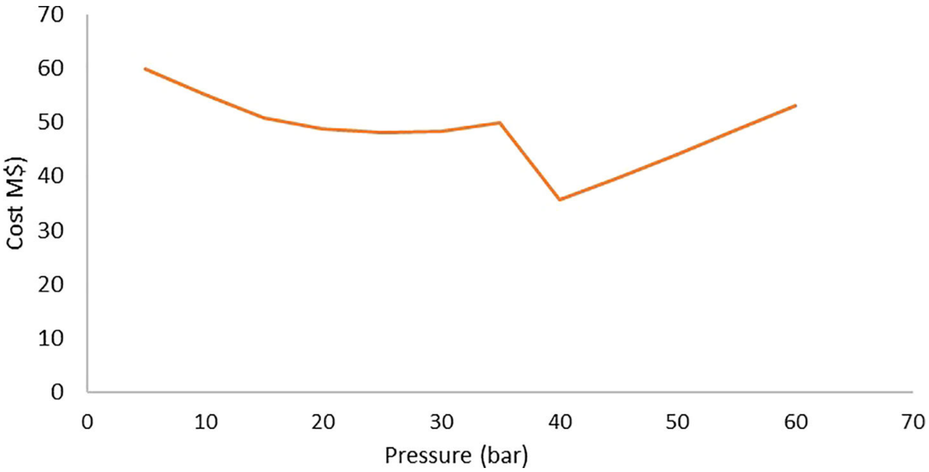


Fig. 15. Capital expenditure costs for onshore storage segment for 150,000 m^3 [59].

of the total costs according to Aspelund et al. [57], and this was also quantified by ZEP [43] to be equivalent to $1,123/m^3 – while the GCCSI [80] estimates the cost to be $16 million (£1 = $1.32 as of March 2019) for a tank capable of holding 10,000 t, made of high-tensile-strength steel; manufacturing costs represent 45% of the total storage tank costs [48]. Wherever land availability is an issue for onshore storage, liquid carbon dioxide tanks could be stored on floating barges. Yoo et al. [49] found that when small volumes of up to 28,000 m^3 are considered, storage tanks can be laid horizontally on the barge, whilst larger capacities would favour vertical orientation. An innovative alternative to new onshore infrastructure for tropical waters such as offshore of Brazil is the floating logistics terminal (FLT), which is an economical and environmentally friendly method to carry all infrastructure for CO_2 shipping terminal. Yamamoto et al. [132] introduce the concept of a FLT composed by several floating bodies. The advantages of the FLT are flexibility, fast installation, and cost effectiveness if such systems are derived from recycled hull from large bulk carriers. The concept of floating logistics could particularly benefit countries such as Japan where the propensity for earthquakes is significant, and generally increase the value of flexibility in the shipping chain.

8.3. Loading

Technical application of loading operations benefits from experience in the LNG and LPG industries. Storage tanks are loaded with a continuous stream of liquefied CO_2 from the liquefaction plant, through a loading system that makes use of high-pressure low-temperature pumps. Liu et al. [133] suggested that cargo tanks should be filled with pressurised gas phase carbon dioxide to avoid contamination with air and formation of dry ice; and that articulated rigid loading arms designed for cryogenic liquids are to be preferred [36,44] over flexible cryogenic hoses due to lower likelihood for mechanical failure and leakage. However, both systems are in use for loading of liquid CO_2 [128]. When loading takes place, the level within the vessel builds up; in order to prevent over-pressurisation of the vessel, this vapour stream must be continuously removed and re-directed back to the liquefaction unit during the length of the operations using a second parallel arm for the CO_2 vapour 'return line' [36,44,134]. Minimising loading time improves delivery efficiency, reduces the number of ships required to discharge a given amount, and requires high flow rates; however, the resulting pressure drop must be taken into account [135]. Flowrates of 2870–3530 t/h [36,72] appear to be appropriate and would enable the loading of a 30,000 m^3 ship in 12 h [36,43,70]; such flowrates would, however, require an adequate Emergency Release System (ERS) to avert outflow of CO_2 in case of failure of the loading arm or unplanned disconnection from the ship [36,38]. During this operation the pressure within the tank will drop, and to avoid freezing, the vapour generated during the voyage in the cargo ship must be recycled back to the storage tank during the operation; this also mitigates against pressure increase in the cargo tank. Formation of dry ice, induced by rapid depressurisation of the system, can be avoided by ensuring appropriate safety margins, however there is no consensus on what they should be. Standard boil-off-gas mitigation measures such as the application of insulation must be performed around the whole loading system as a higher proportion of boil-off gas is generated in comparison with storage [72].

The specific energy requirement for the loading component is given by Aspelund et al. [57] as 0.2 kWh/t CO_2 or 1% of the specific energy requirement in the liquefaction as reported in the same work; costs, including CAPEX, are found to be negligible in relation to the full shipping chain by Decarre et al. [44]. However, such comparative economic assessment appears to be in disagreement with Kokubun et al. [85], who emphasised that loading- related CAPEX represents 37% of the capital expenditure of a two-tankers carrier over a 200 km distance, and 24% of a four-tankers carrier with 400–800 km transport distance. This estimation moreover highlights the fact that expenditure of carrier-loading-system is not related to size of the ship. The significant discrepancy exhibited in the two studies can be mainly attributed to the different project boundaries adopted by the authors; as Kokubun et al. [85] clearly indicates CO_2 liquefaction facilities to be out of the scope of the study, Decarre et al. [44] includes conditioning costs and infrastructure in the economic estimation. Moreover, there is a difference in the transport distances – 200 km and 400–800 km in the former work and 1000 km in the latter – which change the proportional cost of loading facilities. Lastly, the choice of different cargo condition of 223 K, 0.7 MPa for Decarre et al. [44] and 263 K, 2.65 MPa for Kokubun et al. [85] also impacts on the cost of loading facilities as higher pressures require components with higher wall thickness.

8.4. Offloading and injection

After sea transport, carbon dioxide can be unloaded either onshore at a port before being transported by pipeline– in case of port-to-port scenarios – or offshore prior to being directed to the final storage destination. While the former option covering port-to-port shipping is well established through the extensive experience matured in large-scale shipping of similar gases such as LNG and LPG and currently applied in the food, beverage and ammonia industries, offshore unloading is still unproven and still poses some technical challenges related to its implementation [36,63]. Selection of the appropriate offloading solution and related infrastructure still sees no clear consensus and is expected to have a significant impact on the design of vessels, process equipment and costing.

Transfer systems to the wellhead include auxiliary platforms that allow instalment of equipment or direct injection from the ship. The former option allows one to generate a continuous flow into the reservoir, offering a temporary storage to mitigate adverse weather conditions; the nature of continuous operations reduces the risk of cyclical thermal and pressure loading on casings and non-metallic materials [107]. The drawback associated with these systems is the higher capital expenditure required for their implementation [63].

Conversely, offloading to a flexible riser via a buoy for direct injection to the well implies that, conditioning, pressurisation and heating of carbon dioxide must take place on the ship. In order to achieve this, the stream must be pumped to the appropriate pipeline pressure of 5–40 MPa [14,36] and consequently heated to 258–293 K – depending on the site – by means of pre-warmed seawater or waste heat available from the ship. Weather variations and thus seawater temperature fluctuations may compromise the safety of operations in view of the requirement of specific temperature and pressure conditions of the stream in order to avoid hydrate. Direct injection from the ship is found to be achievable for several wells with the integration of compression and heating equipment on board. Brownsort et al. [69] undertook a thorough investigation of offshore offloading technologies and highlighted that selection of single point systems is case-sensitive and related to several factors such as location, stream condition, availability of suitable flexible hoses and design of the ship. Similarly, Vermeulen [36] identified four different Single-Point Mooring (SML) systems that can be implemented to connect the ship with the wellhead, each one exhibiting differences in terms of water depth application and accessibility in relation to conditions of the sea. Offshore discharge is considered a novel procedure in the CO_2 shipping chain, and advanced technology is, therefore, required to mitigate the formation of dry ice during unloading and achieve a consensus on the preferred system [50].

The principal limitation is the limited understanding of the impact of impurities on the phase boundary to ensure that the safety margin from the triple point is maintained during operations [43]. Additionally, sudden stops of injection operations must be avoided at all times to mitigate the risk of dry ice formation [36]. Aspelund and Jordal [53] highlighted optimum injection temperatures to be around 288 K to mitigate against formation of hydrates during operations. When maximum storage capacity is achieved in a particular field, near-well installations have the adaptability to be relocated for injection to another field, thus, adding flexibility to the network and the opportunity to expand a shared transport web within Europe. Direct injection from the carrier is assessed as being feasible for a number of large-scale injection wells, with the exception of shallow depleted reservoirs, and pre-injection conditioning can be achieved through appropriate installations on the ship, where the heating source for injection is provided by seawater or excess heat from the engines [43]. According to Neele et al. [50] injection from the ship increases the costs by 10–25% compared to injection from a temporary platform. By contrast, Ozaki et al. [37] and the IEAGHG [63] found that direct injection from ships can potentially reduce the costs of the project as large-scale offshore installations are omitted, albeit technical and safety aspects require further optimization.

Pre-offloading conditioning consists of heating the carbon dioxide to 273 K and compressing it to ~20–30 MPa, so appropriate heating and compression equipment must be installed on board the vessel. Heat from seawater and the ship's engines can provide the thermal and electrical power required to inject the stream [61]. In scenarios where large volumes are transported for long distances by means of several ships, implementation of a seabed pipeline as a heat exchanger may be a favourable solution [43]. Most studies assume that offshore unloading will be performed in 12–36 h [43,49,50], with lack of temporary offshore storage increasing the injection time to 30–50 h.

9. Technical challenges and process safety

9.1. Selection of materials

The level of dehydration in the stream affects the choice of the type of metal throughout the system. Carbon steel, carbon manganese steel and stainless steel are suitable under low-, medium- and high-pressure carbon dioxide conditions with appropriate foam or vacuum insulation; carbon steel can be used for compressor piping when low water content is achieved, otherwise, stainless steel is required around the compressor in order to prevent corrosion [14,49]. Table 19 summarises the material selection in a CO_2 terminal. The decision on whether to make the whole pipeline and other components (scrubbers, coolers) of stainless steel rather than alternating it with carbon steel is purely based on economics. Despite the absence of water, hydrogen sulphide impurities can still react with the carbon steel, forming a thin film of iron sulphide which tends to coat the inside surface and decrease the rate of heat transfer [39].

Material selection must also account for operational temperature range: liquid carbon dioxide must be handled and transported at temperatures between 223 K and 261 K, depending on preferred pressure conditions, though the eventuality of rapid depressurisation due to sudden shut-down in the system can potentially drop the temperature to as low as 195 K. This creates a hazard from low-temperature effects, particularly in terms of the suitability of materials to ensure the integrity of vessels, pipes and fittings that needs to be addressed in the specific operational risk assessment. Some low-temperature-grade carbon steel variations can operate at temperatures down to 227 K [73], although Omata et al. [58] suggested that heat treatment is required to enable the carbon steel to withstand temperatures below 263 K. However, using materials such as 9% Ni steel, 5% Ni steel or aluminium alloy 5083–0 increase costs by 4–6 times compared to carbon steel. Seo et al. [14] suggest the implementation of A517-grade steel in scenarios where stream's liquefaction temperature is above 228 K, with a recommendation to switch to A537 for conditions that require a liquefied temperature in the range of 213–228 K.

When considering non-metallic components, IEAGHG [136] suggested a range of polymers, such as EPDM, HNBR, PTFE and FKM (Viton®) are appropriate for liquid CO_2 environments. They also suggest that, to avoid issues with the performance of elastomers, it is important to consult the supplier prior to specific applications.

