"Ship Carbon Recycling Working Group" inside Japan Association of Carbon Capture & Reuse (JACCR)* Launches Initiative for Zero-emission Ship Fuels

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1. Introduction

The United Nations Framework Convention on Climate Change (UNFCCC) discusses measures to be taken by the entire world to prevent global warming. The Paris Agreement, which was adopted at the 21st Conference of the Parties to the United Nations Framework Convention on Climate Change (COP21) in December 2015, states the aim of "holding the increase in the global average temperature to well below 2°C above pre-industrial levels and pursuing efforts to limit the temperature increase to 1.5°C."

Meanwhile, in the international maritime field, the Maritime transportation International Organization (IMO) adopted the "Initial IMO Strategy on Reduction of GHG Emissions from Ships"¹⁾ in April 2018, and specified its vision for achieving the following targets with the year 2008 designated as the reference year: (1) Reduction of CO₂ emissions per transport work by at least 40% by 2030, (2) Reduction of total GHG emissions by at least 50% by 2050, and (3) Efforts towards phasing out GHG emissions as soon as possible in this century.

While the international maritime transportation industry introduced the Energy Efficiency Design Index (EEDI) even before the above initial strategy was created, and made efforts to reduce CO_2 emissions from ships, including raising the regulatory values in stages, it is considered that reinforcing the EEDI regulations will not be sufficient and that it is necessary to switch from

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conventional fuels, which are mainly fossil fuels, to lowcarbon or decarbonized fuels in order to achieve the objectives of the strategy.

Based on this movement by the IMO, the Shipping Zero Emission Project was established in April 2018 with the collaboration of industry, academia and government. This project is led by the Japan Ship Technology Research Association (JSTRA), cosponsored by the Ministry of Land, Infrastructure, Transport and Tourism, and assisted by the Nippon Foundation to help maritime transportation, shipbuilding and craft machinery corporations, universities, research institutes, and so forth to study ways to reduce GHG and develop scenarios. In March 2020, the "Roadmap to Zero Emission from International Shipping"²⁾ was announced, stating "LNG to carbon-recycled methane transition scenario" as one of the scenarios for transitioning to alternative fuels in order to achieve the 2050 objectives.

In November 2016, a group including the National Institute of Advanced Industrial Science and Technology (AIST), Hitachi Zosen Corporation, JGC Japan Corporation, INPEX Corporation, and EX Research Institute Ltd. established the Japan Association of Carbon Capture & Reuse (JACCR)³ for the purpose of effectively achieving carbon neutrality by providing an alternative energy involving combining the CO_2 emitted from the industry and hydrogen produced through the use of renewable energy.

In August 2019, Mitsui O.S.K. Lines, Ltd., a member of the association, launched the Working Group for Zero Emission Alternative Fuel⁴ within the JACCR.

In July 2020, Mitsui O.S.K. Lines was joined by EX Research Institute Ltd., Sanoyas Shipbuilding Corporation (currently Shin Kurushima Sanoyas Shipbuilding Co., Ltd.), JFE Steel Corporation, Japan Marine United Corporation, JGC Corporation, Nippon Kaiji Kyokai (Class NK), Nippon Steel Corporation, and Hitachi Zosen Corporation, which agreed with the above

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purpose, and the nine companies together established the Ship Carbon Recycling Working Group⁵⁾ to start examining the feasibility of zero-emission fuels.

This article introduces the results of this Working Group so far.

2. Carbon recycled methane

The stated purpose of this Working Group is to pursue the feasibility of carbon recycled methane produced by methanation, which is considered to be one of the candidates for zero-emission fuel for ships. To achieve this purpose, the following six main issues are to be addressed:

- I. Evaluation of feasibility as a zero-emission fuel
- II. Large CO₂ transport ships
- III. Supply of renewable energy-derived hydrogen
- IV. Methane slip
- V. Supply infrastructure
- VI. Economic efficiency

For Issues II to VI, the major premise is that carbon recycled methane is considered as a zero-emission fuel in Issue I, and therefore it was decided to work on Issue I first.

To evaluate whether carbon recycled methane can be considered as a zero-emission fuel in Issue I, we assumed a supply chain consisting of (1) Separation, recovery and liquefaction of CO_2 emitted from domestic factories, etc., (2) Marine transport of liquefied CO_2 to a location where renewable energy-derived hydrogen is supplied on CO_2 transport ships, (3) Methane synthesis from CO_2 and hydrogen by methanation, and (4) Liquefaction of methane and utilization as a ship fuel, as shown in Fig. 1, and estimated the energy balance of each process.



