Initiatives to Develop CO₂ Capture and Effective CO₂ Utilization Technology Systems



Reducing CO_2 emissions is required to not only employ CO_2 capture technology, but also decide where the captured CO_2 will go and how it can be utilized effectively. At present, as the amount of CO_2 utilized is quite small compared to that of CO_2 emitted, underground storage (carbon capture and storage or CCS) is considered a realistic choice. However, because the locations of storage sites are unequally distributed, some effective methods for CO_2 utilization need to be invented in areas away from these sites. Regarding the efforts of Mitsubishi Heavy Industries, Ltd. (MHI) Group to address this issue, this report presents the applications in chemical products, fuels and direct use in this regard.

1. Introduction

As part of the movement toward decarbonization against a backdrop of global warming, the development of fuel conversion technology for the use of renewable energy and hydrogen is accelerating. However, it is not easy to provide all the energy by means other than fossil fuel combustion. Mitsubishi Heavy Industries Engineering Ltd., which is part of MHI Group, has a technology to capture CO_2 from combustion exhaust gas. Having delivered the system to coal-fired power stations and chemical plants, MHI Engineering boasts the world's top market share. We will expand the application of this technology to other industrial sectors in order to meet social needs for decarbonization.

In the conventional CO_2 capture system, on the other hand, the captured CO_2 is used mainly for underground storage (CCS), enhanced oil recovery (EOR), and urea synthesis. However, if CO_2 capture is to become more widely used in the years to come, other effective CO_2 utilization methods are required. This report presents MHI Group's undertakings for technological development in this regard.

2. CO₂ as a source of carbon

Carbon is a chemical element widely used in chemical products (such as methanol, polyethylene, and carbon black). At present, these products are mainly manufactured from natural gas (methane) or naphtha extracted from crude oil. Although it is technically possible to produce carbon from CO_2 , CO_2 is a stable substance from an energy point of view and using it for production requires more energy than methane or naphtha. **Figure 1** shows energy levels of substances such as CO_2 , methane and methanol. The lower the energy level is, the more stable the substance is, which means that it is more unlikely to react with other substances. Although it depends on the reaction pathway, the figure shows that more energy is required to produce chemical products (such as methanol and ethylene) from CO_2 (-394 kJ/mol), because it is at a higher energy level than methane (-51 kJ/mol) or carbon monoxide (-137 kJ/mol). As this naturally incurs extra costs, society needs to be willing to bear such costs.

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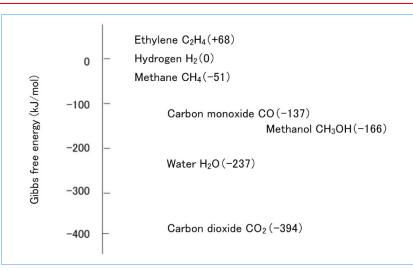


Figure 1 Properties of CO₂ from viewpoint of reactivity

3. Currently available CO₂ storage sites and utilization methods

It is estimated that the current human-related CO_2 emissions are approximately 40 billion tonnes per year. **Figure 2** should be reduced to 4.3 to 13 billion tonnes if carbon neutrality is to be achieved⁽¹⁾. On the other hand, regarding the amount of CO_2 that is required to be captured, the current level of 0.04 billion tonnes should be increased to 4.3 to 13 billion tonnes. According to the International Energy Agency (IEA), the storage potential of CCS is said to be 8 trillion tonnes, which is more than several hundred years' worth of emissions based on the emissions projections for $2050^{(2)}$. Therefore, it can be said that there is a sufficient allocation for CO_2 in total.

At present, the CO₂ that is utilized as a refrigerant, for agricultural purposes, or as a welding gas amounts to approximately 1.2 million tonnes per year. As the annual CO₂ emissions in Japan are 1,000 to 1,200 million tonnes, the amount utilized is just about 0.1% of the total emissions⁽³⁾. Taking the above-mentioned cost issues into consideration as well, we think that CO₂ storage and CCS are the most realistic choices.

However, the locations of currently available storage sites are concentrated in North America or around the North Sea. In the remaining regions, therefore, CO_2 needs to be transported to faraway storage sites or some effective method for utilization should be invented in the neighboring areas of CO_2 capturing sites.