The suitability of elastomers that are frequently applied to the hydrocarbon industry has been questioned [13,137], and it has been noted that cracking of seals is an issue with materials such as nitrile, polyethylene, fluoro-elastomers, chloroprene and ethylene-propylene compounds during rapid depressurisation. The high diffusivity of carbon dioxide inside the molecular structure during pressure cycles, combined with expansion during rapid gas depressurisation, make these compounds unsuitable for decompression cycles that are likely to be encountered during real operations. In response, a number of standards have been developed across the industry to assess suitability or failure of seals and gaskets undergoing ageing and explosive decompression cycles in CO_2-rich environments, though a dearth of experimental findings is apparent in relation to the presence of impurities at different conditions and at different concentrations [138]; Ansaloni et al. [107] notes that little experience exists in relation to measurements of elastomer properties at temperature close to the CO_2 triple point (219 K) which will make it difficult to assess the suitability of materials in relation to conditions typical of sea vessel transport. These authors also suggest that the impact of pressure and temperature cycling and propensity for RGD damage due to fluid absorption at such conditions should be explored to assess the impact on the elastomers' mechanical stability and lifetime of the materials. Qualification of elastomers in low-cryogenic carbon dioxide environments is therefore under-investigated by several groups [107,139]. These considerations are particularly relevant to shipping due to the batch-like nature of its operation, where continuity of loading

Table 19
Material selection in CO_2 terminal [36].

System	Component	Media	Temperature range (K)	Pressure (MPa)	Material
CO_2 Terminal	Liquefaction	Liquefied CO_2	223–373	8	SS300
	Heat exchangers	Liquefied CO_2	223–373	8	Al
	Storage	Liquefied CO_2	223	0.7	P335NL2
	Pumps	Liquefied CO_2	223	1	316L
	Ship loading	Liquefied CO_2	223	1	316L
	HP Compression	Dry CO_2	278–308	8-15	CS,4140

and offloading scenarios poses a risk from thermal and pressure cycling effects on selected metallic and non-metallic materials. Prolonged exposure of materials also needs to be explored in relation to the low-temperature CO_2 environment, although the shipping distance is not specifically expected to have a profound impact, due to the fact that sea vessels and their components need to be designed for a project life of 10–15 years in the first place.

9.2. Boil-off gas generation

When handling liquid CO_2 during real operations, a variable amount of boil-off gas can be generated. The boil-off gas is the vapour produced during sea transport due to the effect of waves' motion on sloshing of the cargo content or caused by ambient heat penetration into the system due to temperature difference during the chain's operations. The rate of boil-off gas is also affected by the distance travelled, level of impurities in the cargo tank, tank pressure design, and operational modes [140]. The rate of boil-off gas per day for LNG carriers is assumed to be 0.1–0.15%, which over a 21 d voyage produces undesirable large quantity of such gas [141]. There are no exact range of values stated in literature predicting the boil-off rate per day for CO_2 carriers, but 0.15% has been inferred as a suitable value by comparison with some of the physical properties with LNG carriers [142]. Chu et al. [143] considered 0.12% of the full cargo content to be the boil-off rate per day for CO_2 carriers. A summary of the factors contributing to the generation of boil-off gas during static operations is provided in Table 20; Zahid et al and Vermeulen [36,72] performed some modelling sensitivities to study these phenomenon; boil-off-gas generation during loading and unloading operations is estimated to be 8–10 times higher than during hold-up conditions [72]. The minimisation of LNG BOG can be regarded to be similar to CO_2 except for differences that exist in storage conditions [44,122].

Commercial designs for BOG re-liquefaction for gas carriers exist for LNG and LPG and can be applied to a CO_2 carrier [141,144,145]. Fig. 16 shows a schematic representation of a potential re-liquefaction system. A study was carried out by Gómez et al. [146] on the different technologies applied for re-liquefaction of BOG on LNG carriers. The Brayton cooling cycle, an external refrigeration method, is normally used for on-board re-liquefaction [146]. The efficiency of the process is considered secondary owing to the importance of other factors such as having a minimal space constraint, displaying stability at sea conditions, easy installation, quick start-up, minimal quantity of equipment [146]. Moreover, a process that utilises the cold energy in the LNG fuel as a refrigerant and as a chilling fluid to re-liquefy the BOG has been considered to be a viable way to deal with boil-off gas by saving cost on purchase of additional equipment and fuel consumed [116]. It was estimated that for the BOG re-liquefaction cycle for both HFO- and LNG-fuelled CO_2 ships, ammonia can be used as an external refrigerant. This is providing the capture system installed on-board uses ammonia solvent for scrubbing emissions [147,148], thereby better utilising ship storage space. Taking into consideration the lower power consumption required by ammonia compared to other refrigerants [122] and its advantages as an absorbent [149], aqueous ammonia would be a reasonable choice as a solvent because no extra solvent storage tank will be needed on the ship. The ammonia content in the ammonia storage tank for the refrigerants could also then be used for the emission absorption process.

Table 20
Factors affecting CO_2 boil-off gas [36,72].

Factor	Desirability	Remarks
Ambient temperature	Low	Lower ambient temperature results in lower heat influx and, hence, boil-off gas
Thermal resistivity and thickness of insulation	High	Results in lower BOG. Thickness is a trade-off between material cost and resulting reduction of boil-off
CO_2 level in the tank	High	Low filling level in the tank leads to a higher evaporation rate of the liquid
Capacity of the storage tank	Low	Assuming the same absolute filling amount, smaller tanks exhibit a lower the rate of pressure build-up due to BOG within the vessel

9.3. Blockages due to hydrates formation

Water solubility in CO_2-rich fluids determines the propensity for slug formation, hydrates formation and corrosion and, hence, dehydration requirements in shipping transport systems. Free water in the stream can create hydrates both in liquid and gaseous states. In order to form, they require adequate amounts of free water (host), a suitable "guest" and the CO_2-rich fluid. Hydrates can lead to blockages in the conditioning systems, particularly within the compression train and, in order to mitigate them, it will be necessary to use chemical inhibitors or operate out of the hydrate-stability zones; the hydrate-water equilibrium is dictated by physical equilibrium as a function of pressure and temperature. As can be seen in Figs. 17 and 18, conditions typical of carbon dioxide shipping near the triple point are within the hydrates-stability zone in both pure saturated and 250 ppmv water-carbon dioxide systems, though the hydrate-stability envelope is wider in the saturated water environment. Li et al. [150] indicated that, when shipping transport conditions are considered, a water content of 100 ppmv lies on the liquid-hydrate equilibrium line, albeit limited experimental data are available to validate existing models; nonetheless hydrates can still form in those regions at 50 ppm concentrations [91].

The presence of moderate quantities of N_2 and O_2 (~2 mol%, each) shifts the hydrate-stability zone to higher temperatures, while other impurities – especially sulphur-related ones such as SO_2 and H_2S – can have a reverse effect. The presence of H_2 increases the liquefaction pressure of the mixture, meaning that during a rapid depressurisation water will be the first impurity to vaporise and bond with the CO_2 to form hydrates, which are potentially dangerous to the system. As such, maintaining a constant operating pressure is essential to prevent two-phase flow and hydrates. Alternatively, controlling the presence of contaminants and a low level of water can prevent the formation of hydrates. In order to assess the predisposition of solid dry ice during depressurisation of the system, a number of equilibria models of carbon dioxide and solids have been generated, albeit that there are some deficiencies in terms of a lack of useful thermodynamic data [152]. Impurities reduce the freezing point of the CO_2-rich mixture. Overall, more extensive investigations on more complex tertiary mixtures are required to cover realistic scenarios [86,88]. A suitable safety margin must also

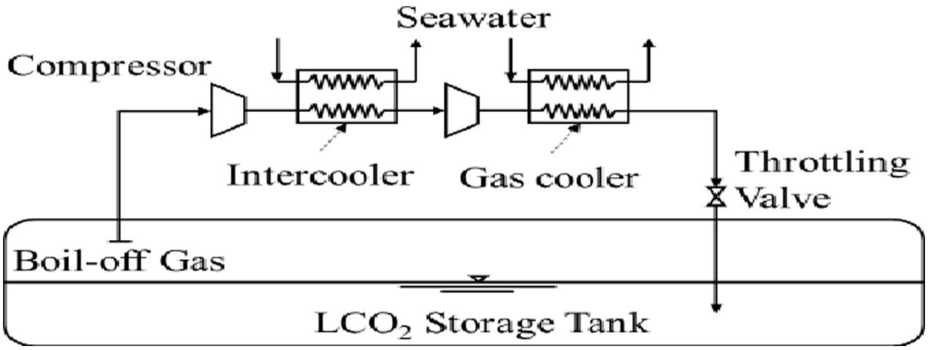


Fig. 16. Open cycle re-liquefaction for LCO_2 transport [142].

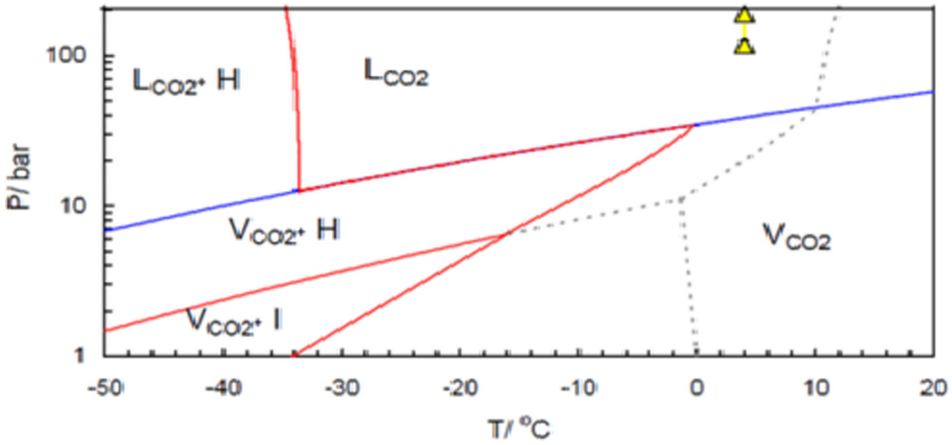


Fig. 17. Hydrate formation in saturated carbon dioxide with 250 ppmv water system adapted from Energy Institute [151]; 'L' indicates a liquid-rich zone; 'V' indicates a vapour-rich zone; 'I' indicates an area where dry-ice will form; 'H' indicates the hydrate-stability zone; the yellow triangles represent CO_2 pipeline condition. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

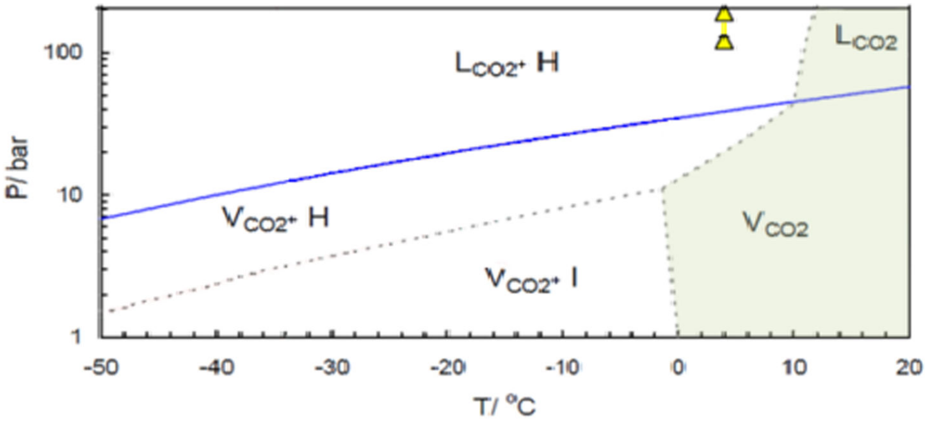


Fig. 18. Hydrate formation in pure saturated carbon dioxide system [151]; 'L' indicates a liquid-rich zone; 'V' indicates a vapour-rich zone; 'I' indicates an area where dry-ice will form; 'H' indicates the hydrate-stability zone; the yellow triangles represent CO_2 pipeline condition. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

be applied as depressurisation below the triple point equilibrium can result in formation of dry ice [57]. This is one of the current challenges related to operation near the triple point. Here, however, removal of volatile impurities to a maximum allowable 0.2–0.5 mol% in the stream can mitigate solid formation near the triple point during liquefaction and transport.

