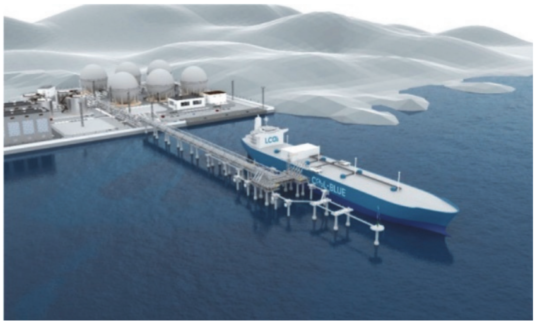
Development of Liquefied CO_2 Carriers and Onboard CO_2 Capture Systems for Realization of Carbon Neutral Society



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Mitsubishi Shipbuilding Co., Ltd. is developing liquefied CO_2 carriers as a means of transporting CO_2 for establishment of a Carbon dioxide Capture, Utilization and Storage (CCUS) value chain, and onboard CO_2 capture systems to reduce CO_2 emissions from ships. In the development of liquefied CO_2 carriers, we select materials for the tank system, design the structures and create the operation process from the perspective of optimizing the entire CCUS value chain, and in the future, we will establish the technology by building a demonstration ship, which will be the world's first liquefied CO_2 carrier for CCUS. As for onboard CO_2 capture systems, we will continue further development toward commercialization based on the results of the demonstration of a capture system conducted in a demonstration plant in fiscal 2021. Through these activities, we will provide the optimal total solutions for business operators that aim to realize a carbon neutral society.

1. Introduction

Mitsubishi Heavy Industries Group (MHI Group) is making various efforts toward "energy transition" for the realization of a carbon neutral society. In addition to the low carbonization of existing technologies and the utilization of new energy such as hydrogen and ammonia, we are working on the development of technologies related to the CCUS value chain, which not only captures CO_2 but also stores or converts it to other usage, with the aim of building a CO_2 ecosystem. It is expected that the CO_2 capture amount required to realize a carbon neutral society will reach 4.3 to 13 billion tons per year in the world in 2050. We anticipate growing demand for liquefied CO_2 carriers as an economical means of transporting this enormous amount of CO_2 to locations where it will be stored or converted to other usage. This report presents, with a particular focus on the liquefied CO_2 carriers, the state of the technological development so far and future prospects.

2. Characteristics of CO_2 and technological requirements for carriers

CO_2 is a colorless and odorless gas that is slightly heavier than air at room temperature and atmospheric pressure. For ocean transportation of CO_2, it is desirable to liquefy it to reduce the volume in the same way as LNG (Liquefied Natural Gas) and LPG (Liquefied Petroleum Gas). When liquefied, the volume of CO_2 becomes about 1/500 of gaseous CO_2. As shown in the phase diagram of CO_2 shown in **Figure 1**, to liquefy CO_2, it needs to be refrigerated and pressurized to 0.52 MPaA or higher. Therefore, for ocean transportation of liquefied CO_2, it needs generally to be kept in a temperature range of -55°C to -20°C and a pressure range of a little less than 1.0 MPaA to 2.0 MPaA. For this reason, materials with high strength and suitable low temperature characteristics are required for a liquefied CO_2 storage cargo tank. Generally, the Type-C tank system that conforms to the pressure vessel standard among the independent tank systems specified in the IGC code (formal name: The International Code for the Construction and Equipment of

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Ships Carrying Liquefied Gases in Bulk) is applied.

If the pressure and temperature of liquefied CO_2 fall to the triple point shown in Figure 1 during operations such as transport and loading/unloading, dry ice may be generated, which may cause operational problems such as blockage of piping. Therefore, within the pressure and temperature condition range of the transported liquefied CO_2 described above, it is necessary to select actual design condition in consideration of various factors.