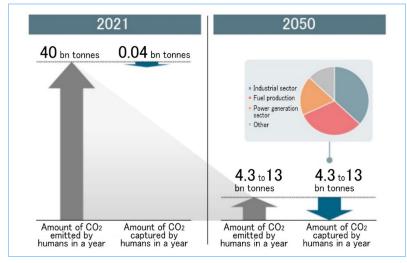


Figure 2 Necessary CO₂ reductions

4. Reuse of captured CO₂

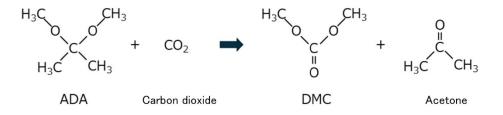
When reusing CO_2 after capture, it is hoped that such reuse leads to CO_2 fixation or reduced consumption of fossil fuels for decarbonization. In our group, several research projects on the reuse of CO_2 are under way. Below are application examples for chemical products, fuels, and direct use.

4.1 Dimethyl carbonate (DMC)

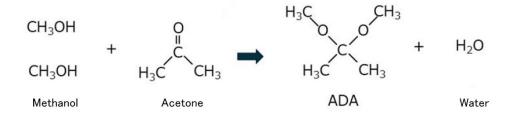
Dimethyl carbonate (DMC) is a chemical product used as an electrolyte in lithium batteries. As such batteries will be used over a long time, they can be used as a means of carbon fixation. It is also expected that the usage of lithium batteries will increase as their application becomes more common in the future. In other words, if CO_2 fixation into DMC becomes practically and commercially viable, this will make it possible to develop a new resource circulation model, for example, by collecting CO_2 from power station exhaust gas and distributing it to the market as an electrolyte for lithium batteries. In this way, we can contribute to decarbonizing our society.

In the generally adopted DMC synthesis, CO is used as a raw material. We have successfully established a process in which CO_2 is used as a raw material⁽⁴⁾. The synthesis method is shown below. Optimization of the process is under way.

DMC is synthesized from CO_2 and methanol, in which acetone dimethyl acetal (ADA) serves as an intermediate. The reaction takes place in two stages. CO_2 is first reacted with the above-mentioned ADA in the presence of a catalyst, to produce DMC. This is followed by the acetone, a by-product in the first stage, being allowed to react with methanol for the ester exchange reaction, through which ADA is reproduced. ADA is thus circulated for use within the process (Equations [1] and [2] and **Figure 3**).



Equation [1] Chemical reaction for DMC synthesis



Equation [2] Chemical reaction for ADA synthesis

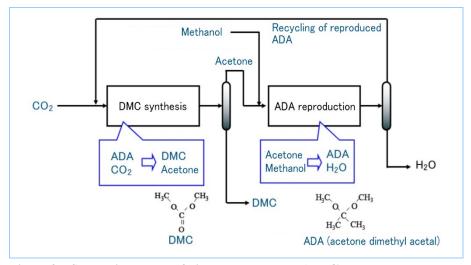


Figure 3 Synthesis method of dimethyl carbonate (DMC)

When it comes to DMC demand, the average annual growth rate of the market will be 8% at the maximum. The demand is expected to grow markedly, especially for on-board car battery

applications. While the annual demand was about 700,000 tonnes in 2020, this amount may rise to around 1.4 million tonnes in 2028 (**Figure 4**)⁽⁵⁾. Especially high-demand regions are Europe, the United States, and Asia (China in particular). The 2020 forecast for the demand proportions is: China (26%), Japan (11%), North America (12%) and Europe (15%) (**Figure 5**)⁽⁵⁾. As a certain level of demand is expected in East Asia, which is distant from the CO₂ storage areas, DMC synthesis can be expected to be of use for CO₂ utilization.

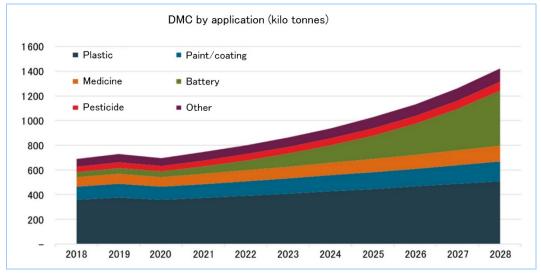


Figure 4 DMC demand forecast

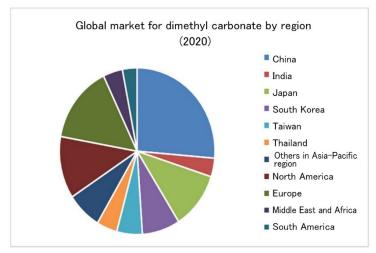


Figure 5 DMC demand by region

4.2 Methane (methanation)

Methane is used as the city gas. If produced from CO_2 , it will lead to reduced consumption of natural gas (a fossil fuel). Methanation is the production of methane by allowing CO_2 to react with hydrogen under high-pressure and high-temperature conditions. It is represented by the following chemical equation [3]:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$
 Equation [3]

Hydrogen is required in this reaction. Hydrogen itself can be used as a fuel and is carbon-free. However, it has a lower heating value than methane. Therefore, blending with the city gas (i.e., existing methane) will result in a drop in the heating value of the blended gas. If hydrogen is reacted with captured CO_2 to produce methane, such a drop in the blended gas can be prevented. Moreover, the existing city gas infrastructure can be used for the blended gas without necessitating modifications or causing problems.