9.4. Process safety, dispersion of inventory and boiling liquid expanding vapour explosions

Health and process safety is a critical aspect of industrial processes, and the CO_2 terminal is no exception [151]. The UK's Health and Safety Executive produced a comprehensive analysis of the danger potential of carbon dioxide systems [153] with specific reference to the CCUS chain. Considerations of engineering aspects such as formation of dry ice, emergency protocols and integrity issues related to structural integrity are suggested as research topics in the area of CO_2 transport, especially in relation to liquid, cryogenic systems. Moreover, hazards resulting from loss of inventory of large CO_2 vessels must be investigated, and implementation of stringent risk assessments is recommended to reduce such hazards. In order to protect people and limit the impact to the plant and the surroundings, Zahid et al. [72] emphasized that terminals should include emergency shutdown (ESD) system. Such systems close the flow between the carrier and terminal in case of an unplanned emergency, similarly to what happens in hydrocarbon terminals. An ESD system normally includes fast-response valves, loading arms coupled with emergency release systems and it will be operating automatically in relation to some key operational parameters. For instance, initiation can be caused by an atypical tank pressure, level or a leakage at the terminal or ship. An ESD should always employ appropriate safety protocols. As previously noted, low-pressure shipping systems near the triple point are associated with high uncertainty and propensity for dry-ice and hydrate formations in case of depressurisation of the system, and thus maintaining a robust safety margin from the triple point is recommended. Accordingly, Noh et al. [154] undertook a preliminary hazard analysis (PHA) in the CO_2shipping chain and identified the unloading system and storage tanks as the highest-risk components in the storage terminal. With reference to the unloading system, they found that the extensive implementation of ESD systems throughout the terminal, coupled with low- or high-pressure alarms can successfully reduce the risk of low-temperature gas and solid phase leak caused by failure of the unloading arms and recirculation line. An ERS could mitigate the risk of CO_2 leakage in case of rupture or mechanical failure of the unloading arm or recirculation line; and for the CO_2 storage tanks, the integration of process safety valves, level gauges and alarms can aid in minimising the damage caused by CO_2 leakage in case of rupture or overpressure of intermediate storage vessels. The study can be considered a point of reference to generate a safe CO_2 transportation infrastructure in future commercialisation of CCUS technology.

The rate of incidents relating to large-scale CO_2 carriers cannot be determined due to lack of commercial implementation; experience with CO_2 pipelines systems suggests that failures are mostly related to third-party interference, corrosion or material defects. However, similarly to pipeline applications, current empirical data on operations are insufficient to establish the failure probability of a system with the same accuracy as for hydrocarbon systems [131]. The rate of incidents for different types of carriers was investigated by Doctor et al. [34] as showed in Table 21. One advantage of CO_2 transport is that it exhibits lower risk from fire in comparison to LPG/LNG tankers. CCUS infrastructure is considered to be at lower risk from fire due to the fact that carbon dioxide is non-flammable, though the risk of hypercapnia and hypercarbia and even asphyxiation during collision and related tank rupture cannot be ruled out. This risk can however be reduced by applying rigorous standards of construction and operation in LPG to carbon dioxide shipping [34].

According to De Visser et al. and Det Norske Veritas [102,155], potential impurities such as CO, amines, NOx and glycol should also be considered when making health and safety assessments, with H_2S and SO_2 implying significant additional measures. Managing the presence of such impurities is possible through more sophisticated emergency response and training which inevitably result in higher capital and operational expenditures. The Health and Safety Executive [153] found that the hazard distance for an unplanned discharge from a vessel may be up to 400 m when large, cold, liquid phase stored inventory is considered. However, there is considerable uncertainty in the models of releases of liquid, cryogenic CO_2; this implies the need for experimental investigations.

Table 21
Rate of incidents for different types of carriers [34].

Ship type	Number of ships (2000)	Serious incidents (1978–2000)	Frequency (incidents/ship year)
LPG tankers	982	20	0.00091
LNG tankers	121	1	0.00037
Oil tankers	9678	314	0.00144
Cargo/bulk carriers	21,407	1203	0.00250

In case of a carrier accident the liquid CO_2 tanker would release the fluid onto the water surface, and despite the fact that interactions with the environment are not completely understood at this stage, potential formation of dry ice and hydrates are expected. Release of liquid-phase CO_2 inventory into the atmosphere is followed by a phase transition as the media releases; Vermeulen [36] indicated that the release rate of liquid CO_2 will be regulated by the differential pressure between the tank and the environment, the size of the crack, and the nature of the vessel's failure as well as the receiving medium. A greater pressure differential leads to a greater release velocity such quick dispersion will result in a high-speed, cryogenic stream that can result in cryogenic burns and impact injuries to personnel caught in the jet of gas and/or a 195 K solid phase [156]. Additional considerations on material selection must be made in order to maintain process integrity. Carbon dioxide tends to pool and in case of strong winds, this could cause asphyxiation or affect engine performance rupture or failure of a vessel will result in an expansion of the inventory to ambient pressure, which has a remarkably high initial momentum due to loss in expansion energy. Upon release, the liquid phase will gradually make a transition to a two-phase gas and solid mixture. As illustrated in Fig. 19, during releases with liquid phase starting points (A and B), solids will form depending on the rate of enthalpy change: the closer this intersection to the vapour line, the lower the proportion of CO_2 solids. Prediction of potential solid CO_2-accumulation regions is important to develop appropriate safety protocols and dispersion behaviour will be strongly affected by ambient conditions, including wind speed. Experimental investigations are still required to comment on the reliability of these prediction models in real scenarios. Han et al. [157] undertook experimental work on the behaviour of liquid inventory during loss of mechanical integrity of a CO_2 container. Here the focus of this work was the investigation of flow characteristics in CO_2 carriers, and it was found the liquid inventory must be promptly discharged to avoid operational issues by applying a 'jettisoning' process. During this operation, the liquid carbon dioxide undergoes two distinct phase transitions – the first one from liquid to liquid + vapour and the second from liquid + vapour to solid + vapour. These phase changes dictate the dispersion behaviour as the phase transition into solid and vapour takes place irrespective of the length of the experimental pipe. Moreover, the magnitude of pressure change is related to the friction pressure drop rather than due to the momentum pressure drop. An experimental validation of liquid CO_2 release at pressures of 4–5.5 MPa was performed by Pursell [158]; however, this work did not consider leakage and discharge behaviour of liquid carbon dioxide relevant to CO_2 shipping near the triple point, such as 0.7–1 MPa and 220 K to 226 K. Wetenhall et al. [91] found that dispersion behaviour in the case of a release in both pipeline and ship systems can be affected by the presence of impurities, although no further assessment was made in their work.

In some instances, the high evaporation rate of carbon dioxide into ambient air can cause a BLEVE that ruptures the containment vessel [159]. An empirical study focusing on the rapid decompression of liquid CO_2 in a vertical tube found that for a pressure of 3.5 MPa and 5.5 MPa, a velocity of 20–30 m/s for the liquid–vapour occurs [160], though thermodynamic-related properties could not be obtained due to lack of temperature and pressure measurements. Experimental work has also been performed by Van der Voort [161] using liquid CO_2 bottles of 40 L capacity in order to determine the temperature dependence of BLEVE occurrence; a homogenous nucleation temperature of 271 K was determined, although even below such temperature the risk of BLEVE only decreases, but does not completely disappear. Low-pressure CO_2 shipping, both for the storage at terminal and shipping cargo conditions of

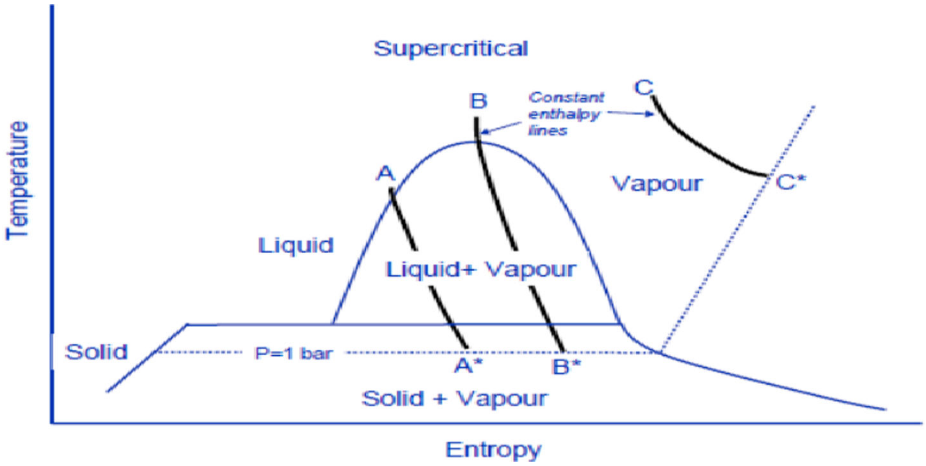


Fig. 19. Thermodynamic path of CO_2 release [36].

223 K and 0.7 MPa, is considered to be subject to low-risk of BLEVE as there is little potential superheat available. However, the risk of BLEVE cannot be dismissed when medium- and high-pressure CO_2 shipping (1.5 MPa, 248 K and 4.5 MPa, 283 K, respectively) are considered.

The non-flammable nature of CO_2 prevents the ignition and acceleration of boil-off gases in generating further BOG, and as a result, a CO_2 BLEVE is also known as a 'cold BLEVE' [67]. Large-scale experiments are required to validate available models and develop appropriate risk assessments [162].

A preliminary assessment finds liquid CO_2 releases to have a significantly less stringent long-term impact on the environment in comparison to oil spills, although interactions with marine environment can lead to pH changes and generation of hydrates. Dispersion of the release due to effect of the wind may result in failure of the ship's engine [34].

10. Environmental impact assessment

10.1. Shipping emissions and control measures

The black smoke produced from a ship plume visibly indicates the adverse effect of shipping on the environment; in fact, exhaust emissions are estimated to contain 450 different compounds [163], including greenhouse gases, water vapour, nitrogen and sulphur oxides, non-combusted hydrocarbons, and particulate material. The majority of ships today use residual fuel (e.g., HFO) mainly because of its low cost, and this is a major cause of air pollution [164,165]. Marine pollution was not considered in the Paris Agreement, but it is a significant concern that must be addressed. Approximately global GHG emissions from shipping operations amounts to 1.1Gt [17,166], a consequence that cannot be avoided due to the need to meet rising energy demand and a vast increase in population growth. The third greenhouse gas study by the IMO stated ship transport accounted for 2.6% of global anthropogenic CO_2 emissions in 2012 [16,167]. In comparison to the 3.5% determined for 2007, this reduction resulted from slow steaming and increase in vessel size [16,168].

