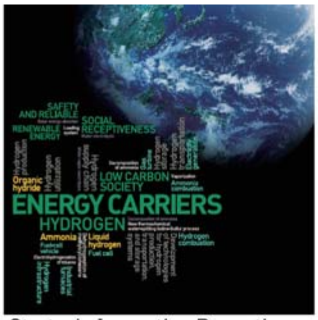
CO_2-Free Energy (Ammonia)



Strategic Innovation Promotion Program (SIP) Energy Carriers[1]

MASAKI IIJIMA[*1] MAKOTO SUSAKI[*2]
HIROYUKI FURUICHI[*3] TAKAHITO YONEKAWA[*4]
NORIAKI SENBA[*4] HIROMITSU NAGAYASU[*5]

In order to abide by the Paris Agreement, it is necessary for CO_2 emissions to be reduced to net zero in the second half of this century, and in other words, fuel that emits no CO_2 (CO_2-free fuel) is in demand. Among such fuel, ammonia is a portable fuel which is easy to carry, and it can be easily produced from natural gas. In addition, the capture and storage of CO_2 emitted in the production of ammonia prevent the emission of CO_2. The production of ammonia has a long history, and it is now distributed at relatively low prices throughout the world. The use of ammonia by direct combustion is also becoming feasible through research on Energy Carriers in the Strategic Innovation Promotion Program (SIP). We hope that a system for using CO_2-free fuel will be developed and such fuel will be used to prevent global warming.

1. Introduction

(1) Paris Agreement and zero CO_2 emissions target

In December 2015, the Paris Agreement was adopted. The general objective of the Paris Agreement is to cap the increase in the global average temperature at 2°C above pre-industrial levels. In addition, in consideration for countries especially vulnerable to climate change, it stipulates that efforts to limit the temperature increase to 1.5°C should be pursued.

To that end, the long-term goal that total global greenhouse gas emissions should be limited to the amount that the ecological system could absorb in the second half of this century was set. This goal is intended to reduce greenhouse gas emissions by human activities to substantially zero.

In order to abide by the Paris Agreement, CO_2 emissions reduction in every field, the reduction of CO_2 emissions to zero in the second half of this century and the introduction of methods for reducing CO_2 in the atmosphere known as negative emission technologies, are necessary.

(2) Need for CO_2-free fuel

In recent years, the introduction of renewable energy such as solar power and wind power has been promoted, and the ratio of renewable energy used in the electric power sector will further increase. In the future, the need for CO_2-free fuel will be diversified, for example, for use in time zones that cannot be covered by renewable energy, for the load adjusting function of electric power, for uses as heat sources of general industries where it is difficult to use renewable energy and for use in fields such as transportation where CO_2 capture and storage cannot be applied.

In Japan, the study of the use of hydrogen energy has been promoted since the WE-NET

*1 Senior Chief Engineer, CO_2 Capture and Environmental Business Development Department, Mitsubishi Heavy Industries Engineering, Ltd
*2 General Manager, CO_2 Capture and Environmental Business Development Department, Mitsubishi Heavy Industries Engineering, Ltd
*3 General Manager, Basic Engineering Department, Mitsubishi Heavy Industries Engineering, Ltd
*4 Group Manager, Basic Engineering Department, Mitsubishi Heavy Industries Engineering, Ltd
*5 Chief Staff Manager, Research & Innovation Center, Mitsubishi Heavy Industries, Ltd.

Project was carried out. Recently, the use of hydrogen has been studied for the purpose of preventing global warming rather than enhancing energy security.

For the transportation of hydrogen, the use of liquefied hydrogen, organic hydride and ammonia has been studied. If the production of hydrogen without the emission of CO_2 is made possible, the remaining challenge is how to transport and use hydrogen in economical ways.

In any case, the provision of inexpensive and CO_2-free fuel will be demanded in various fields in the future.