Our group companies of Mitsubishi Heavy Industries Engineering, Ltd. and Mitsubishi Heavy Industries Environmental & Chemical Engineering Co., Ltd. (MHIEC) are collaborating

with the City of Yokohama and Tokyo Gas Co., Ltd. on a pilot test for CO_2 capture and methanation (**Figure 6**; publicly announced in January 2022). Specifically, a small CO_2 capture system will be installed at an incineration plant in Yokohama City to collect CO_2 from combustion exhaust gas of a city waste incinerator. Meanwhile, water will be electrolyzed to produce hydrogen using solar power generation or surplus electricity. Methanation converts these two substances into methane. We are currently moving ahead with the pilot test project, in which we will conduct recovery testing.

The biggest advantage of methanation in the reuse of CO_2 lies in enabling the existing city gas infrastructure to continue to be used in the way it is now. However, from where hydrogen can be obtained and how much it costs are the challenges to deal with.

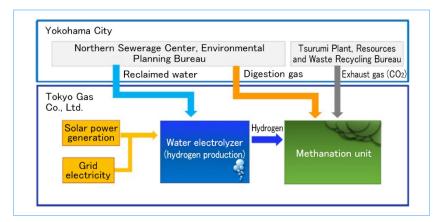


Figure 6 CO₂ capture/methanation from city waste incinerator

4.3 Agricultural use

In protected horticulture, attempts are under way to improve the quality of crops and their yields by controlling the environment in the greenhouses. One of the methods is CO_2 application (CO_2 fertilization). Plants take in CO_2 through stomata on the leaf surface, and light energy is used to produce oxygen and sugar from CO_2 and water in the plants (photosynthesis). Generally speaking, high CO_2 concentrations speed up the rate of photosynthesis. This often results in the closing of stomata and reduces water evaporation (transpiration) through the stomata, which enables plants to lose less water. It is assumed that the CO_2 concentration in the greenhouse is maintained roughly in the range of 400 ppm to several thousand ppm, which is equivalent to the CO_2 levels in the air. Therefore, high-purity CO_2 such as a raw material for chemical synthesis is not necessarily required. The generally practiced CO_2 application methods are the combustion (kerosene and LPG) and the use of the product (liquefied carbon dioxide). The issues to address include: the prevention of formation of harmful substances through complete combustion, high costs of fuels/liquefied carbon dioxide, and stabilization of carbon dioxide procurement (small quantities and supply chain diversity).

In June 2022, our group company Mitsubishi Heavy Industries Engineering, Ltd. delivered the first unit of a compact CO_2 capture system to Taihei Dengyo Kaisha Ltd. in Hiroshima, Japan. With this system, CO_2 is captured from the exhaust gas of a biomass-fired boiler. This CO_2 is sent to a newly built plastic greenhouse on the premises of the power plant and is used for agricultural purposes. Thus, depending on the surrounding environment, the agricultural application can be one of the solutions.

5. Conclusion

For the reduction of CO_2 emissions, not only CO_2 capture but also fixation/storage are critical challenges. From a quantitative point of view, CCS is the most realistic choice. However, the locations of the storage sites are concentrated in North America and around the North Sea. In the areas away from these sites, effective utilization of captured CO_2 and fixation technology are required.

MHI Group is trialing various applications in this regard, for example, in chemical products, fuels and direct use, thus dedicating itself to establishing a carbon cycle from CO_2 capture to reuse and fixation. However, as CO_2 is a chemically stable substance, its use as a raw material of a

chemical product or fuel has many problems from an economic point of view. To tackle these challenges, we continue to work on technological development to contribute to CO_2 reduction, while cooperating not only among our group companies but also with any related organizations such as companies and municipalities.

References

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- (2) Global CCS Institute, 2020, The Global Status of CCS : 2020, Australia
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- (5) Dimethyl Carbonate Market Global Forecast to 2025 (Market and Market TM)