Despite this improvement and considering a business-as-usual scenario with no further measures taken to mitigate shipping emissions, future emissions are expected to rise between 50% and 250% by 2050 as a result of economic growth and development (see Fig. 20) [16,169,170]. Within 400 km of land, shipping-related emissions [171] cause morbidity and death to several millions [172,173]. More surprisingly, it was recently concluded that aerosols from ship engine exhaust contributed to storm intensification and increased lightning activity in the north-eastern Indian Ocean and the South China Sea, which represent two of the busiest shipping lanes in the world [174]. It is, therefore, important to reduce these effects, possibly using alternative source of fuels and abatement methods to reduce emissions. A report by Element Energy et al. [38] quantified the amount of CO_2 emissions in terms of ship size and distance (assumed fuel type is LNG). In Fig. 21, CO_2 emissions were expressed as a percentage of transported CO_2, and it can be seen that higher emissions occur when very small ships are used (1 kt CO_2) resulting in high numbers of trips and longer distances travelled.

The IMO has decided to adopt a strategy to reduce CO_2 emissions by 2050 to half its 2008 levels. This was considered early 2018 and was the first time the shipping industry has defined a strict limit on carbon emissions similar to the Paris Agreement. Required actions for the implementation of the IMO initial GHG strategy have been classified into different measures, one of which is the adoption of new reduction mechanisms [175]. A mechanism or innovative direction which has not been fully explored is the use of carbon capture technology whilst combusting fossil fuels [166]. Combustion of marine fuels contributes nearly 2.3 Mt of sulphur dioxide, which is 13% of global emissions [16,168,176]. Residual fuels represents 72% of the total fuel consumed in 2015, whilst the remaining is accounted for by distillate fuels and natural gas [165] (Fig. 22). The bulk of ship owners use HFO and MGO, containing a sulphur content of 3.5% and 0.1% respectively [177]. Certain regions known as the sulphur emission control areas restrict high sulphur content fuel usage as compared to other areas. The IMO Marine Protection Committee reduced the global sulphur content limit of 0.5% on bunker fuels (from the previous 3.5%) (Fig. 23), this year. The sulphur content limitation and the adopted strategy for CO_2 emissions reduction gives examples of strong enabling policies in the shipping industry that can spur on innovations to tackle the climate challenge [178].

Han [180] classified mitigation measures for shipping emissions into the following, technological, market-based and operational. Retrofitting or upgrading older ship infrastructure with more efficient ones are classified as a technological measure. Operational measures involve modifying vessels operations while on sea or at dock. Market-based strategies are designed strategically to ensure polluters pay for what they pollute (emission trading systems), thereby leading to the deployment of operational and technological measures. Some of these measures are listed in the section below for corresponding carbon and sulphur emissions, as there is no single or best solution that fits all ship types [181]. Bunkering infrastructure availability and engine modification are amongst many challenges that can result from the change to alternative fuel options such as natural gas or biofuels, in pursuance of global sulphur limit [182]. At the same time there is an accelerating worldwide trend towards reducing CO_2, NO_X and particle emissions. All of these justify the search for sustainable technologies that can help the shipping industry to solve the challenges ahead.

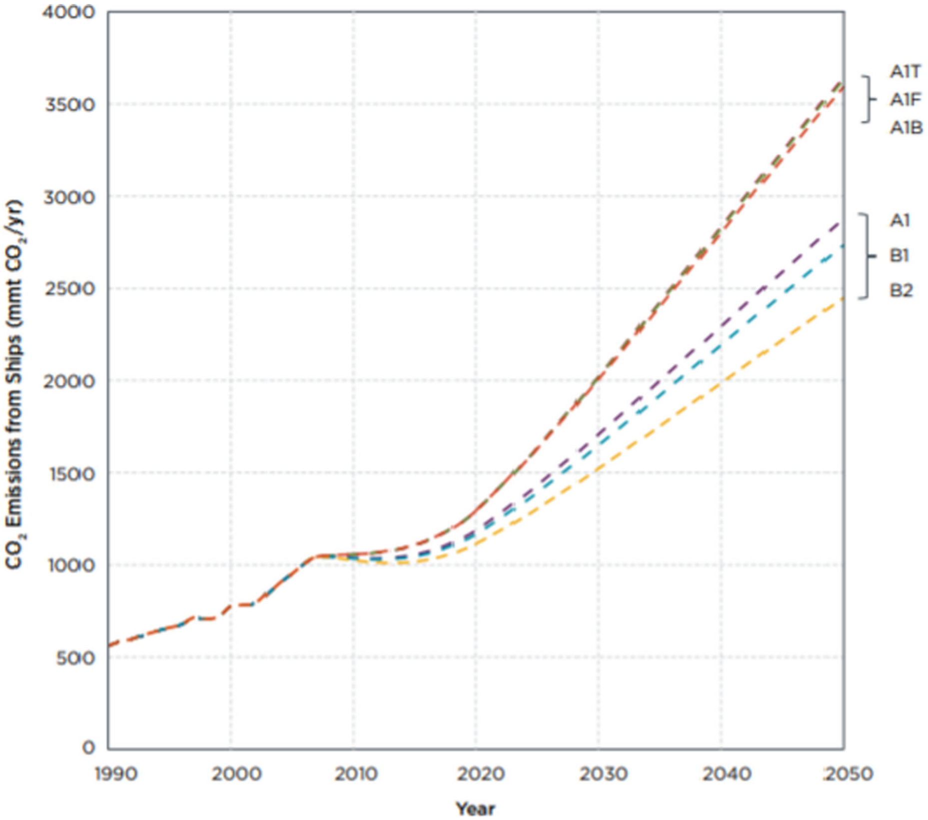


Fig. 20. Projections of maritime CO_2 emissions from shipping [16,169,170]. A1F, A1B, A1T, A2, B1, B2 are emission growth scenarios based on global differences in population, economy, land use and agriculture. The six scenarios were used by the IMO expert group to form six growth scenarios for the shipping industry.

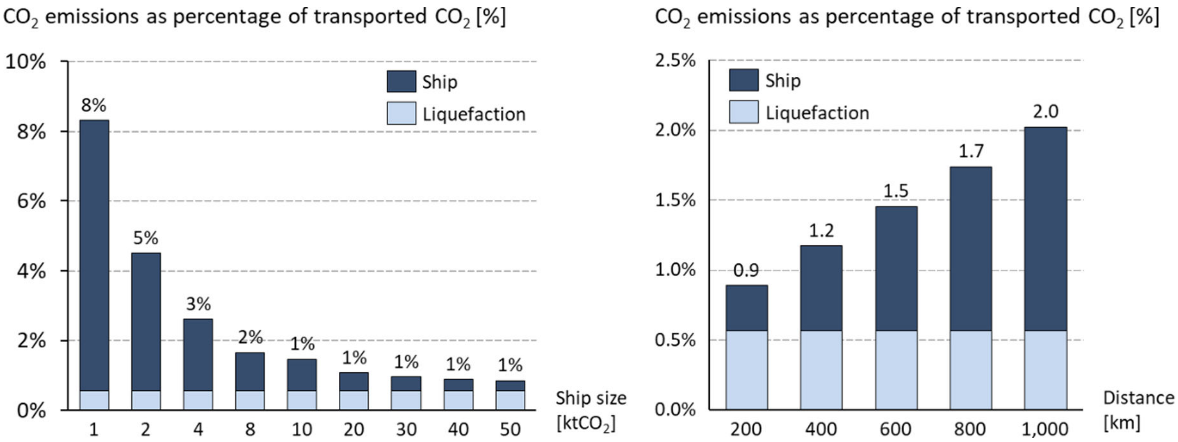


Fig. 21. Emissions from CO_2 shipping (ship fuel combustion and liquefaction) [38].

10.2. Emission control measures

10.2.1. Carbon emissions

The generation of carbon emissions is due to fossil fuel combustion. Most ship engines operate on oil-based fuels (residual or distillate fuels) depending on the size. Large commercial vessels like cargo ships use HFO while smaller ones operate on distillate fuels. In 2008, two measures were introduced by IMO to address the sector's GHG emissions, the Ship Energy Efficiency Management Plan (SEEMP) and the Energy Efficiency Design Index (EEDI). SEEMP is directed towards methods that can spur on better energy efficiency methods and the EEDI measures are a set of standards for newly built ships. EEDI is compulsory for ships manufactured after 1 January 2013 [183]. Regardless of the adoption of energy efficiency standards, in the EU by 2050, 86% increase of CO_2 emissions above 1990 levels is expected if no action is taken [184]. For this reason, in 2015 the European Union Monitoring, Verification, and Reporting (EU MVR) regulation was inaugurated and adopted for reducing maritime GHG emissions. It is expected to reduce CO_2 emissions for every journey covered within the EU zone by up to 2% [18]. Every shipping company must report its annual carbon emissions and quantity of fuel consumed within the EU area; data collection started in 2018 [184]. The IMO CO_2 Data Collection System (IMO DCS) was also taken on in 2016 to collect fuel consumption for all ships and this began officially in 2019. The EU MVR and IMO DCS lays out strategies to diminish carbon emissions from ships. With the current technologies and combination of measures, emissions can be reduced by more than

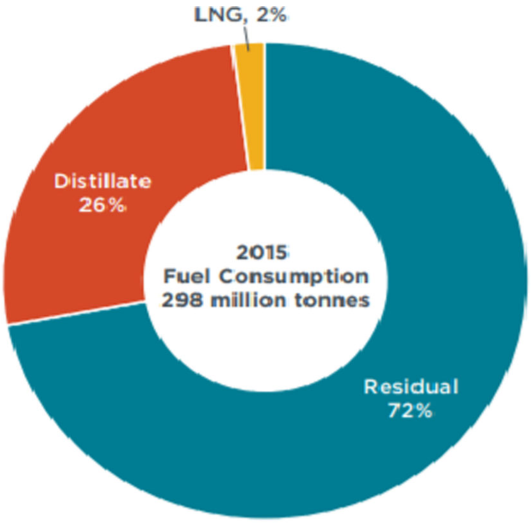


Fig. 22. Fuel consumption by global shipping fleet in 2015 [165].

75%, if policies and regulations are focused on achieving these reductions [168]. The options below show the current status of different pathways that can be taken in achieving carbon reduction, with their effectiveness and gaps.

- Alternative fuels

Switching to alternative fuels with lower life-cycle emissions (production, refining, distribution and consumption) automatically results in the reduction of carbon emissions [170,185]. Ships are very fuel-efficient compared to other modes of transport [170], but the HFOs used by almost 80% of the world's shipping fleet is problematic [18]. It is more carbon-intensive than other fuels (Fig. 25) and produces other air pollutants. Fuels of the diesel quality are the most used in the shipping sector (HFO, low sulphur HFO and low sulphur distillates fuels), vegetable oils and biodiesel are potential fuels (but are not produced in sufficient amounts for global needs), similarly bio-fuels can offer lower CO_2 emissions compared to conventional HFOs [170,185]. With the 2020 global cap on sulphur, most ships will end up burning more refined oil grades in the near future because they are cleaner and produce fewer polluting emissions. Solid fuels such as the coal were used to fire steam boilers but these are now almost entirely restricted to heritage vessels [186]. Amongst gaseous fuel, LNG has been identified as having a lower life-cycle of CO_2 emissions than HFOs [170,185]. The use of alcohols as a marine fuel is not yet widespread, but they can serve as a suitable alternative to high-sulphur fuels, thereby reducing carbon footprint of shipping operations. Methanol is widely available and used in chemical industry and can be produced from either natural gas or biomass (bio-methanol). This can also be regarded as a future-proof fuel to reduce GHG emissions, unlike LNG or conventional fuels. Fig. 24 below describes the two type of ship fuels characterised with lower life cycle emissions.

a. LNG

Natural gas has a negligible sulphur content and higher hydrogen-to-carbon ratio when compared to diesel fuel types. This culminates to a 20–30% lower CO_2 emissions on combustion [187]. LNG is thus, often considered as a future fuel because it complies with the strong regulations currently in force. LNG offers CO_2 savings compared to HFO, but this highlight the importance of methane slip according to life-cycle assessment studies [178,179,188]. Methane slip (2–5%) has been reported for LNG engines, although it is lower for dual- fuel 2-stroke engines (high-pressure) [189,190]. The reduction of methane emissions cannot excluded when appropriately considering LNG as a GHG reduction strategy, and application of best practices for methane control in the LNG supply chain could yield 10–27% GHG reduction compared with conventional fuels [191], although, usage may be limited due to the lack of LNG in harbours worldwide. Worldwide, there are only 67 (as of April 2018) LNG supply locations in operation, 26 decided and 38 planned [192]. The majority of these locations are in Europe, the rest include Asia, America, Middle East and Oceania. The greater the spread of various LNG supply locations across the world, the more ship owners are likely to use LNG propulsion, as the LNG price seems attractive. The price of LNG is lower than MDO and HFO (Fig. 25), but there is much uncertainty with respect to the cost of new LNG infrastructure and variable gas price [21].