For example, to reduce the risk of dry ice generation during operations, it is generally desirable to transport liquefied CO_2 with the pressure kept as high as possible to provide a sufficient margin against the triple point. However, in such cases, the cargo tank needs to be able to withstand relatively high pressure and its size is limited from a structural strength standpoint. On the other hand, to improve the transportation efficiency, it is desirable to keep the liquefied CO_2 pressure as low as possible to increase relatively the volume of the cargo tank. However, in such cases, the liquefied CO_2 during transportation and loading/unloading will be under conditions closer to the triple point, so careful attention is required during operations to prevent the generation of dry ice caused by the conditions falling to the triple point. In addition, since the triple point is generally affected by the properties (impurity composition) of CO_2, it is necessary to consider the difference in properties between pure food-grade CO_2 and CO_2 captured from plants for CCUS.

Furthermore, the density of liquefied CO_2 is larger than that of other liquefied gases, about 1.1 ton/m^3 to 1.2 ton/m^3, and the draft of a CO_2 carrier tends to be deeper, so it is necessary to develop a ship dimension that takes into consideration the compatibility with existing terminals.

In this way, in the development of liquefied CO_2 carriers, it is necessary to select the conditions for liquefied CO_2 to be transported, as well as the optimum ship and cargo conditions throughout the CCUS value chain, consider the appropriate cargo tank material and structure, and develop process designs and operational processes to avoid or mitigate the risk of dry ice generation.

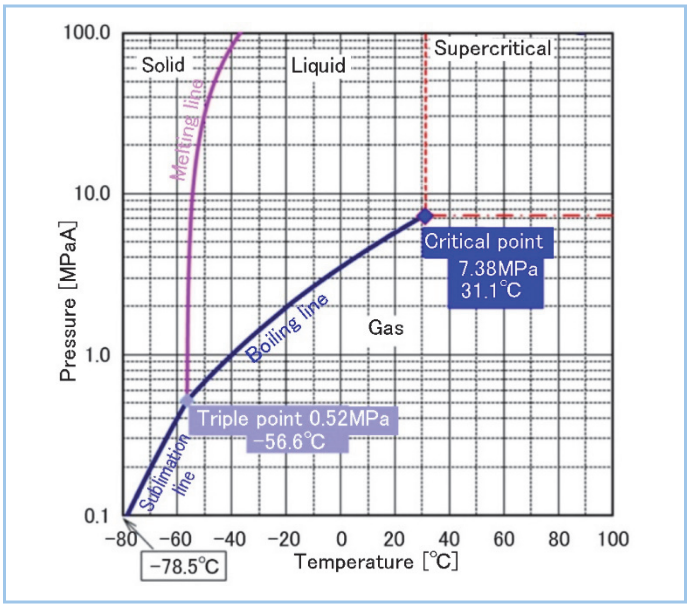

Figure 1 CO_2 phase diagram
In order to be liquid state , CO_2 needs to be kept in a low-temperature and high-pressure state.

3. Technological development status of liquefied CO_2 carrier

We have been studying liquefied CO_2 carriers in anticipation of the times so far, utilizing its knowledge of advanced structural analysis technology, material evaluation ability, and gas handling technology cultivated through the building of liquefied gas carriers (LNG carriers and LPG carriers), and also participated in the IEA (International Energy Agency) Greenhouse R&D program in 2004 to study sea transportation of CO_2. In particular, in response to the growing expectations of the CCUS value chain for the realization of a carbon neutral society in recent years, we are accelerating the development of various technologies in order to bring liquefied CO_2

carriers to the market soon. The following sections describe the development status of a cargo containment system and cargo handling system as examples.

3.1 Development of cargo containment system

As described above, since it is necessary for the liquefied CO_2 carrier to keep the cargo, CO_2, in a low-temperature and high-pressure state, materials having high strength and suitable low temperature characteristics are used for the cargo containment system. Possible material options include heat-treated steel, low-temperature steel, and Ni steel, and the most suitable material from the viewpoint of safety and economy varies depending on the liquefied CO_2 transported and the conditions required for the ship. We have acquired abundant and extensive knowledge of steel materials for ships, including knowledge of materials applicable for low-temperature conditions obtained through the development of liquefied gas carriers and knowledge of high-strength materials obtained through the development of large containerships. Also in the development of liquefied CO_2 carriers, we are selecting the most suitable materials for the cargo containment system quickly and accurately to meet various demands that differ depending on the customer and the market.