(3) SIP Energy Carriers

We have conducted research and development on liquefied hydrogen, organic hydride and ammonia as "Energy Carriers" in the Strategic Innovation Promotion Program (SIP). The research and development of the production of carriers (i.e., production from petroleum, natural gas and coal and production from renewable energy), transportation and utilization (i.e., use as hydrogen and direct use of ammonia) have been conducted in the 5-year plan since fiscal year 2014. In the production of CO_2-free fuel such as hydrogen and ammonia from fossil fuel such as petroleum, natural gas and coal, CO_2 capture and storage (CCS) is indispensable. We also conducted testing and research for the inexpensive production of hydrogen through the electrolysis of water using electric power and high-temperature heat produced from renewable energy. **Figure 1**[(1)] shows an overview of testing and research on energy carriers.

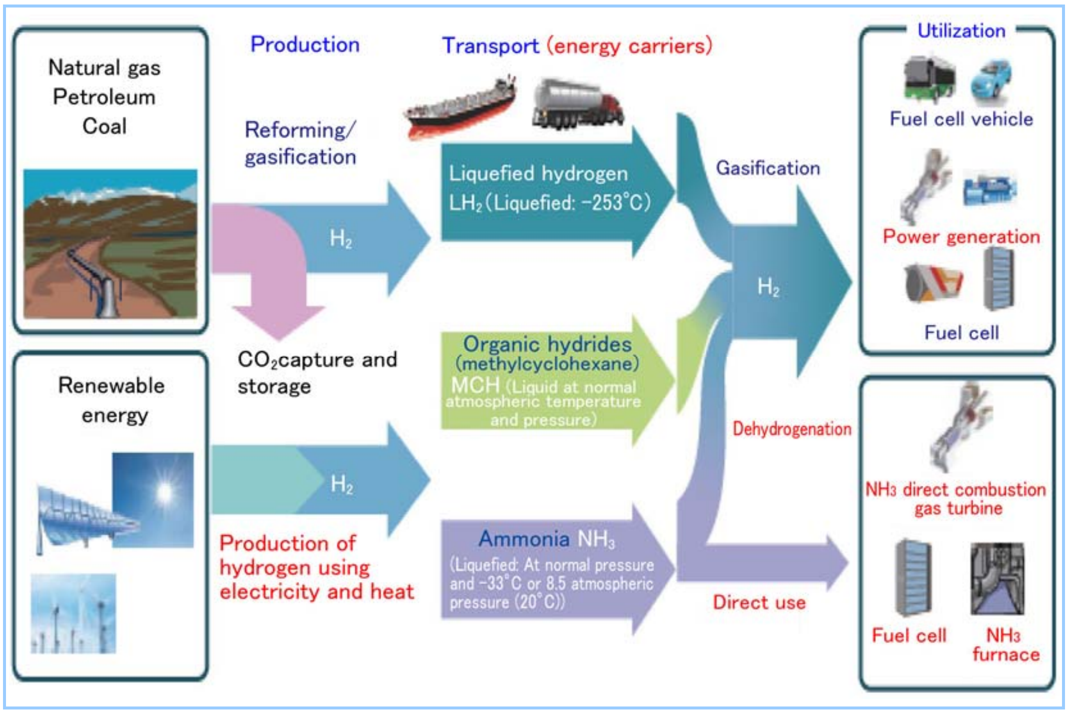


Figure 1 Testing and research on energy carriers

2. Efforts for SIP Energy Carriers

(1) Testing and research on energy carriers as fuel

Testing and research on Energy Carriers[(1)] have been conducted in the 5-year plan from FY2014 to FY2018 and three methods for carrying hydrogen have been evaluated.