There were about 247 LNG fuelled vessels in operation or on order as at April 2018 [192], the majority of which will be in the EU considering large expansive emission control areas (ECAs) (Fig. 26). For vessels sailing majority of their time in ECAs, LNG propulsion is a reasonable choice compared to those that spend less than 5% of their time [193]. Vessels that spend shorter periods of time in ECAs, switch to MDO or other distillate fuels and some continue to use HFO whilst in non-ECAs. Economic incentives and targeted policies are likely to be necessary to ensure worldwide uptake of fuel change to LNG [21]. The use of LNG has been identified as achieving annual cost savings for different emission reduction levels (economic and environmental) when compared to other

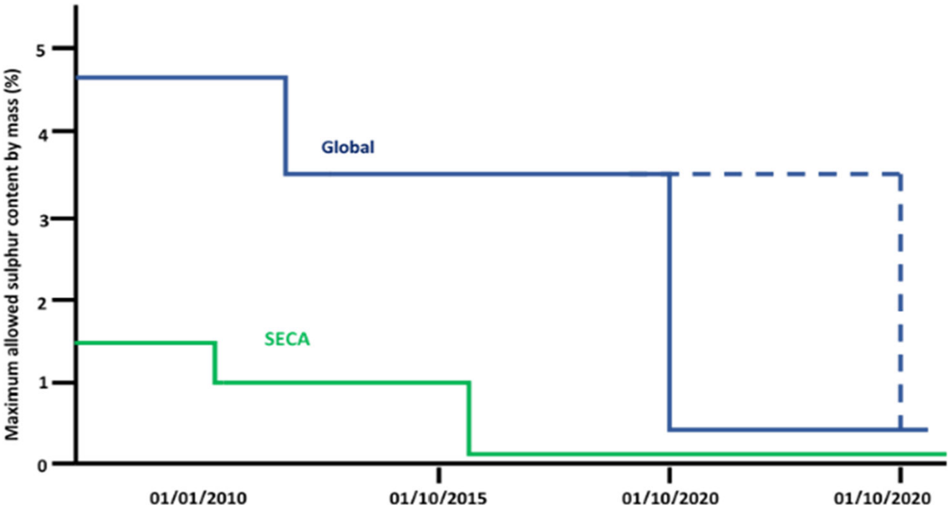
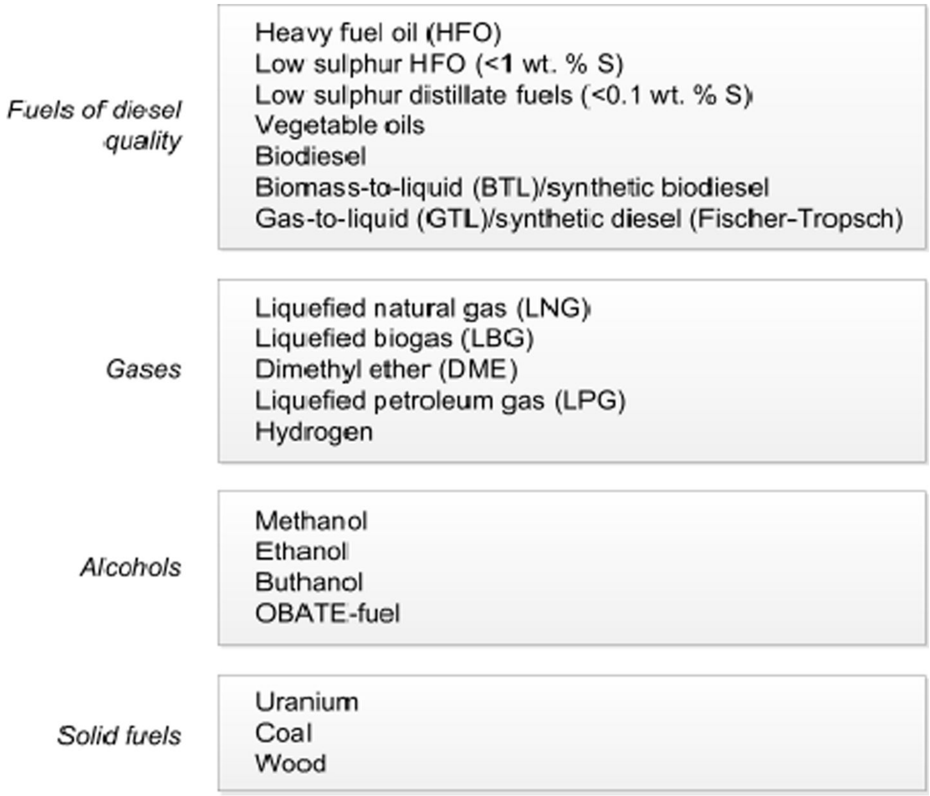


Fig. 23. IMO regulation on sulphur content in bunker fuels [177].



Fuels of diesel quality	Heavy fuel oil (HFO) Low sulphur HFO (<1 wt. % S) Low sulphur distillate fuels (<0.1 wt. % S) Vegetable oils Biodiesel Biomass-to-liquid (BTL)/synthetic biodiesel Gas-to-liquid (GTL)/synthetic diesel (Fischer-Tropsch)
Gases	Liquefied natural gas (LNG) Liquefied biogas (LBG) Dimethyl ether (DME) Liquefied petroleum gas (LPG) Hydrogen
Alcohols	Methanol Ethanol Buthanol OBATE-fuel
Solid fuels	Uranium Coal Wood

Fig. 24. Marine current and future fuel types [179].

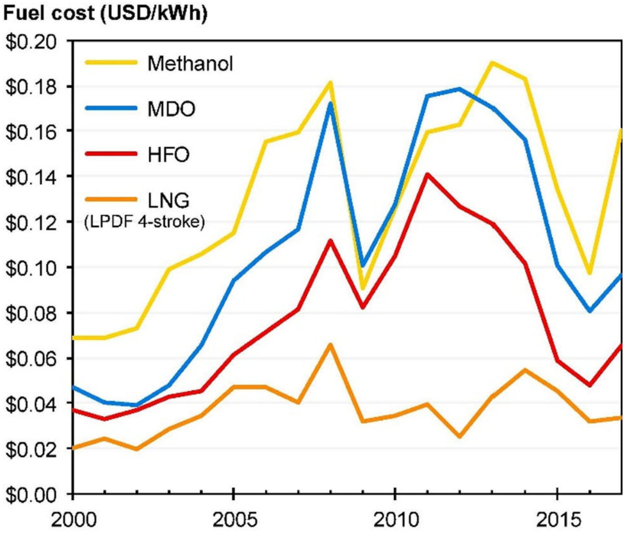


Fig. 25. Marine fuel costs for different fuels in $/kWh of engine output [21].

strategies on a passenger ship [194].

b. Biofuels

The combustion of biomass if used in a sustainable way, emits the same amount of CO_2 as was captured by the plant during photosynthesis, therefore these have been considered by researchers as a potential marine fuel [195]. First-generation biofuels such as hydrotreated vegetable oil (HVO), straight vegetable oil (SVO), fatty acid methyl ester (FAME), and bio-ethanol are available for use; however, large scale production is constrained due to sustainability issues [21]. Second-generation biofuels are generated from non-food biomass and have a lower GHG emissions than conventional biofuels. They include pyrolysis oil, lignocellulosic ethanol (LC Ethanol), bio-ethanol, Fischer-Tropsch diesel (FT-diesel), etc. Biofuels based on using microalgae appear to be promising because cultivation can be achieved close to ports and less refining is needed [196]. Diesel-like biofuels can be used in ships requiring minimal engine modifications and can also use the same bunkering infrastructure. Biofuels can offer NO_X, SO_X and PM emissions reduction and are biodegradable as compared to fossil fuels; that is, if they escape to the environment they are easily biodegradable [195,197]. The limitations to biofuel uptake are cost and availability. The price for FAME and HVO were 1040 $/t and 542 $/t respectively in 2017, which is more than double the prices of LNG (270 $/t), HFO (290 $/t) and MDO (482 $/t) [198]. Second-generation biofuels costs are much higher due to the complexity in the production process. Availability of biofuels is dependent on the utilisation of resources such as food, water, land space and fertilisers for growing crops (first- and second-generation). These resources must be managed to minimise a negative impact on the broader agricultural system [170,185,199]. Strong GHG reduction policies or carbon pricing are needed in order for them to gain a competitive advantage with fossil fuel alternatives [21].

- Energy efficiency

The EEDI aims to optimise fuel consumption through the development of efficient equipment for new ships, in essence, improving energy efficiency by changes in ship design such as propulsion systems, hull superstructure, design speed and capability. Ship owners can currently meet the SEEMP's demand for increased level of energy efficiency by various operational measures such as speed reduction, voyage optimisation, ballast and trim optimisation, bulbous bow, using existing larger ships, hull cleaning, coating and lubrication, weather routing, cargo load factor increment, increasing energy awareness, regularly scheduled polishing and autopilot adjustment [18]. The state-of-the-art technologies or routes used to achieve energy efficiency, classified into design

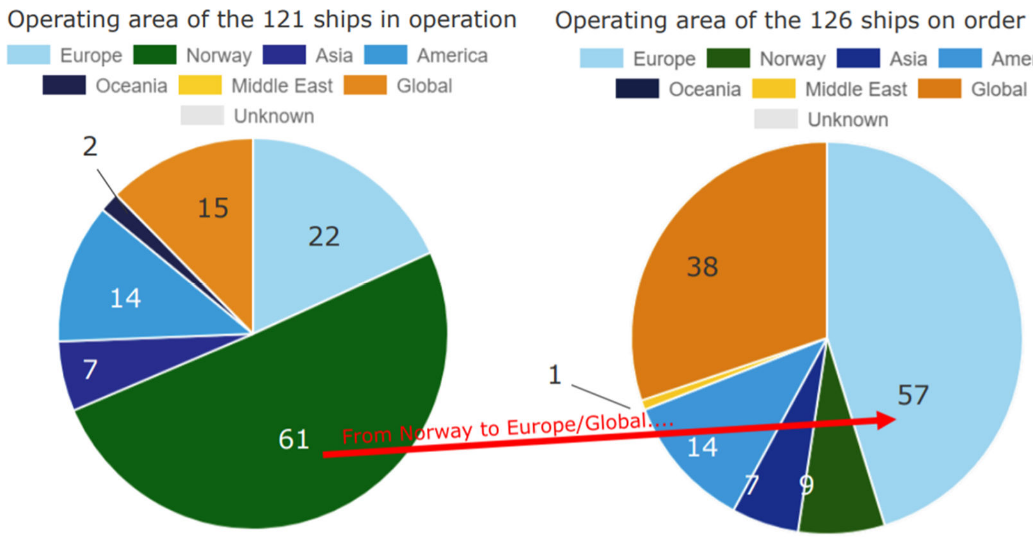


Fig. 26. LNG fuelled vessels in the world (Operating areas) [192].