Fig. 1 Assumed supply chain and processes to be evaluated

Specifically, the annual amount of $150,000 \text{ t } \text{CO}_2$ emitted from domestic factories, etc. is separated and recovered by a chemical absorption or physical adsorption method, then converted into the liquefied state at 0.7 MPaG and -46°C (hereafter referred to as liquefied CO₂ conditions) to transfer it by sea on 11,000 t CO₂ transport ships. The transferred liquefied CO₂ is unloaded at a location where renewable energy-derived hydrogen is supplied, and methane is synthesized through the methanation reaction after re-vaporization. This synthesized methane is liquefied to be used as a ship fuel.

Prior to trial calculation, we specified the boundary conditions for handing over the intermediates and product substances between processes. We also specified the transport volume and distance conditions as follows:

Condition 1: CO_2 is put into the liquid state at 0.7 MPaG and -46°C for transport.

Figure 2 shows the state diagram for CO₂. We selected the transport conditions in Condition 1, as the IMO International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk stipulates "the pressure shall be maintained at 0.05 MPa above higher than the triple point for CO₂ during international marine transport."

Condition 2: The marine CO_2 transport distance was set to 5,000 nautical miles (1 nautical mile = 1,852 m).

Condition 3: The annual amount of CO_2 separation, recovery and transport is set to 150,000 t.

Condition 4: The calculation for each process is conducted by using publicly known technologies and information at present.

Condition 5: We assumed the year 2030, when the achievement of zero-emission ships is expected, 0.370 kg-CO₂/kWh, which is the value published⁶⁾ by the Federation of Electric Power Companies of Japan (September 2015) based on the "Long-term estimate of electricity demand" for Japan as the CO₂ emission factor for electricity, and the Phase 3 regulatory values as the Energy Efficiency Design Index (EEDI) used in marine transport. In addition, we used 0.060 t-CO₂/GJ, which is the value for industrial steam in "List of calculation methods and emission factors in calculation, reporting and publication systems"⁷⁾ by the Ministry of the Environment, as the CO₂ emission factor for steam.

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Fig. 2 Temperature and pressure for marine transport of CO₂

The items to be evaluated to calculate the CO₂ emissions are described below.

We calculated the CO_2 emitted within the supply chain for CO_2 separation, recovery and transport, and synthesis and liquefaction of carbon recycled methane that was described previously.

We set the CO₂ emission factor for hydrogen, which is derived from renewable energy and supplied, to zero.

In addition, there is the issue of "allocation," which means which country should be responsible for counting the CO_2 emitted, including international maritime transportation, as our assumed supply chain would cover multiple countries. However, we decided not to handle this issue, as no international framework or agreement has yet been established.

The energy balance results for each process that we calculated based on the above conditions are described in Chapters 3 to 6, and the results of tabulation for each process and its analysis in Chapter 7.

3. Energy balance in the CO₂ separation and recovery process

Techniques to separate and recover CO_2 include chemical absorption, physical adsorption, and membrane separation, and many other separation techniques are being developed. In this chapter, we calculated the energy balance for the chemical absorption method and the physical adsorption method assuming CO_2 recovery from the exhaust gas at steelworks.

Chemical absorption method:

The chemical absorption method refers to the technique of separating CO_2 by utilizing the chemical reaction of CO_2 absorption solution. In this method, a solution that can dissolve a large volume of CO_2 selectively is brought into contact with the blast furnace

gas to capture the CO_2 into the solution by the reactive absorption principle to subsequently separate and recover the CO_2 gas in a high concentration. The method is suited to separating and recovering large volumes of CO_2 from process gas, etc. at normal pressure. Physical adsorption method:

The physical adsorption method refers to the CO_2 separation technique in which CO_2 is adsorbed to a solid adsorbent such as activated carbon and zeolite under high pressure or low temperature, to be desorbed at low pressure or high temperature. The Swing method, which uses multiple adsorption towers filled with adsorbent and changes the environment such as pressure and temperature, is often used. There are the Pressure Swing Adsorption (PSA) method to swing the pressure, the Thermal Swing Adsorption (TSA) method to swing the temperature, and the Pressure Thermal Swing Adsorption (PTSA) method, which combines the PSA and the TSA methods.

Dehumidification may be necessary before CO_2 separation and recovery, depending on the type of adsorbent.

 3.1 CO_2 separation and recovery by the chemical absorption method

The chemical absorption method selectively separates and recovers CO_2 from combustion exhaust gas or blast furnace gas by using the chemical reaction between a basic substance such as an amine and CO_2 , which is an acidic substance. Figure 3 shows the concept of the chemical absorption method⁸⁾.