Although the Type-C independent tank system specified in the IGC code, which is generally adopted for cargo tanks of liquefied CO_2 carriers, is well proven for small LPG carriers, etc., the adoption of this tank type to liquefied CO_2 carriers requires appropriate consideration of the impact of greater specific gravity of the liquid cargo (more than twice compared to LPG). For this reason, we ensure the reliability of the entire cargo containment system by conducting detailed numerical analysis of structural strength including the tank support structure (**Figure 2**).

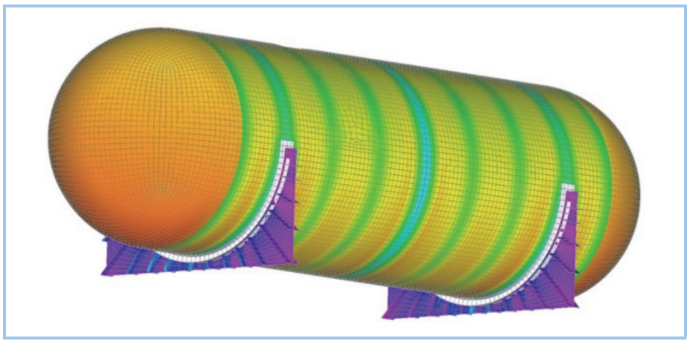

Figure 2 Example of structural strength analysis of liquefied CO_2 cargo tank
Detailed analysis including the tank support structure is carried out to ensure reliability.

Furthermore, one of the issues for onboard transportation of liquid cargo that needs to be fully considered and requires measures is sloshing, which is a phenomenon where the fluid inside a tank oscillates greatly when the tank is fluctuated by external forces. Especially in the case of liquid cargo carriers, the fluid load due to sloshing increases when the period of the ship motion and the natural period of the free surface in the tank are synchronized, which may damage the structure and other fittings inside the tank. Since the specific gravity of the liquid also affects the fluid load (pressure) generated when this sloshing occurs, we conduct detailed numerical simulation by using Computational Fluid Dynamics (CFD) calculation (**Figure 3**). First, the ship motions are estimated under various sea conditions, and then the sloshing behavior in the cargo tank excited by the ship motion is predicted by CFD calculation. Based on the result thereof, the pressure of liquefied CO_2 acting on the structure and other fittings inside the tank is appropriately evaluated and necessary measures are taken.

In addition to the examples shown above, we conducted comprehensive technical verifications such as appropriate evaluation of the effects of thermal stress caused by low-temperature cargo. As a result, our cargo containment system for liquefied CO_2 carrier has obtained Approval in Principle (AIP) from Bureau Veritas.

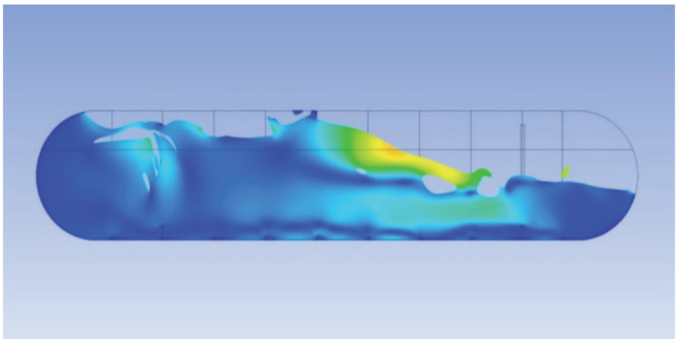

Figure 3 CFD sloshing simulation of liquefied CO_2 cargo tank
Predicting sloshing behavior due to ship motion and evaluating the generated pressure

3.2 Development of cargo handling system

As explained in chapter 2, the onboard transportation of liquefied CO_2 needs to maintain conditions that can provide a certain margin against the triple point in the phase diagram. Since liquefied CO_2 during transportation and loading/unloading is subjected to various changes in conditions (pressure and temperature) in the cargo tank and piping, it is necessary in various operation processes to properly anticipate changes in the conditions and give consideration so that transportation and loading/unloading can still be carried out without causing the conditions to fall to the triple point.