and operational measures [16,170,185] and they are explained below.

a. Concept, speed and capability

The design of the beam and draught (key parameters), size and speed have significant impact on a ship's energy efficiency [170]. The average lifetime of a ship may exceed thirty years, retrofitting operations should be considered at the design stage in order to achieve flexibility in operations. The speed for which a ship is designed can be changed due to specific reasons such as increased fuel costs and lower freight rates [185,200]. For instance, large container vessels, initially designed for 25 knots speed or greater have been changed after 2008 to 21–23 knots as a result of increased fuel costs and lower freight rates [201]. This subsequently reduces the cost and emissions per freight unit transported; however, high-value goods sometimes demand higher speeds [21], which might be compensated by being airfreighted, which unfortunately increases total emissions. A weakness with the state-of-the-art design practice regarding concept, speed and capability, is the dependence on improving existing designs instead of challenging today's practice [201]. Although, reducing the design speed is applicable to all vessels, it has low-to-medium payback time [200]. The global uptake of speed reduction requires regulation, and market-based mechanism (tax levies or cap-trade systems) [202] and would also be difficult to enforce [203,204].

b. Hull design

Hull design measures focus on reducing resistance during operation and improving propulsive efficiency [170]. Vessel size increase, hull shapes, bow optimisation, light-weighting, hull coating, use of resistance reduction devices and lubrication are different measures used to reduce emissions per unit transport work in hull design [168]. This abatement technology is applicable to all ship types and available on the market [185].

c. Power and propulsion systems

The generation of power on-board is done either by low- or medium-speed diesel engines. Energy efficiency in propulsion engines can be attained in different ways. Old engines can either be upgraded or replaced, recovery of energy from exhaust gases can either be used for steam or electricity generation or both [170,205]. Energy recovered in the exhaust gas can be effectively used to drive auxiliary machines resulting in 12% savings on fuel consumed and hence, CO_2 emissions [206]. Bouman et al. [168] classified different measures such as propulsion-efficiency devices, hybrid power propulsion, on-board power demand, power system/machinery, and waste heat recovery, already in force for cutting down CO_2 emissions. They estimated that the potential reduction of emissions by these measures is low, reflecting the challenges in implementation, especially for hybrid propulsion systems.

d. Fleet management, logistics and incentives

Energy efficiency can be improved by the choice of the right kind of ship. Thus, for example, using larger ships wherever possible reduces energy consumption. Fuel consumption per tonne mile is higher for smaller ships than for larger ships; therefore, fuel savings can be generated provided there is sufficient demand for transport [185]. Reducing wait time and quicker turnaround times in ports; through efficient port procedures cut back on fuel usage, is becoming the rule in most ports [205].

e. Voyage optimisation

Voyage optimisation means finding the shortest route possible between the port of embarkation and delivery within several constraints like weather, currents and wave data, vessel characteristics, logistics, scheduling and other contract arrangements. Weather routing, advanced route planning, ballast and trim optimisation and just-in-time arrival are measures used to minimise energy consumption whilst cutting back on fuel usage and emissions [170,205]. Efficiency improvements based on these measures are highly variable and difficult to access because shipping operations vary distinctly [170]. McCord et al. [207] concluded that fuel savings of 11% can be achieved for a 16-knot vessel (in a case study) by utilising the ocean currents.

f. Energy management

Energy management is necessary to reduce the on-board energy consumption. Besides the power needed for propulsion, electric power is essential for auxiliary operations and sustenance of the crew. Certain cargoes require refrigeration or heating. The heat could either be supplied by the steam boiler or from the exhaust [205]. Exhaust gases can be used to operate absorption air conditioning units as a heat recovery application [194]. To achieve the reduction of on-board energy consumption, the following are some measures taken to ascertain optimal operation: economiser cleaning, steam and compressed-air systems leakage detection, optimisation of steam plant, waste heat recovery, use of fuel cells, optimisation of fuel clarifier/separator, optimised heating, ventilation and air conditioning operation on board, and electric power integration [170]. Upgrading to automation and process control for temperature and flow control may help to reduce energy consumption, but this varies distinctively on different ship types.

- Renewable energy sources

Renewable energy sources can be generated either on board ships (wind, solar and wave) or onshore for storage while berthed. Wind power has been exploited in various ways such as kites, sails, and Flettner-type rotors [170,199,205] and the annual emission reduction potential for their use on board are in the range of 5–10% [208]. The placement of solar cells on ships with sufficient deck space has been tried. The Japanese Nissan car carrier, Nichioh Maru, with room for 1380 cars has its deck space covered with 281 solar panels, powering LED lights to the accommodation quarters. For this reason, the need for a diesel-fuelled generator was eliminated, resulting in consuming 13 t less fuel for the round trips (twice every week) [209]. Measures focusing on wind energy were observed to have higher reduction potential than for solar energy, although this is strongly dependent on ship size, route and surface area [168,210]. Energy can also be generated on-shore to power ships while at berth, this is called cold ironing and is also known as Alternative Marine Power [205]. This is applicable to any ship size, reducing local air pollution considerably, but is dependent on the travel time spent in ports. Fuel cells are also another abatement option that can be used to replace part of the energy supplied by the auxiliary engines [205]. The only products produced are water, heat and electricity, eliminating pollution caused by burning fossil fuels. The vessel Viking Lady, for example, has a fuel cell installed producing a significant part of the energy that would have been produced by the auxiliary engines, hence reducing CO_2 emissions by 20% and also eliminates SO_X and soot emissions [211].

- Emission reduction technologies – Carbon capture, storage and utilisation (CCUS)

There are various emission-reduction technologies available for reduction of CO_2 from exhaust gases such as absorption processes, use of membranes and solvents [212], but none has been considered commercially viable for ships. One challenge currently recognised is that current CCUS methods used on land cannot be used on ships due to the impact on their performance. The increase in power consumption and the amount of space required for CCUS equipment to be installed must be considered to minimise their impact [213]. Pre-, oxy- and post-combustion are the three major capture processes that can be considered. The integration of any of these processes excluding post-combustion, on a ship requires significant changes to the energy system of the ships. Application of a post-combustion process will require little or no change to the engine type, but instead, to the flue gas treatment equipment processes [22]. Det Norske Veritas and Process Systems Enterprise (PSE) described a process for capturing CO_2 emissions on-board ships. Publicly available result estimates the capability of the process in reducing carbon emissions is of the order of 65% [214]. The concept consists of a SO_2 scrubber and a CO_2 capture process using an amine solvent (Fig. 27). A solidification process has been proposed for storage on-board ships to minimize the effect of the unavoidable movement caused by ocean waves [213]. The CO_2 emitted forms a stable compound, precipitated calcium carbonate, stored safely on-board or unloaded whilst onshore. Another solvent-based process was developed by Luo and Wang [215] to capture CO_2 emissions from a medium size cargo ship. The level of capture achieved was 73% using the available utilities on-board. A gas turbine was added to increase the level of capture to 90%. A study was carried out on a LNG-fuelled vessel to capture CO_2 from the exhaust emissions, the vessel's length was increased by 6 m accommodating the additional separation equipment [216]. A study also has evaluated the use of aqueous ammonia for the combined removal of CO_2 and SO_2 on-board for HFO fuelled ships and only CO_2 removal for LNG fuelled ships [147,148]. The thermal energy of the exhaust gas was used to regenerate the solvent to minimise utility cost. An inland and a cargo vessel fuelled by either LNG or diesel was also investigated to analyse the effect of a potential capture system integration using piperazine and aqueous monoethanolamine (MEA) solvent [217]. It was concluded that piperazine offered a lower cost of capturing CO_2 compared to MEA, due to its higher desorption pressure for both vessels. The cost of capture is dependent on the ship size, the fuel used and the selected capture rate and technology [217]. Integrating a CCUS system on-board requires extra capital cost and expansion due to retrofitting, although this could be reduced if the captured CO_2 can be sold to be used in greenhouses or in the food industries [218]. Owing to a literature gap, there is a need to understand the effect of a capture system integration on a ship for CO_2 reduction in terms of cost and other operational measures.

10.2.2. Sulphur emissions

The main source of sulphur emissions is from the fuel; sulphur content is higher in residual fuels than distillates because residuals are the heaviest fractions obtained from a refining process. Sulphur dioxide emissions annually from the shipping industry is about 2.3 Mt, and due to their solubility in water, sulphur compounds cause acidification, affecting marine life and human health [16,166]. The 70th session of the Marine Environment Protection Committee in 2016 organised by the IMO has set a mandatory limit to the amount of sulphur content in marine fuels used globally, reducing it from 3.5% to 0.5%, this took effect in January 2020 [177]. This can be considered as an extension of the 0.1% sulphur cap in ECAs. The ECAs include the North Sea, Baltic Sea, the English Channel, around the US Caribbean Sea with the North coastlines [219]. The reason for the difference in the global and the stricter regional limits can be considered as a compromise to attain a global limit and meet concerns of acidification over sensitive environments [18]. The European Union Directive 2012/33/EU is another regulation scheme that considers the reduction of sulphur content in marine fuels. This directive incorporated all the dates and limits included in the revised MARPOL 73/78 Annex VI in 2008 with the exception that the 0.5% global limit will be mandatory in the EU waters [220]. The directive also prohibits the use of marine fuels of 3.5% sulphur content with the exemption of ships running in a closed mode operation emission abatement methods [220]. Currently, fuels used at berth have a sulphur content of 0.1% and this is still the case in EU ports. In order to reduce sulphuric emissions from shipping, three abatement options have been identified, namely: retrofitting of scrubbers to allow continuous use of HFO; fuel switching to de-sulphurised residual fuel oils; or switch to alternatives (LNG and methanol) [221]. Each distinct abatement method is dependent on the ship owner's choice with regard to cost. Rynbach et al. [181] identified three primary fuel alternatives (HFO + scrubbers, MGO and LNG) for use in the ECAs and worldwide, as compared to HFO, for SO_X reduction, but in conclusion, they stated that no single option fits all ship types. The impact on performance, service requirements, costs and benefits of various options are currently weighed by ship owners to determine the best choice [181].