a. High-temperature solar heat supply system
b. Hydrogen production using heat
c. Development of ammonia synthesis process using CO_2-free hydrogen
d. Basic technology for hydrogen station using ammonia
e. Ammonia fuel cell
f. Ammonia direct combustion
g. Development of hydrogen supply technology using organic hydride
h. Development of cargo loading/unloading system for liquid hydrogen and the relevant rules for operation
i. Development of hydrogen engine technology

j. Safety assessment of energy carrier

This research on hydrogen production and the utilization of hydrogen/ammonia was conducted with the aim of evaluating which methods (including hydrogen transportation methods) are desirable, and to represent Japan's trailblazing development of hydrogen utilization technology ahead of other countries. In the latter half of the 5-year plan, research mainly focused on the direct use of ammonia, and testing and research on ammonia direct combustion in gas turbines, reciprocating engines, boilers and industrial furnaces and direct ammonia use in solid oxide fuel cells (SOFC) were conducted. In July 2017, ammonia mixed combustion testing was conducted at a coal-fired power plant of Chugoku Electric Power Co., Inc. Through this testing and research, the prospect of putting ammonia direct combustion into actual use was obtained, which was a significant outcome of testing and research on energy carriers.

(2) Evaluation of three methods

Japan has few petroleum, natural gas and coal resources, all of which have been conventionally used for fuel. Even if renewable energy is introduced to the fullest extent possible, it is said that it cannot cover all the energy required in Japan. Therefore, it is absolutely necessary to produce CO_2-free fuel from overseas energy sources or import it. In the case of the transport of materials such as fuel in large amounts, the most economical method for liquid or gaseous fuel is to use pipelines, but when transporting over long distances or across the ocean, it must be liquefied and transported by ship.

The liquefying temperature of hydrogen is very low at -253°C and the amount of power required for liquefying it is very large. Furthermore, it is not easy to maintain the temperature at -253°C.

Ammonia becomes a liquid at -33°C and under atmospheric pressure. On the other hand, when ammonia is pressurized, it becomes a liquid at 8.5 atm and at ambient temperature, providing the advantages of ease of handling and its usability as a direct fuel. Concerning organic hydride, methylcyclohexane produced by adding hydrogen to toluene can be transported at ambient temperature and under atmospheric pressure, but a large amount of energy is required for extracting hydrogen from methylcyclohexane.

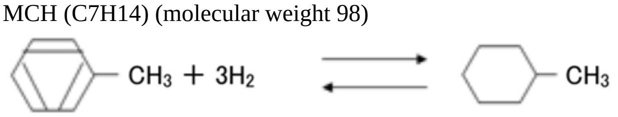
Based on the physical and chemical properties of ammonia and the fact that it is currently distributed throughout the world, the conclusion was reached on "Energy Carriers" in the SIP that ammonia can play an important role as a CO_2-free fuel.

Table 1[(2)] presents a comparison of the physical properties of compressed hydrogen, liquefied hydrogen, methylcyclohexane and ammonia.

Table 1 Physical properties of NH3 and major energy carriers

	Hydrogen content (weight %)	Hydrogen density ($kg \cdot H_2/m^3$)	Boiling point (°C)	Hydrogen release enthalpy change* ($kJ/molH_2$)	Other properties**
Ammonia	17.8	121	-33.4	30.6	Acutely toxic, corrosive
Methylcyclohexane (MCH)	6.16	47.3	101	67.5	Inflammable, irritant
Liquefied hydrogen	100	70.8	-253	0.899	Highly inflammable, highly combustible, explosive
Compressed hydrogen (350 atm)	100	23.2	–	–	
Compressed hydrogen (700 atm)	100	39.6	–	–	

* Carrying hydrogen using the difference of hydrogen between MCH toluene (C7H8) (molecular weight 92) and MCH (C7H14) (molecular weight 98)



* Hydrogen release enthalpy change: Energy required in extraction of hydrogen

** The descriptions in "Other properties" were excerpted from the summary of "Hazardous information" in the MSDS. For the exact properties of each material, see the MSDS for each material.

(3) Effectiveness of ammonia

The physical properties of ammonia are almost the same as those of LPG, and ammonia can be transported using LPG vessels. At present, the production of ammonia amounts to 180 million tons/year globally. About 80% of the production volume is used in fertilizer such as urea, and about 10%, which is 18 million tons/year, is internationally distributed.

At the present time (October 2018), the price of ammonia on an FOB basis in the Gulf of Mexico region in the U.S. is 250US$/T. This price is converted to 14.3US$ in terms of 1 million BTU (MMBTU), which is equal or slightly higher in terms of calorific value compared with the price of crude oil of 70US$/BBL (13.5 US$/MMBTU) (WTI price).