Therefore, we have conducted dynamic process simulations in various operations to identify risks that the pressure or temperature of the liquefied CO_2 falls to the triple point, and consider measures against the risk. For instance, **Figure 4** shows examples of data variations at unloading operation obtained by a simulation using a process simulator ASPEN PLUS DYNAMICS. This simulation model consists of elements such as tanks, pipes, valves, cargo pumps and vaporizer, and the characteristics of each element are properly applied.

In this way, now we are continuously studying to predict liquefied CO_2 behavior in detail generated in each part of the handling system in various operations and to incorporate them into process design and handling operations of liquefied CO_2.

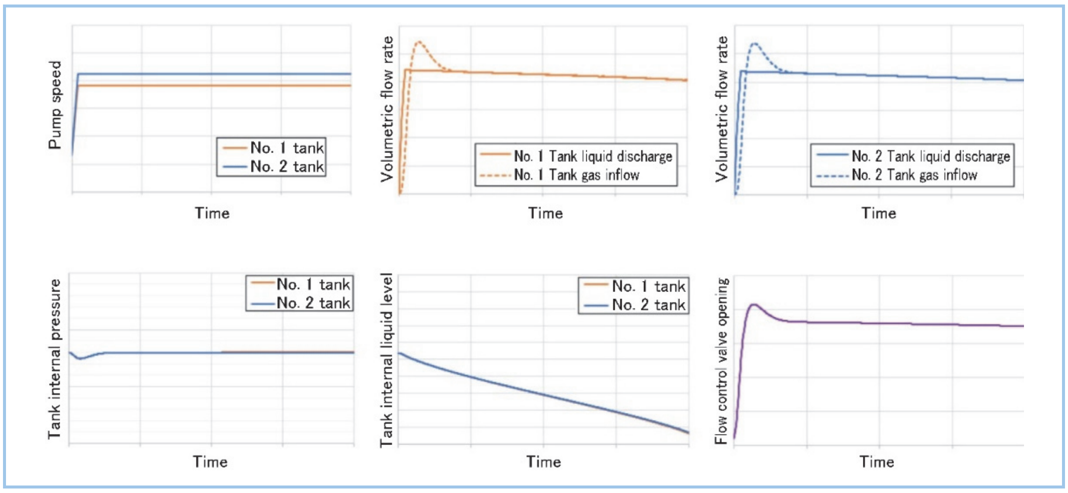

Figure 4 Examples of data variations at unloading liquefied CO_2
Predicting changes in the pressure, etc., during operation and avoiding the risk of dry ice generation

4. Initiatives in liquefied CO_2 transportation demonstration project for NEDO

We have signed a contract with Sanyu Kisen K.K., which performs ship management for domestic and ocean-going ships and other business, to build a demonstration ship for liquefied CO_2 transportation to be used in Research, Development and Demonstration of CCUS Technology, Large-scale CO_2 Capture and Storage (CCS) Demonstration Testing at Tomakomai, and CCUS R&D and Demonstration Related Project / Large-scale CCUS Demonstration Project in

Tomakomai / Demonstration Project on CO2 Transportation by New Energy and Industrial Technology Development Organization (NEDO). Table 1 shows the principal particulars of the demonstration ship, and **Figure 5** shows the schematic external view.

This NEDO project aims to establish liquefied CO_2 onboard transportation technology for realization of large-capacity and long-distance CO_2 transportation. Engineering Advancement Association of Japan, one of the contractors of the NEDO project, will charter the demonstration ship from Sanyu Kisen K.K.,and transport liquefied CO_2 for the project.

The demonstration ship will be delivered in the second half of fiscal 2023 prior to a liquefied CO_2 carrier built for the Norwegian "Northern Lights Project", one of the world's leading CCS (CO_2 capture and storage) projects, and is expected to be the world's first liquefied CO_2 carrier for CCUS.

We are in charge of the entire design and construction of the demonstration ship, including the cargo tank system installed thereon, utilizing the knowledge cultivated so far in the construction of liquefied gas carriers.

In the development of the demonstration ship, we will develop a cargo management system that can deal with the technical issues mentioned in chapter 2, especially the CO_2 component unique to CCS, which has properties different from those of food, for avoiding and responding immediately to the generation of dry ice, and install it on the ship. Then we will verify the effect of the development during the subsequent demonstration period to establish the world's first large-capacity and long-distance CO_2 transportation technology.