A plant employing this method consists of an absorption tower, regeneration tower, reboiler, etc. The gas that contains CO_2 , such as combustion exhaust gas and blast furnace gas, is pressurized in blower (B1) in Fig. 3, supplied to the bottom of the absorption tower, and travels upward inside the tower. The chemical absorption solution is dripped from the top of the tower at the same time and moves to the bottom along the surface of the filler inside the tower. The CO_2 in the supplied gas reacts selectively with the chemical absorption solution and is absorbed through gas-liquid contact during this process. As a result, approximately 90% of the CO_2 contained in the supplied gas is absorbed by the absorption solution and recovered by the time the gas reaches the top of the tower.



Fig. 3 Conceptual drawing of a plant employing the chemical absorption method

As the chemical absorption solution, amine solution is mainly used for CO₂ recovery from combustion exhaust gas, blast furnace gas, etc.

The chemical absorption solution that has reacted with and absorbed CO_2 is called the rich solution. This rich solution is extracted from the bottom of the absorption tower, fed by Pump P1 to be introduced at the top of the regeneration tower via a heat exchanger. The rich solution is heated inside the regeneration tower to 100– 120°C and releases the CO_2 . This CO_2 is then recovered from the top of the regeneration tower with a concentration of 99% or higher. The absorption solution after releasing CO_2 is called the lean solution, and it is recovered from the bottom of the regeneration tower. The lean solution is fed by Pump P2 and is dripped from the top of the absorption tower again after passing through a heat exchanger.

The CO_2 absorption reaction in the chemical absorption method is exothermic, and so the energy corresponding to this reaction heat needs to be supplied in order to desorb the CO2 in the regeneration tower. In addition, energy must be supplied to increase the temperature of the absorption solution and provide the thermal energy that is lost at the top of the tower for CO_2 recovery. The sum of these heats—reaction heat for absorption solution, heat for temperature increase, and heat lost at the top of the tower—is the energy required for CO_2 separation and recovery. The chemical absorption solution offers higher performance as this CO_2 recovery energy is smaller. The reboiler supplies this CO_2 recovery energy as steam.





Figure 4 shows the scope of examination in this chapter. We examined the processes to liquefy the CO_2 recovered from the blast furnace gas with the chemical absorption method, store it for a certain period in the storage tank, and transfer it to the CO_2 transport ship with a transfer pump. We set the CO_2 concentration in the blast furnace gas at 22%, and the conditions of liquefied CO_2 to be loaded onto the CO_2 transport ship at 0.7 MPaG and -46°C.

In the chemical absorption method, the energy of the steam used in the reboiler accounts for more than 90% of the total energy consumption. We therefore calculated the CO₂ emissions for the amount of steam consumption in the reboiler. In this trial calculation, we used the value of 2.3 GJ/t-CO₂, the CO₂ recovery energy value for ESCAP®, which was commercialized by Nippon Steel Engineering Co., Ltd.⁹⁾ This value is a world top class value among the amine absorption solutions that have been commercialized. Assuming that the thermal efficiency of the reboiler is 80%, the steam energy required for recovering CO₂ from the amine absorption solution with CO₂ recovery energy of 2.3 GJ/t-CO₂ is calculated as 2.9 GJ/t-CO2. Therefore, it is calculated that 0.17 t of CO₂ is emitted when recovering 1 t of CO₂ assuming the CO₂ emission factor stated in Chapter 2.

Meanwhile, amine absorption solutions are still being researched. For example, a NEDO project¹⁰⁾ is developing an amine solution with CO_2 recovery energy of 1.6 GJ/t-CO₂ as a target to be achieved by the end of fiscal 2022. By using this absorption solution, it is calculated that 0.12 t of CO₂ would be emitted when recovering 1 t of CO₂.



Fig. 5 CO₂ liquefaction process

Figure 5 shows the process flow for producing liquefied CO₂ under liquid CO₂ conditions from the CO₂

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gas at the temperature of 40°C and pressure of 0 MPaG that was recovered by the chemical absorption method. The figure also shows the state and processed amount of CO_2 . The CO_2 that is recovered by the chemical absorption method is pressurized to 0.6 MPaG by Compressor 1. Its temperature increases to approximately 200°C under this pressurization, and it is mixed with the liquefied CO₂ that is being circulated after being cooled to 40°C while consuming little energy by using seawater, etc. This gas mixture is then pressurized to 1.7 MPaG by Compressor 2, allowed to swell and decompress to 0.6 MPaG, and heated slightly to obtain liquefied CO_2 in the intended state.