1. Switch to low-sulphur fuels

In a refinery process, the crude fractions that remains after the extraction of lighter fractions is called residual fuels [222]. However, in compliance with the sulphur limit, vessels must run on fuels with less than 0.5% sulphur content (marine gas oil or diesel oil). This is the easiest option for most ship owners because no engine modification is necessary [18]. In ECAs, low sulphur fuels are regularly used. Some vessels operates a hybrid type solution that allows the flexibility of switching between high- and low-sulphur fuel considering the areas they operate in [221]. The decision to sell residual fuels has been an option

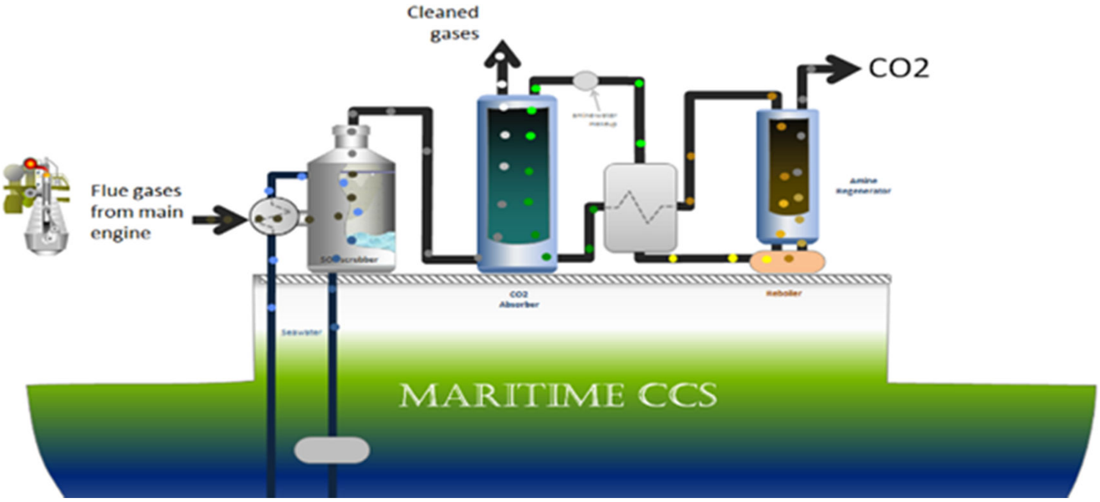


Fig. 27. Process schematic for the carbon capture process on a typical vessel [214].

for refineries to installing process equipment needed to convert them into distillates. But in order to meet this demand, desulphurisation and conversion capacity of refineries would need to increase to ensure adequate availability for the shipping sector [223].

2. On-board scrubbers

On-board scrubbers are an alternative approved by IMO in meeting the sulphur regulation [194]. The continuous use of high sulphur fuel is allowed only if a scrubber is attached to the exhaust system of the ships [205]. This has been readily deployed on ships and is available in the form of dry and wet scrubbers. Dry scrubbers mostly use calcium-related materials to react with sulphur while the wet scrubbers (open, closed and hybrid) use alkaline containing liquids, usually sea water. Positive results on scrubber installations on ships and high removal rates have been reported by Warsitila and Lloyd’s Register [25,224]. The treatment is in line with the IMO Exhaust Gas Cleaning Systems Guidelines for pH, turbidity, polycyclic aromatic hydrocarbons, and temperature [225]. Sodium hydroxide combined with freshwater can be used as the scrubbing medium in closed-loop scrubbers. The freshwater flow rate can be approximately 20 m^3/MWh [25]. The wash water is recirculated in contrast to the open-loop system. The hybrid scrubber combines both principles. It can be operated as open and closed mode at sea and in sensitive areas respectively. The most common types installed on ships are the hybrid and open-loop scrubbers [226]. Dry scrubbers use calcium hydroxide pellets instead of wash water, and its power consumption is 10% of a wet scrubber mainly because of the absence of wash water [227]. The use of scrubbers is a maturing technology for ships, the cost of scrubbers starts at the price of 1.5 million USD (dependent on engine size) [222], this is lower compared to prices experienced in previous years [25,228,229]. However, the energy consumption increases by 2% when using a scrubber compared to using low-sulphur fuels [222]. The use of scrubbers is developing rapidly, spurred on by the global sulphur limit, thus for instance, Hyundai is set to install them on 19 of its ships [230].

3. Alternative fuels

LNG has no sulphur content and meets the IMO 2020 regulation without any further restrictions. LNG fuel can be seen as an insurance against possible future tighter regulations, although it is more expensive compared to the use of scrubbers, and it completely eliminating sulphuric emissions. Retrofitting existing vessels is costly because of the extra storage capacity needed, typically 3–5 times more space is needed for fuel storage than for the conventional HFO [21,231]. Dual-fuel marine engines exist, therefore, they can accommodate MDO, MGO and LNG [232]. However, reduction in methane emissions is needed if LNG is to contribute to the reduction of both GHG and sulphuric emissions [21].

11. Future developments and challenges

11.1. Shipping for CCUS

Until recently, a crucial impediment to the implementation of CO_2 shipping was the London Protocol, a regulating agreement which impeded cross-border transport of CO_2 for CCUS. The amendment of the London Protocol at the 14th meeting of the Contracting Parties in October 2019 means that Contracting parties are now able to choose to legally transport CO_2 across their borders; moreover, no additional legislations and regulations are deemed to pose any significant constraints to transnational shipping of CO_2 [63].

Several operational challenges are still associated with large-scale CO_2 shipping, mainly due to lack of implementation of CCUS projects, though none of them are considered project-stoppers (Table 22). Maintaining CO_2 in liquid phase near the triple point on both ship and terminal during loading and unloading is the main challenge faced during real operations; therefore, appropriate safety protocols will need to be implemented to reduce the risk of dry ice formation and preserve the integrity of the system. This is particularly relevant to transport conditions at lower pressure, in proximity to the triple point, where lack of implementation prevents a thorough understanding of the reliability and risks of real operations throughout the chain. When considering other technical challenges such as BOG, the IMO gas code allows for venting of gaseous streams in order to maintain required pressure and temperature. Overall, there appears to be a dearth of process safety protocols and projects addressing the impact of impurities on system integrity of CO_2 shipping systems for CCUS. In order to make a successful transition to real, commercially relevant scenarios, further experimental work is required to assess the effect of potential impurities – including simple binary mixtures – on phase behaviour of CO_2, while modelling work on more complex mixtures and compositions is still required [13]. Determination of the solubility of water in CO_2 with the presence of N_2 and H_2S content is key to maintain integrity of the systems yet still needs further attention. Generally, the lack of commercial implementation makes it difficult to accurately assess some critical technical aspects – such as offshore offloading and direct injection from the ship – and determining the reliability of cost estimations in the literature. As such, demonstration projects could provide invaluable information and facilitate commercialization.

Table 22
Uncertainties associated with ship transport of carbon dioxide [35].

Challenge	Remarks
Direct injection	Uncertainty of the logistical arrangements and investment of the required process units in compliance with maritime regulations.
Maritime regulations	Technical challenges related to ship construction for high-pressure operating conditions. A regulatory classification would be required to permit the use of LNG as fuel and avoid the vessel being classified as an LNG transport carrier
Ship dimensioning – flexibility	Enhancing flexibility is challenging in medium and high-pressure solutions due to the limited scale of the vessel. Low-pressure solutions are associated with a higher degree of flexibility with regards to ship dimensioning.
Interface capture/ storage	Low pressure conditions imply higher conditioning costs and more stringent engineering solutions to handle the CO_2 in the liquid state. Medium and high-pressure state exhibit fewer complex operations and lower conditioning costs

Despite this, the risk surcharge of the new technology is expected to decrease significantly after five projects, similarly to the experience with LNG ships [38]. However, unlike LNG and LPG and except for EOR, CO_2 is perceived as a waste product, so it is anticipated that CO_2 shipping will require government incentives to generate a business framework and build momentum in the industry.

Optimisation of the energy requirement in the chain would be relevant, particularly in relation to the liquefaction stage, which is the most energy intensive and thus costly element in producing a suitable CO_2 stream for transportation. The potential for recovery and utilisation of the cold energy prior to offloading, is also currently being explored; however, this can potentially require an additional offloading hub [56].

The construction of storage tanks that can be submerged or situated on the seabed, thus acting as a heat exchanger to heat the CO_2 up prior to offloading can lower and mitigate the required heating duty on-board. Despite the numerous technical challenges associated with this approach, particularly in relation to material selection, its successful application would result in less stringent energy requirements and, thus, cost savings in the shipping chain.

As shown in Fig. 28, Aspelund and Gundersen [70] proposed a more complex 'Liquefied Energy Chain' in the power industry that combines natural gas production with CCUS. Natural gas is liquefied along with the captured carbon dioxide. Liquid nitrogen production is a possibility if oxy-fuel combustion is employed (as it is continuously produced in the air separation unit that generates liquid oxygen for the oxy-fuel combustion system. The liquefied natural gas, CO_2 and N_2 are transported on the same ship. Offshore, the cold energy from the liquid nitrogen and carbon dioxide are used to liquefy natural gas in the field, allowing for the CO_2 gasification, heating and injection at high pressures to EOR fields; LNG can then be transported back to the power plant. The cryogenic exergy in LNG is utilised to liquefy CO_2 and nitrogen produced because of injection and EOR activity, thereby forming a closed loop. This results in added efficiency and optimised investments but relies on suitable logistics and the presence of all the required elements within an appropriate distance. Zhou and Wang [213] proposed and analysed a novel chemical process for carbon solidification (CPCS) technique for carbon dioxide on-board storage as $CaCO_3$ (calcium carbonate). Potentially, calcium carbonate can be reused or sold as a by-product in the construction and plastic industries, albeit that it is a relatively low-cost material; CPCS can overcome challenges such as high requirement for storage tanks, ship instability, safety margin of liquefied CO_2 near the triple point in the light of higher density and profits from selling the end product. Additional studies are, however, required to verify current experimental results and scale-up the process.

Despite the indicated technical and operational challenges, near-future developments appear to have unlocked the potential of CO_2 shipping. Thus, Japan is set to deploy sea vessels to transport carbon dioxide, seeking to become among the first players to commercialise such technology for mitigating effect global warming [233]. Similarly, Norway launched the 'Northern Lights' full scale CCUS demonstration which will collect form 3 industrial emitters and transport 400,000 tons of carbon dioxide per year by means of ships [71]. In the UK, the Acorn project [84] has synergies with the 'Northern Lights' and aims to establish a European CO_2 transportation infrastructure and import emissions from other European countries via shipping, thus building the required momentum in CCUS.

11.2. Management and reduction of emissions from ships

While shipping is least energy-intensive way to carry goods compared to other transport types, GHG emissions are increasing due to global economy growth. The challenge is to meet the rising demand while at the same time curbing dangerous emissions. With the emergence of these regulations (IMO 2020 limit and the initial GHG strategy), ship's energy efficiency for both new and old are required to improved using different measures [175,177]. The second IMO GHG study proposed several measures that ship operators could adopt [170], but their uptake is dependent on the impact on the company's performance, cost effectiveness and emission reduction potential [234,235]. Several studies have shown the various existing measures with a range of emissions reduction potential [168,170,185,236]; however, the rate of implementation is rather slow for existing fleet, implying the need for more stringent regulation [168,199,235]. Extracted data [168] from 150 reviewed studies on technical and operational measures on CO_2 emissions reduction potential is shown in Fig. 29. The solid horizontal

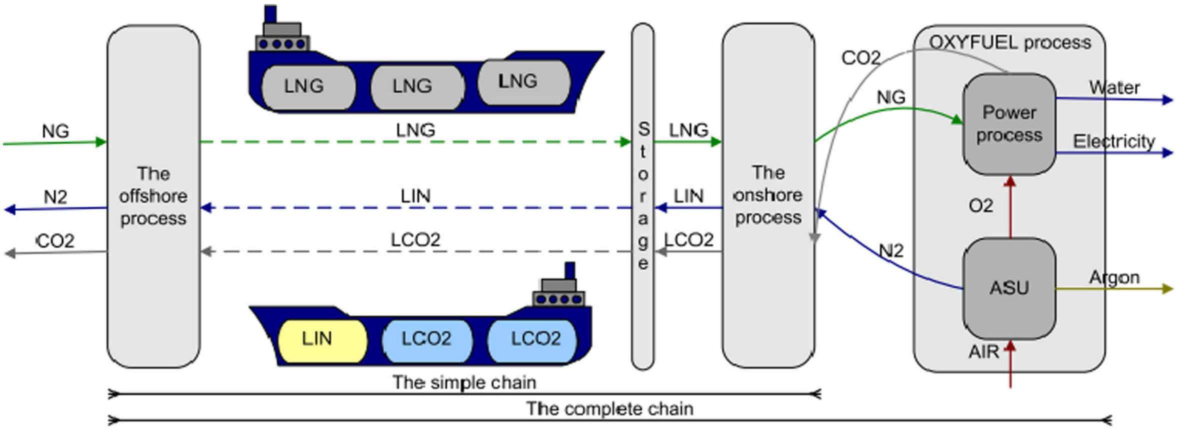


Fig. 28. Schematic representation of the liquefied energy chain [70].

bar represents the entire range of potential CO_2 reduction for the measures discussed, but the widest range for each measure indicates poor agreement in the literature due to some limitation in studies on vessel type and different model assumptions [168,237]. This level of performance uncertainty together with investment costs for some measures indicate the challenges of steering the industry towards a low–carbon direction. The CO_2 reduction cost for technical measures ranges between 50 and 200 $/t on average (Fig. 30) [238] exceeding the emission-trading price in the US [237]. The decision to implement cost-intensive technical measures is dependent on the commitment and risk a company is willing to take [235]. With adequate financial support from the government via incentives, companies are likely to implement measures with very siginificant fuel consumption and emission reduction effects.