Table 1 Principal particulars of liquefied CO_2 demonstration test ship for NEDO

Registration	Japan
Length overall	72.0 m
Beam	12.5 m
Draft	4.55 m
Tank capacity	1,450 m^3

Figure 5 Conceptual image of the liquefied CO_2 demonstration ship for NEDO
Establishing the world's first large-capacity and long-distance CO_2 transportation technology through the demonstration project

5. Development of onboard CO_2 capture system

As part of the above-mentioned MHI Group's aim of building a CO_2 ecosystem, we are also working on the development of onboard CO_2 capture systems to reduce CO_2 emitted by ships. This chapter introduces our latest initiative related thereto, an onboard CO_2 capture system demonstration project “CC-Ocean (Carbon Capture on the Ocean)”[*1], which was jointly implemented with Kawasaki Kisen Kaisha, Ltd. and Nippon Kaiji Kyokai.

In this project, we conducted a demonstration test of a small-scale CO_2 capture demonstration plant (hereinafter, demo-plant) under commercial operating conditions, which was the first time in the world, by installing the demo-plant on a coal carrier "CORONA UTILITY" operated by Kawasaki Kisen, Ltd. in order to verify CO_2 capture technology offshore and deal with requirements for onboard use of the technology.

The project was conducted over a two-year period. A HAZID evaluation of the demo-plant and a safety evaluation of the equipment and system were conducted by Nippon Kaiji Kyokai, and then the demonstration plant was fabricated, installed on the coal carrier, and operated in an offshore environment for approximately six months for measurement and checking of the performance. The demo-plant installed on the coal carrier is a CO_2 capture system that is originally for onshore plant exhaust gas treatment employing the chemical absorption method and has been converted for onboard installation. **Figure 6** shows a schematic illustration of the demo-plant.

In this project, the demo-plant achieved higher performance values than planned for CO_2 capture amount, CO_2 capture rate and captured CO_2 purity, and the equipment could be operated and maintained by the crew of the coal carrier without any problem. We also verified the effects of engine load fluctuations and ship motion on the CO_2 capture performance and the effects of exhaust gas on the CO_2 absorbent. We summarized the guidelines for safety measures associated with ship operations, such as measures against leakage of the CO_2 absorbent, ventilation concepts for equipment installation areas, etc., as requirements for operating CO_2 capture systems in an offshore environment.

In the future, based on the knowledge and technical issues obtained and found in this demonstration, we will promote efforts toward the commercialization of the onboard CO_2 capture system through establishing the concept of the entire system including liquefaction and storage onboard, examining the optimization of the system as an offshore system, considering the unloading of CO_2 onboard to land, etc.

*1 This project is supported by Assistance Project for Research and Development of Technological Advancements in Marine Resource Development, a project subsidized by the Maritime Bureau of the Ministry of Land, Infrastructure, Transport and Tourism.

Figure 6 Illustration of installed small demonstration plant of onboard CO_2 capture system
We were the first in the world to demonstrate CO_2 capture onboard and confirm the performance.

6. Conclusion and future prospect

This report described liquefied CO_2 carriers' role in the realization of a carbon neutral society and their future demand, and presented the required technical elements, our development thereof and our efforts on the technology for CO_2 capture from ships.

In the future, we will develop and hold CO_2 handling technology in a world-leading way, taking advantage of the opportunity to design and build the world's first liquefied CO_2 carrier for CCUS. And by selecting the optimum transportation conditions from a bird's-eye view of the entire CCUS value chain through collaboration with the MHI Group's products, we will provide optimal total solutions for business operators.

Mitsubishi Shipbuilding co., Ltd, which plays a part in the energy transition strategy promoted by the MHI Group, established the “Marine Decarbonization Business Development Group” on February 1, 2022. By integrating the functions of technology development, market research, and business strategy planning to execution in this organization to accelerate technological development and new business creation in the decarbonization field with use of the advanced technology cultivated in our long-established shipbuilding experience, we aim to respond immediately to global trends and market needs toward the realization of a carbon neutral society in the maritime industry.