Energy is mainly consumed by the compressors in this liquefaction process, and the theoretical values under the processing conditions shown in Fig. 5 are 39 kWh for Compressor 1 and 35 kWh for Compressor 2. Based on these values, the theoretical electric energy required to produce liquefied CO_2 in the liquid CO_2 conditions from 1 t of CO_2 gas that is recovered is 74 kWh/t- CO_2 . Assuming that the efficiency of the compressor is 0.7, the electric energy required to liquefy 1 t of CO_2 is approximately 104 kWh/t- CO_2 .

Table 1 shows the energy consumption and CO_2 emissions of each process for CO_2 recovery, liquefaction, storage and transfer when 150,000 t of CO_2 is recovered. We calculated CO_2 recovery by the chemical absorption method and CO_2 liquefaction by using the unit amounts described above, and the energy consumption for each process was calculated as 431,000 GJ for CO_2 recovery and 15,600 MWh for CO_2 liquefaction.

For storage of CO₂, we assumed that 10,000 t of CO₂ is stored at a temperature of -46°C and pressure of 0.7 MPaG in two tanks each with a capacity of 5,000 m³, which are thermally insulated with polyurethane foam. As we specified that the CO₂ evaporating due to thermal conduction from outside the tank during storage is reliquefied and recovered, CO2 is generated due to the use of electricity by the cooling device for this process. Here, estimating that the amount of heat infiltrating into the CO2 storage tank is 100 kW, we specified 170 kW as the power required for the cooling device to be used for liquefaction of the CO2 that evaporates under the infiltrating heat in consideration of device efficiency. Using this value and assuming that 10,000 t of CO₂ is stored for an average period of 20 days and replaced 15 times, we calculated 1,220 MWh as the electric energy necessary for storing a net CO₂ amount of 150,000 t.

We determined that the electric power required for the transfer pump to transfer the CO_2 from the storage tank to the CO_2 transport ship would be 250 kW. If it takes 20 hours for one transfer and the transfer is performed 15 times, the electric energy required for CO_2 transfer is 75,000 kWh.

We calculated the CO₂ emissions in Table 1 by multiplying the energy consumption by the CO₂ emission factor for the energy source in Chapter 2. As shown in this table, the CO2 emissions from each process are 25,900 t for CO₂ recovery, 5,770 t for liquefaction, 453 t for storage, and 27.8 t for transfer. The total CO₂ generated in all four processes we examined was approximately 32,200 t for the amount of CO2 handled, which was 150,000 t. Of this value, CO₂ recovery accounted for 80.4%, and CO₂ liquefaction for 17.9%. While the results show that the CO₂ emissions were high for the CO_2 recovery process, it is expected that the CO_2 emissions would decrease from 25,900 t to 18,000 t if the new absorption solution with CO₂ recovery energy of 1.6 GJ/t-CO₂, which is being developed by a NEDO project,¹⁰⁾ can be used, and that the total CO_2 emissions in Table 1 can also be reduced from approximately 32,200 t to 24,300 t.

Table 1 Energy consumption and CO₂ emissions



3.2 CO₂ separation and recovery by the physical adsorption method

In this trial calculation, we adopted the PSA separation and recovery method¹¹).

For the raw material gas, we assumed combustion exhaust gas with CO_2 concentration of 24% and moisture

 -5- Journal of The Japan Institute of Marine Engineering Vol.56, No.4 (2021) of 3%. Figure 6 shows the configuration of the process.



Fig. 6 Separation and recovery process flow by physical adsorption method

Moisture is removed with a dehumidifier, and gas is supplied to the adsorption tower with a blower. The CO_2 collected by a vacuum pump is liquefied by the liquefaction equipment and stored in the tank. In addition, we specified that a steam heater would be used for regeneration in the dehumidifier.

Based on our assumed annual transport amount of 150,000 t, we specified the CO₂ production amount as 18 t/h, and the raw material gas supply volume as approximately $64,000 \text{ m}^3/\text{h}$ in consideration of the separation and recovery efficiency, etc. We selected models that suited these assumptions for the devices used in the process such as blower and vacuum pump, and made a simple estimation of the required energy based on their rated power values.

The heat quantity necessary for regeneration at the dehumidifier is calculated as 42 kJ, and the annual CO_2 emissions are calculated as 2,500 t when using the CO_2 emission factor for the steam that is used, as indicated in Chapter 2.

When the power for other devices is electric energy, the total required energy is estimated as 64.5 GWh.

Assuming the CO_2 emission factor for electric power given in Chapter 2, the annual CO_2 emissions are calculated as 23,865 t.