Another immediate concern for the shipping sector is in addressing the global fuel sulphur content limit; fuel switching to low-sulphur fuels and the use of LNG (likely solutions) to tackle this challenge do little to address CO_2 emissions in the longer term [199]. The use of LNG provides a short-term measure for reducing carbon emissions but not in the long term. Its use also provides the opportunity to address the challenge of sulphur and CO_2 emissions together. If CO_2 is not considered, the effort taken to meet the current sulphur regulation could hinder future measures for reducing CO_2 emissions [239]. Scrubbers are also used to curb sulphur emissions; and considered the only solution that enables ship owners to have their cake and eat it. However, the use of open-loop scrubbers, a type of wet scrubbers, emits approximately 45 tons of acidic and contaminated wash water and heavy metals into the ocean [240]. A short-sighted approach for tackling sulphur emissions without the thought for carbon emissions can be avoided by the use of post-combustion capture.

There is no single silver bullet solution sufficient to achieve the considerable shipping sector-wide reduction; instead, combinations of solutions including alternative fuels, energy efficiency, operational measures, renewables and exploration of CCUS potentials are needed. Some technologies that could offer co-benefits in the reduction of CO_2 and SO_2 emissions are energy storage and fuel cells; these can be used for small vessels operating in coastal waters [168,237]. Also, wind-assisted propulsion can be used on vessels operating on the high seas [168]. In the exploration of new technologies and retrofit options, ship owners should identify solutions that satisfy the sulphur limit whilst in the short term without limiting the potential for GHG reduction in the longer term. For instance, LNG use should be integrated with CCUS and the necessary fuel supply infrastructure is also made capable of supporting low-carbon fuels such as biogas, hydrogen or ammonia in the future.

The Integrated Green Energy Solution has developed a solution for the global crisis of plastics in waterways. The first plastic-to-fuel factory is being built and located at the port of Amsterdam. This project would turn an estimate of 35,000 Mt of non-recyclable plastic waste into 30 million L of fuel annually, preventing 57,000 t CO_2 annually and, thereby, giving value to materials that would ordinarily go to waste [241,242]. The fuel produced by the plant would be sold to the maritime industry. Innovative and urgently needed technology that will enable

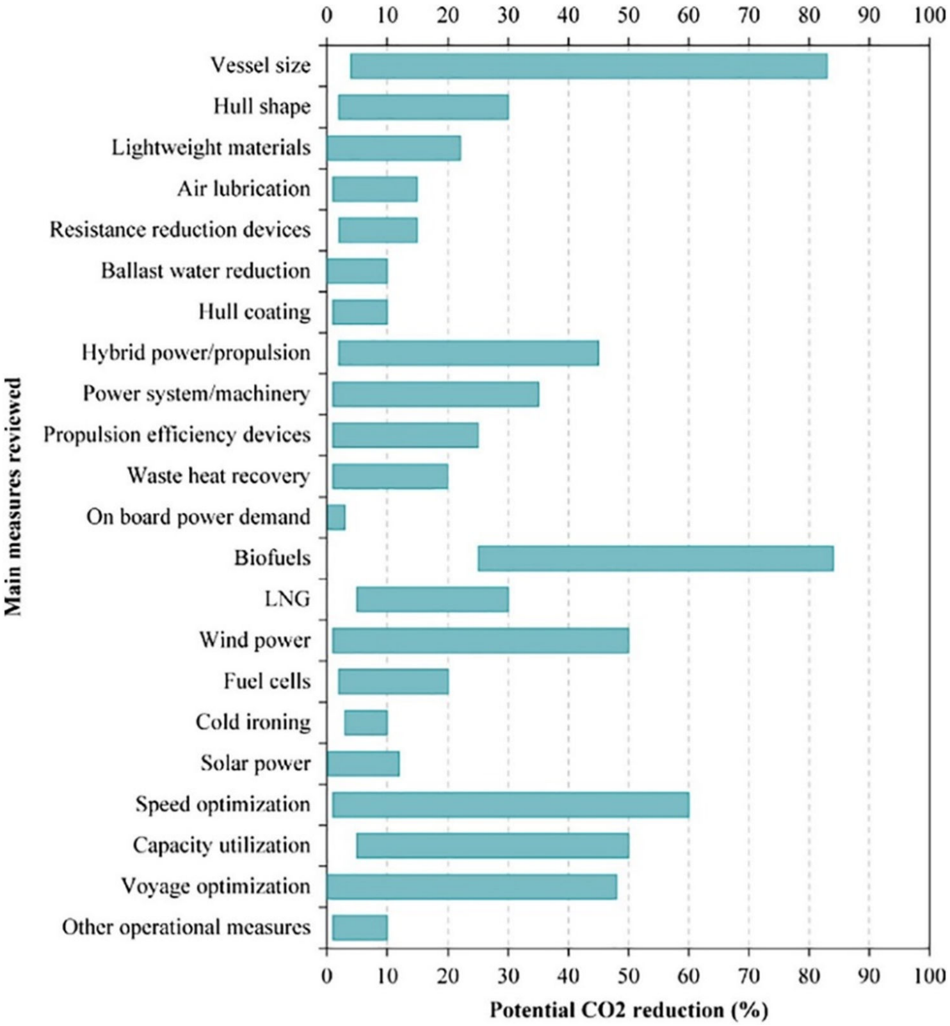


Fig. 29. Potential CO_2 reduction from an array of technical and operational solutions [168,237].

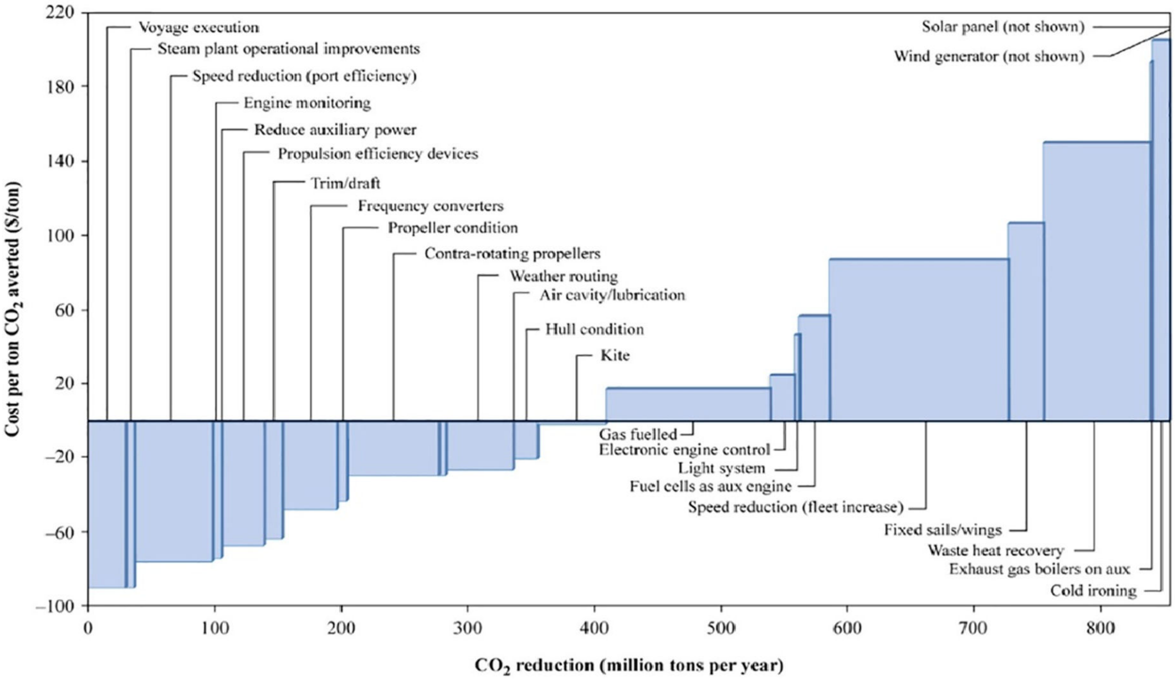


Fig. 30. CO_2 cost reduction cost per option for existing and new builds – world shipping fleet in 2030.

the shift from reliance on fossil fuels and addressing the challenge of plastic waste should be a political priority.

Nonetheless, in order to reduce CO_2 emissions from large carrier vessels, a project called ‘Wind Challenger Project’ has been developed by the University of Tokyo and its industrial partners with the aim of utilising ocean wind energy for the propulsion of a cargo carrier. This will be achieved by integrating large rigid sails made of light composites on the upper deck, which are expected to generate enough forward thrusts to drive an 180,000 deadweight tonnage carrier at a speed of 22 km/h when the wind velocity is 43 km/h. Preliminary field studies suggest that 30% of the propulsion energy can be obtained from the wind [243].

12. Conclusions

As CCUS builds momentum in industry and establishes its role as a significant carbon reduction technology, CO_2 shipping will likely have a key role in supporting its execution in the UK and worldwide. Despite some technical and operational gaps, the implementation of carbon dioxide shipping can facilitate early de-carbonisation in numerous countries and industries. No major drawbacks have been highlighted in the literature in relation to the implementation of this technology, although demonstrational projects are necessary to build confidence in the supply chain and demonstrate continuous operations. Moreover, the use of flexible carrier ships can turn CO_2 transport and storage into a profitable industry for countries which have significantly higher storage capacities than they require, particularly after the abolishment of the constraints previously posed by the London Protocol.

Carbon dioxide shipping often has lower costs than the equivalent pipeline project, depending on size, location and duration of the project, as well as transport distances and pressure specifications, with ship and liquefaction dominating the costs. However, it is characterised by high operational expenditures and fuel costs and, therefore, carbon dioxide shipping exhibits its cost-effective potential relative to pipelines when short duration projects characterised by low flowrates and longer distances are considered.

The key challenges to be addressed are mainly operational, and include amendment of existing regulations, mainly the London Protocol – and the establishment of a viable business model. However, due to the lack of experience with carbon dioxide shipping at the required scale, demonstration projects will be required to meet port restrictions in preparation for the implementation of any dedicated infrastructure in the longer term. It is expected that government incentives and economic strategies will be essential to build momentum in the CO_2 shipping industry, especially because, unlike the LNG and LPG fields, carbon dioxide is perceived as a waste rather than a valuable product.

CO_2 shipping has the potential to extend de-carbonisation to those countries and industries where CCUS is essentially infeasible due to geographical or infrastructural reasons and reduce the cost of early projects through its sink-source matching, low up-front capital expenditure requirement and high degree of flexibility. With countries such as Japan, Norway and the UK now actively seeking to commercialise large scale CO_2 shipping as part of their decarbonisation strategies, near-future developments appear to be promising.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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