As with LPG, ammonia becomes a liquid when it is pressurized at ambient temperature and it is a portable fuel that is easy to handle in final use.

In particular, when it is used as a fuel for transportation, its ease of transportation at ambient temperature is a significant advantage. However, ammonia is toxic and emits an odor when it leaks, and if it is used near ordinary households, it may cause problems. Therefore, it is considered that ammonia will mainly be used in controlled areas such as in power plants, factories and cargo vessels.

3. Production method of CO_2-free ammonia

In 1913, Germans Haber and Bosch commercialized the process for synthesizing ammonia from hydrogen and nitrogen using an iron-based catalyst, and today the method is used in the production of ammonia. Mitsubishi Heavy Industries Engineering, Ltd. (MHIENG) has delivered many ammonia plants to various countries around the world since 1958. In current ammonia synthesis, natural gas is generally used as a feed stock.

By passing natural gas through a catalyst while heating it together with steam using a steam reformer, the natural gas is converted into hydrogen and CO. After that, air is injected, and the oxygen in the air is used for further combustion to convert the remaining methane into hydrogen and CO, and at the same time, nitrogen is supplied. Steam is added to the CO, which is converted into CO_2 and hydrogen using a catalyst. After that, the CO_2 is separated to produce hydrogen and nitrogen, and then ammonia is synthesized from the hydrogen and the nitrogen.

Figure 2 depicts the balance of CO_2 at a 2000 T/D-scale plant which is a standard ammonia plant. At the ammonia plant, about 2/3 of the CO_2 is separated from the process system, and about 1/3 of the CO_2 is discharged from the exhaust gas of the steam reformer and the auxiliary boiler. By capturing the CO_2 from this flue gases and storing it underground together with the CO_2 from the process system or using it for Enhanced Oil Recovery (EOR), this ammonia plant emits no CO_2. Thus. an ammonia fuel system that does not emit CO_2 can be established.

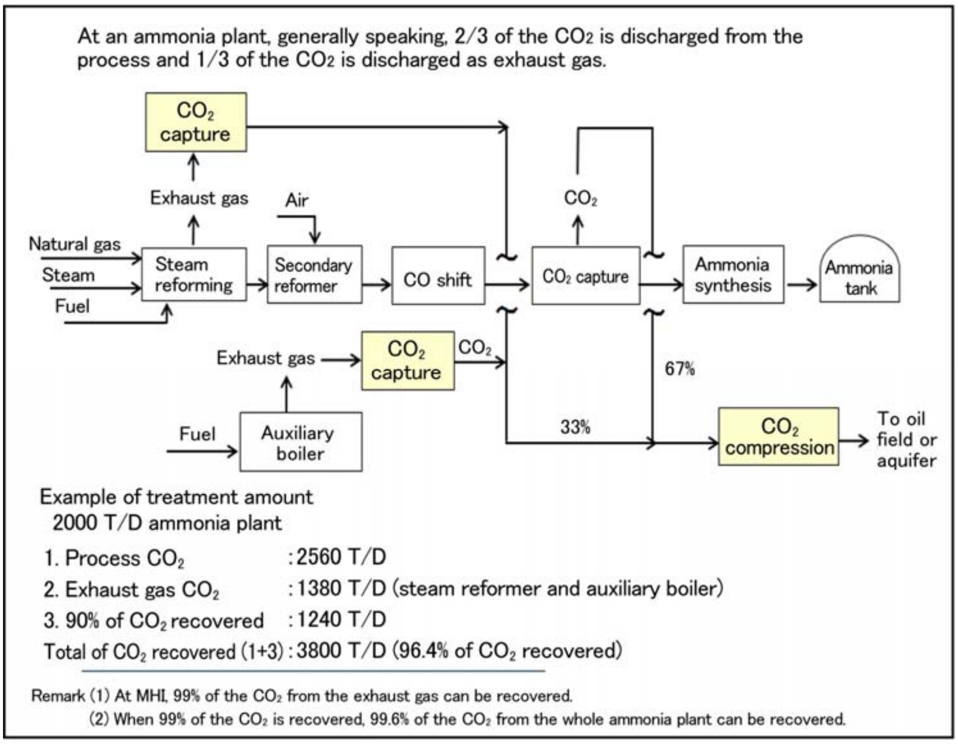
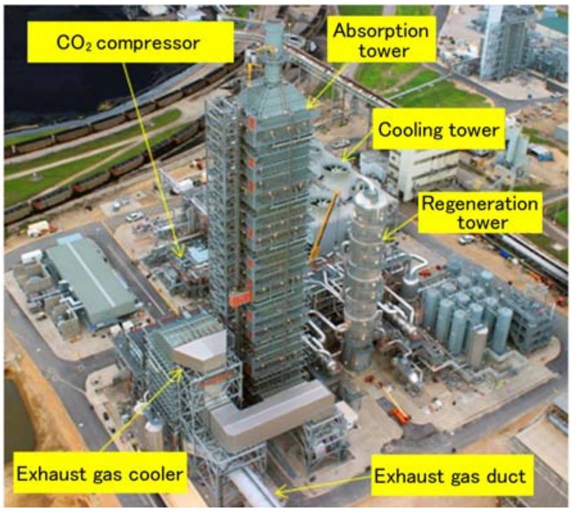