Therefore, combining steam and electric power, the annual overall CO_2 emissions of the CO_2 separation and recovery process by the physical adsorption method are calculated to be 26,365 t.

4. Energy balance in the CO₂ transport process

The transport process is the process of transporting the liquefied CO_2 from where it is recovered to where the methane is produced, by sea. Unlike other processes, there is no energy balance due to a change in material state such as chemical reaction, pressure or temperature. The energy balance of this process is therefore mainly

due to the operation of the CO₂ transport ship.

The objects of the energy balance calculation due to the operation of the CO_2 transport ship include the propulsion plant of the ship including the main engine, equipment used for CO_2 cargo handling and maintaining the state of the conditions of CO_2 during transport, the accommodation facilities for the crew, and other matters related to operation of the ship. The power and electricity required for the operation of the transport ship is obtained from the main and auxiliary engines, and the CO_2 emissions from these engines were calculated based on using of low-sulfur fuel oil as its energy.

As described above, the various conditions such as the operating conditions, cargo-related facilities, and accommodation facilities have a significant impact on CO_2 emissions from transport ship operations. On the other hand, new ships engaged in international shipping are subject to CO_2 emission regulations using the Energy Efficiency Design Index (EEDI)^{12) 13)}. In this examination, we calculated the CO_2 emissions based on these regulatory values, and added the consideration for the re-liquefaction equipment and liquefied CO_2 pump, which have large effects on the CO_2 emissions during transport and cargo-handling of liquefied CO_2 , to estimate the CO_2 emissions in the transport process.

Furthermore, we took into consideration the ballast voyage for the CO_2 transport ship to return to the loading location in addition to the laden voyage from the loading location for transporting liquefied CO_2 to the unloading location. We also considered the operation of the auxiliary engines during the loading or unloading in the terminal in the CO_2 emissions calculation.

The conditions for examining the CO2 emissions are as follows:

a) Total annual transport amount: 150,000 t

b) Net annual number of times of transport: 15

c) Distance for one transport: 5,000 nautical mile/oneway

The particulars of the CO_2 transport ship are as follows:

a) Deadweight: 11,000 t

b) Cargo capacity: 10,000 m³

c) Vessel speed during voyage: 10 kt

(1 kt is the speed of a ship which moves 1 nautical mile in 1 hour.)

d) Number of ships in operation: 2

We examined the CO₂ emissions by dividing the transport process into the following four modes:

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- a) Loading: Liquefied CO₂ is loaded onto the CO2 transport ship from the shore manifold at the loading location.
- b) Laden voyage: Liquefied CO₂ is transported from the loading location to the unloading location.
- c) Unloading: Liquefied CO₂ is unloaded from the CO₂ transport ship to the shore manifold at the unloading location.
- d) Ballast voyage: The CO₂ transport ship is taken from the unloading location to the loading location.

In calculating the CO₂ emissions, we used the values described in the EEDI Calculation Guidelines¹³⁾ as the CO₂ emission factor and the fuel consumption rates of the main engine and the auxiliary engines.

We set the output of the auxiliary engines that is used to provide the electricity for services onboard while the ship is moored (main engine is stopped) to 5% of the rated output of the main engine. Since the EEDI is an indicator of the CO2 emissions of a new ship, estimated in the number of grams emitted when carrying a cargo of 1 t over a distance of 1 nautical mile under certain conditions at the stages of design and construction, it can also indicate the ship's performance.

The EEDI regulations stipulate that the Attained EEDI of a new ship must be less than the Required EEDI that is determined by the type and capacity of the ship.

In this examination, we calculated the CO₂ emissions under the voyage mode while considering that the Required EEDI determined based on the conditions of the CO₂ transport ship assumed above is equal to the Attained EEDI of this ship, and added the emissions by operating the re-liquefaction equipment under the voyage mode, emissions by operating the CO₂ pump under the unloading mode, and emissions from the auxiliary engines while the ship is moored, to calculate the total CO₂ emissions in the transport process as follows:

I. Navigation days and cargo handling time

Navigation days: 42 days (per round voyage)

Cargo handling time: 20 hours (per round voyage)

Moored days: 4 days (per round voyage, including cargo loading or unloading time)

II. Net number of days in each mode

- b. Laden voyage: 315 days
- c. Unloading: 30 days
- d. Ballast voyage: 315 days

III. EEDI for the CO₂ transport ship (3rd level

regulation)

EEDI: 11.257 g-CO₂/t • nautical mile

IV. Total CO₂ emissions: Approx. 20,500 t

There are many technical issues that need to be solved regarding the liquefied CO2 transport ship described in this chapter, including the development of devices such as the re-liquefaction equipment. The energy balance presented here is a rough estimate based on assumptions for both the items described in this section and those that are not.

5. Energy balance in the methanation reaction process

As shown in Fig. 7, methanation is an exothermic reaction which is given by:

 $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O - \triangle 165 \text{ kJ/mol}$ (1)This is commonly known as the Sabatier reaction. Since the thermal energy of 4 mole of hydrogen, which is 967 kJ, is converted into the thermal energy of 1 mole of methane, which is 802 kJ, in this reaction, it is theoretically possible to convert hydrogen into methane with more than 80% of the energy efficiency as follows:

$$802 \text{ kJ} / 967 \text{ kJ} \times 100 = 82.9\%$$

In addition, as it is an exothermic reaction, the reaction proceeds autonomously without supplying external energy.

As shown by Eq. (1), a reverse reaction also occurs whereby the water that is formed as the reaction proceeds reverts to CO2 and hydrogen again. Therefore, the reactor has two stages as shown in Fig. 7 so that the water generated in the first stage is removed before the gas is introduced into the second stage of the reactor. This allows conversion of approximately 96% in the first stage, and the remaining 4% is introduced into the second stage, achieving a conversion rate of 99% or higher.

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a. Loading: 30 days

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Fig. 7 Flow of methanation

5.1 Energy consumption by CO2 vaporization

Since the liquid CO₂ transported by a CO₂ transport ship is vaporized to supply into the methanation plant in this process, energy to maintain the temperature in the storage tank and energy to vaporize it are needed.

The liquefied CO_2 in the transportation is at 0.7 MPaG and $-46^{\circ}C$, and the energy necessary to maintain the temperature in a tank is 170 kWh, which indicates that 1,489,200 kWh is required each year.

Next, as the vaporization energy from the liquid CO_2 into gas at 0.7 MPaG and 20°C, the electric power consumption is calculated based on the enthalpy difference between the two phases, which is 400 kJ/kg- CO_2 , as follows:

150,000 t-CO₂ × 400 kJ/kg-CO₂ / 3,600 s

= 16,667 MWh

The annual electric power consumption is thus calculated as

1,489 + 16,667 = 18,156 MWh.

Multiplying this by the CO_2 emission factor for electric power, 0.370 kg- CO_2 /kWh, we obtain

 $18,156 \text{ MWh} \times 0.370 \text{ kg-CO}_2/\text{kWh} = 6,718 \text{ t-CO}_2$ as the annual CO₂ emissions.

5.2 Material balance in the methanation process

Table 2 shows the material balance in the process shown in Fig. 7 when 150,000 t of CO₂ is methanized under the assumed conditions for 8,000 hours operation annually.

The CO_2 flow rate supplied from the CO_2 tank is calculated as

 $150,000 \text{ t} \times 22,400/44 \text{ Nm}^3/\text{t} / 8,000 \text{ h} = 9,545 \text{ Nm}^3/\text{h}$ and it is supplied into the reactor in combination with four times the amount of renewable energy-derived hydrogen. By this methanation reaction, 54,458 t-CH₄ of methane is manufactured annually.

Table 2 Material balance in methanation

| Process | | CO ₂ supply (from evaporator) | Methanation (1st stage reactor inlet) | Methanation outlet (to liquefaction facility) |
|------------------------|------------------|---|--|--|
| | CO ₂ | 9,545 | 9,545 | 15 |
| Flow rate | H ₂ | 0 | 38,182 | 61 |
| (Nm³/h) | CH ₄ | 0 | 0 | 9,530 |
| | H ₂ O | 0 | 0 | 33 |
| Pressure | MPa(G) | 0.5 | 0.5 | 0.4 |
| Temperature | °C | 40 | 40 | 40 |
| Composition (dry・%) | CO ₂ | 100.0% | 20.0% | 0.2% |
| | H ₂ | 0.0% | 80.0% | 0.6% |
| | CH4 | 0.0% | 0.0% | 99.2% |

5.3 Energy consumption by the methanation process

Since the methanation process is an exothermic reaction, no external energy is required for carrying out the reaction, and electric power consumption consists of the power for auxiliary machines such as pumps, control panel and startup heater (cooling water and instrumentation air are not taken into consideration as supplied utilities).