Figure 2 CO_2 balance at an ammonia plant

MHIENG delivered the world's largest CO_2 recovery system to a coal-fired power plant in Texas in the U.S. in January 2017, where the recovered CO_2 is used for EOR at the West Ranch oil field and crude oil is recovered, and CO_2 are stored in an oil reservoir. **Figure 3** gives an overview of the facility for recovering CO_2 from the coal-fired power plant.



NRG Energy, Inc. and JX Nippon Oil & Gas Exploration Corporation
Photo of Petra Nova project

Figure 3 Facility for recovering CO_2 from a coal-fired power plant

Since 2011, in Alabama in the U.S., MHIENG has conducted CO_2 capture from a coal-fired power plant and a demonstration test for storing the captured CO_2 in an aquifer (implemented by SECARB[※1]) jointly with Southern Company. **Figure 4** illustrates an overview of the CO_2 capture and storage project. As such, CO_2 capture and storage has been conducted on a commercial basis, and the technologies for CO_2 capture from exhaust gas at ammonia plants and the production of CO_2-free ammonia have already been established.

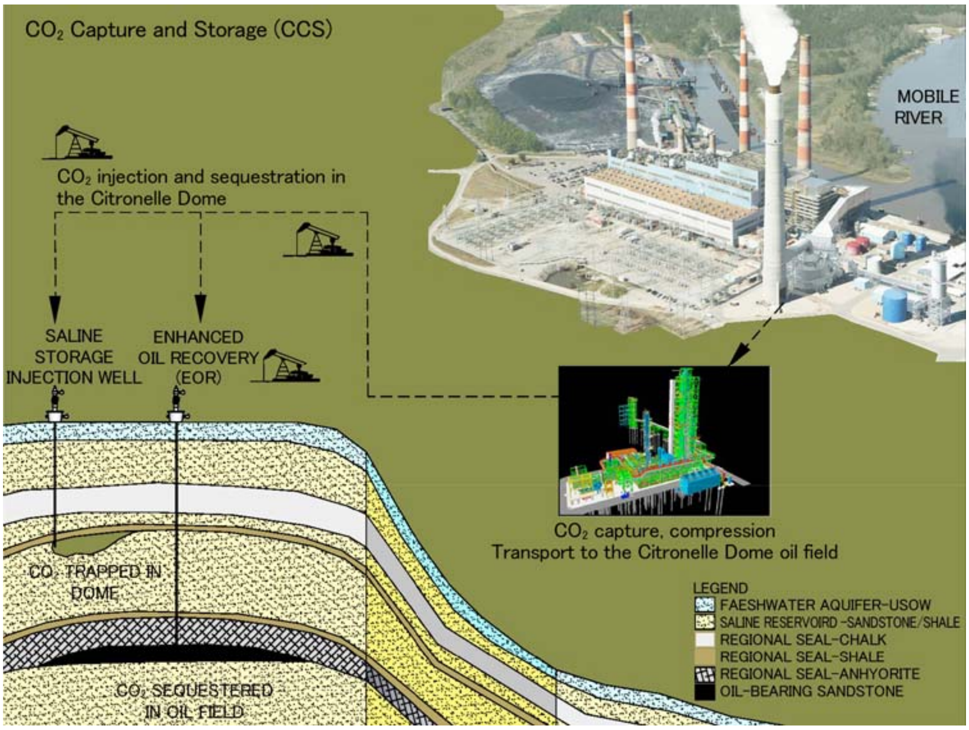


Figure 4 Overview of CO_2 capture and storage project

CO_2 from the process system can be stored as it is a total of 90% of the CO_2 from flue gas can be captured by the CO_2 recovery technology with which MHIENG has a significant amount of experience (KM CDR Process®[※2] developed in cooperation with Kansai Electric Power Co., Inc.), and the captured CO_2 is stored together with CO_2 from the process. As a result, 96% of the CO_2

generated in the production of ammonia can be stored. If 99% is captured from exhaust gas, 99.6% of the CO_2 can be stored, allowing the production of ammonia with almost no CO_2 emissions into the atmosphere.

There is another CO_2-free ammonia synthesis method in which electricity produced from renewable energy is used to electrolyze water and separate nitrogen in the air for the synthesis of ammonia. At present, inexpensive natural gas is produced in massive amounts in various places around the world, and therefore ammonia can be produced at a much lower cost by synthesis from natural gas compared with the use of renewable energy.