Assuming that the process start/stop occurs 15 times per year, the electric power consumption by the process for startup operation and 8,000 h of rated operation is calculated as 2,042 MWh, which results in annual CO_2 emissions as follows by multiplying by the CO_2 emission factor of 0.370 kg- CO_2 /kWh:

 $2,042 \text{ MWh} \times 0.370 \text{ kg-CO}_2/\text{kWh} / 1,000 = 755 \text{ t-CO}_2.$

5.4 CO₂ emissions from the methanation process

Table 3 shows the electric power consumption and CO_2 emissions that occur due to the operations of the re-liquefaction facility to maintain the liquid CO_2 in the CO_2 tank at 0.7 MPaG and -46°C, the heater to evaporate it, and other equipment in the methanation process.

Based on these results, the annual CO_2 emissions from the methanation process are calculated as follows: (551 + 6,167 + 755) t-CO₂ = 7,473 t-CO₂.

Table 3 CO₂ emissions results

| Facility | CO2 tank | Evaporator | Methanation reactor | |
|--|------------------------------|--|---|--|
| Major equipment that consumes electric power | Re-liquefaction facility | Heater for keeping reaction temperature | Heater for startup, pump, meters, control panel | |
| Energy source | Energy source Electric power | | Electric power | |
| Annual power consumption(MWh) | 1,489 | 16,667 | 2,042 | |
| $\begin{array}{c} \text{Annual CO}_2 \text{ emissions} \\ (\text{CO}_2 t/y) \end{array}$ | 551 | 6,167 | 755 | |

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6. Energy balance in the carbon recycled methane liquefaction process

This process includes the facilities to liquefy the methane gas synthesized in the methanation reaction process, store the liquefied methane and supply it to ships as ship fuel.

Figure 8 shows the configuration of the main facilities and equipment in this process. The synthesized methane gas, which becomes the feed gas, is pressurized, and impurities such as CO_2 and moisture which would cause solidification and clogging at low temperature are removed to ppm order during the stage before the liquefaction facilities.

The chemical absorption method using an amine solution as the absorbent is used to remove CO₂.

Next, moisture is removed by a dehydration facility using molecular sieves. By installing two dehydration towers in the dehydration facility and conducting operation and regeneration alternately, the facility can be operated continuously. The synthesized methane from which impurities have been removed to levels that would cause no problem is pressurized and fed to the liquefaction facilities.

In the methane liquefaction facility, methane is liquefied through a liquefaction system by refrigerant to remove the heat from the methane gas by the vaporization heat of the circulated refrigerant. While various liquefaction methods for the liquefaction refrigerant process are possible, we adopted the propane precooling/mixed refrigerant method with the highest thermal efficiency in this study.

Liquefied methane is stored in a tank, pressurized after going through a cryopump and supplied to the LNG fuel ship as ship fuel.

The product gas from the methanation facility contains a small amount of hydrogen, and it is not efficient to completely liquefy it. It is therefore accumulated at the top of the liquefied methane tank as vaporized gas, and the gas is continuously released from the top of the tank. The vaporized gas in the tank contains methane for equilibrium composition in addition to hydrogen, and our system effectively utilizes it as fuel for in-house power generation.

Table 4 shows the results of estimating the energy consumption and CO_2 emissions for each facility. The major energy consumption by facilities other than the generator is for rotary machines such as compressors and

pumps, and is in the form of electric power. The CO_2 emissions were calculated from electric power consumption by using the CO_2 emission factor in Chapter 2.

Electric power is consumed mainly by the refrigerant compressor in the liquefaction facility, followed by the feed gas compressor. The dehydration facility conducts dehydration by heating the gas in the tank and aerating it, and we neglected the CO_2 emission from this facility as its energy consumption is quite small. The CO_2 emissions were calculated by subtracting the electric power generated by the gas turbine generator using the gas in the tank as the fuel from the overall electric power consumption for this process. We counted the CO_2 emissions from the gas turbine generator by combustion as the CO_2 emissions from this process.

Table 4 Estimation of CO₂ emission from methane liquefaction process

| Facility | Feed gas pressurization | CO ₂ removal | Dehydration | Methane liquefacti on | Liquefied methane Tank/shipment | Generator |
|--|--|-------------------------|-------------|--|---|---------------------------------------|
| Main equipment | Feed gas compressor Air-cooled heat exchanger | Circulation pump | | Coolant compressor Air-cooled heat exchanger | Loading pump Vaporized gas compressor | Gas turbine Generator |
| Energy source | Electric power | Electric power | - | Electric power | Electric power | Vaporized gas from this process |
| Consumed (generated) electric power, kW | 1,060 | 10 | - | 3,320 | 60 | (1,800) |
| Electric power received from an external source, kW | 2,650 (consumed power - generated power) | | | | | |
| CO2 emissions, t/year | 7,840 ⁽¹¹⁾ (CO ₂ emissions related to electric power received from an external source) | | | | 9,520 | |

(*1) CO₂ emission factor is calculated with 0.370 kg-CO₂/kWh as base.

The annual CO2 emissions calculated by multiplying the electric power supplied from an external source by the CO2 emission factor are approximately 7,840 t, and the annual CO2 emissions from this process are estimated as approximately 17,360 t by adding the annual CO2 emissions of approximately 9,520 t from the gas turbine generator.



7. Overall evaluation of the supply chain

As shown in Fig. 9, dividing the energy balance for the entire supply chain, accumulating the processes which were calculated in Chapters 3 to 6, by the lower calorific value of methane gives approximately 27 g-CO₂/MJ.



Fig. 9 CO₂ emissions per unit calorific value of zero-emission methane fuel for ships

In addition, it is expected that the CO₂ emissions per unit calorific value for the entire supply chain can be reduced to approximately 20 g-CO₂/MJ by improving the efficiency of the separation and recovery technique, and using electric power derived from renewable energy and methane as the fuel for the CO₂ transport process.

The CO_2 emissions per unit calorific value (approximately 27 g- CO_2/MJ) for the amount of energy input in each process estimated by our Working Group are comparable with the CO_2 emissions of biodiesel, hydrogen refined from methane, and hydrogen formed by electrolysis of water using renewable energy, which are considered zero-emission fuels in general (see Fig. 10). It is also worth noting that the Working Group considered the allocation of the recovered CO_2 and the CO_2 generated in the production of H₂ that is input into the methanation reaction process outside the boundary.

8. Conclusion

In order to verify whether synthetic methane, which is one of the alternative fuel candidates for reducing GHG in marine transport, can be considered a zero-emission fuel, the Ship Carbon Recycling Working Group conducted a trial calculation on the energy balance in each process of the assumed supply chain.

We were able to confirm that its value (approximately 27 g-CO₂/MJ) is comparable with those of other alternative fuel candidates by comparing it with the CO₂ emissions per unit calorific value of main alternative fuels published by DNV^{14} as shown in Fig. 10, since the IMO has not given a definition of zero-emission fuel. We found that the methane synthesized by methanation could be deemed a zero-emission fuel.



Fig. 10 CO₂ emissions per unit calorific value for major alternative fuels by DNV

In the future, we plan to continue examining the feasibility of the remaining Issues II to VI (large CO₂ transport ships, supply of renewable energy-derived hydrogen, methane slip, supply infrastructure, economic feasibility, etc.) and keep promoting carbon recycled methane fuel.

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Reference

- Initial IMO Strategy on Reduction of GHG Emission from Ships, IMO MEPC 304(72), 2018
- Roadmap to Zero Emission from International Shipping, Shipping Zero Emission Project, March 2020
- 3) CCR(Carbon Capture & Reuse) HP https://ccr-tech.org/
- Press Release "Working Group for Zero Emission Alternative Fuel - Project Aims to Reduce GHGs Emissions across Industries", August 6, 2019
- Press Release "Nine companies have started "Ship Carbon Recycling WG" of Japan's CCR Study Group - Crossindustry initiatives for zero-emission ship fuels through methanation technology", July 16, 2020
- 6) Environmental Action Plan by the Japanese Electric Utility Industry - Voluntary Approaches toward a Low Carbon Society (Phase II), The Federation of Electric Power Companies of Japan, 2015
- Ministry of the Environment HP, https://ghgsanteikohyo.env.go.jp/files/calc/itiran 2020 rev.pdf
- Survey on the Carbon Capture and Storage process Comparison of the chemical absorption process with the physical absorption process for CO₂ capture, JST Center for Low Carbon Society Strategy, LCS-FY2015-PP-08
- Nippon Steel & Sumikin Engineering Co.,Ltd Technical Review, vol.5 (2014), p.73
- 10) NEDO Project,

https://www.nedo.go.jp/content/100525415.pdf

- 11) Adsorption Technology Handbook (third edition), published by NTS, 2020
- 12) Amendments to the annex of the protocol of 1997 to amend the international convention for the prevention of pollution from ships, 1973, as modified by the protocol of 1978 relating thereto (Inclusion of regulations on energy efficiency for ships in MARPOL Annex VI), IMO MEPC.203(62), 2011
- 13) Guidelines on the method of calculation of the attained energy efficiency design index (EEDI) for new ships, IMO MEPC 212(63), 2012

14) Assessment of selected alternative fuels and technologies, DNV-GL, 2019

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