※1 The Southeast Regional Carbon Sequestration Partnership

※2 KM CDR Process® is a registered trademark of Mitsubishi Heavy Industries Engineering, Ltd. in Japan, the U.S., European Union (EUTM), Norway, Australia and China.

4. History of use of ammonia as fuel

Some people may not be familiar with the use of ammonia as fuel, but looking back to the Second World War, 100 ammonia-powered buses were used in Belgium.

At that time, diesel fuel could not be procured, and out of necessity, ammonia was used as fuel.

In another example from 1959 to 1968, the X-15 manned jet fighter of the U.S. Air Force used ammonia as fuel, and it reached a record speed of Mach 6.7 at an altitude of 107960m. The temperature was very low at an altitude of 100,000 meters, and it is assumed that the fact that ammonia does not solidify at low temperatures was the reason it was chosen as fuel.

5. Conclusion

CO_2-free fuel is strictly intended to prevent global warming. In order to achieve the target of +2°C or lower based on the Paris Agreement, global CO_2 emissions must be reduced to 1/2 by 2050, and advanced countries must reduce CO_2 emissions by 80%. To that end, CO_2-free fuel that can be used everywhere will become more important. MHIENG has already established commercial CO_2-free ammonia production technology and is ready to provide it at any time.

However, ammonia is more expensive than coal or LNG on the basis of its calorific value, and it is more expensive than even crude oil. For ammonia to be widely used as CO_2-free fuel, it seems that some political incentive is necessary in the early stages of introduction.

We are grateful to the people involved with the promotion of the research and development of "Energy Carriers" in the Strategic Innovation Promotion Program (SIP) who were helpful in writing this article.

References

(1) “Cross-ministerial Strategic Innovation Promotion Program (SIP)” brochure, Energy carrier Cabinet Office,, Japan Science and Technology Agency.
http://www.jst.go.jp/sip/pdf/SIP_energycarriers2016.pdf

(2) F.Shiozawa, Ammonia: Potential as an energy carrier (Part1,Part2) , Journal of the Hydrogen Energy Systems Society of Japan Vol.42 No.1.
http://ieei.or.jp/2017/05/expl170523/
http://ieei.or.jp/2017/05/expl170525/