Fuel Gas CO_2 Recovery Utilization, Disposal, and Business Development

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Mitsubishi Heavy Industries, Ltd. (MHI) has developed a process for recovering CO_2 effectively from the exhaust gas of boilers and other devices in cooperation with the Kansai Electric Power Co., Ltd., which has already been commercialized in the production of urea. This paper presents a review of applications for utilizing CO_2 recovered by this process together with methods for fixing CO_2 as means for helping to prevent global warming. It also describes conditions for making the utilization and sequestration of CO_2 feasible.

1. Introduction

(1) Recent developments in negotiations on the Framework Treaty of Global Warming

The Seventh Session of the Conference of the Parties to the United Nations Framework Convention on Climate Change (COP 7) was held at Marrakesh in Morocco from October 29, 2001. Despite of the unwillingness of the Administration to join the United States (U.S.) from the Kyoto Protocol, other countries concerned reached an agreement that seeks to realize the effective implementation of the Protocol. According to this agreement, these countries are taking steps to ratify the Protocol. Japan also ratified the Protocol in June of this year (2002).

(2) Developments in different countries

The United Kingdom (UK) and the Netherlands have begun a greenhouse gas emission trading system, while other EU countries intend to begin taking part in the system from 2005. Hence, the EU countries are preceding other states in national action.

In the U.S., President Bush announced a new energy policy that seeks to curb the increase in the import of crude oil and the drastic rise in the price of natural gas after declaring the unwillingness of the Administration to join the Protocol. This policy focuses on the long-term development of clean coal technology and the resumption of nuclear power generation.

In Japan, the government decided new general rules for promoting the prevention of global warming. However, it has not yet announced the implementation of the greenhouse gas emission trading system or carbon tax. In the near future, it is expected that the prevention of global warming will be rapidly embodied in Japan, on the basis of ratification of the Kyoto Protocol in June 2002.

2. Standpoints towards the recovery and sequestration of CO_2 in the prevention of global warming

(1) Announcement of IEA at GHGT-5

In addition to these developments on the political front, the international conference of Greenhouse Gas Control Technologies (GHGT) has been held every two years to present the results of recent research as a latest technical movement for the prevention of global warming. Dr. Stoke Orchard and others of the International Energy Agency (IEA) put forth the following view, as a topic deserving of further attention at the fifth conference of GHGT in Cairns, Australia[(1)] in 2000. In short, they note that technologies for making the prevention of global warming practically effective, recovery and sequestration of CO_2 are essential both in terms of scale and cost in order to reduce CO_2. This is because the high efficiency utilization of energy, conversion of fossil fuels into energy with less carbon content, and the use of natural energies such as solar and wind power are not sufficient either in terms of scale or cost. Therefore, the recovery and sequestration of CO_2 will play a major role in the future. Accordingly, the recovery and sequestration of CO_2 must be positively developed and large-scale demonstration tests of suitable methods are absolutely necessary.

(2) Action of different countries in recovery and sequestration of CO_2 and the feasibility of large scale projects

Projects in which the recovery and sequestration of CO_2 are currently being carried out around the world are summarized as below.

In Norway, CO_2 that has been separated from natural gas produced at the Sleipner Gas Field is injected into aquifers on a scale of about one million tons of CO_2 each year. In Canada, Enhanced Oil Recovery (EOR) using CO_2 has been commenced by transporting offgas CO_2 through a pipeline from a coal gasification plant in North Dakota, USA, to the Weyburn Oil Field in Saskatchewan, Canada. This EOR approach not only improves oil recovery, but also the sequestration of CO_2 into oil reservoirs can be carried out practically.

In Japan, a pilot project is being undertaken with the aim of sequestrating a total of 20,000 tons of CO_2 into aquifers in Niigata Prefecture.

Practical CO_2 sequestration projects are being carried out in some countries as outlined above, while some EU countries are able to ensure plenty of areas suitable for the sequestration of CO_2 because aquifers and oil and gas fields are widely distributed mainly in North Sea. The U.S. and Canada have thick sedimentary layers in the plains in their central regions, which also make it possible to provide enough places that are suitable for sequestration CO_2.

On the other hand, Japan does not have sufficient sedimentary layers because it is a volcanic country. In addition, any areas that could potentially be used for sequestration could be easily damaged and destroyed by faults due to volcanic activity and earthquakes. In Japan, therefore, it is quite difficult to find areas that could be adequately secured for sequestrating CO_2. In spite of such a negative conditions, investigation of areas for sequestrating CO_2 is currently being undertaken under the leadership of Research Institute of Innovation Technology for the Earth (RITE), as an effort to expand the possibility of sequestrating CO_2 in Japan.

(3) Utilization of CO_2 for producing energy (petroleum and natural gas)

A very widely used method of producing energy using CO_2 is EOR. CO_2 forms a miscible state (a state where crude oil and CO_2 are freely mixed with each other at a supercritical pressure) in an oil reservoir, so that the viscosity of crude oil is reduced significantly, the fluidization of crude oil is increased in the oil reservoir, and recovery ratio of crude oil is dramatically increased.

Some 200 000 barrels of crude oil are currently being produced each day using this method, mainly in the western region of Texas in the U.S. [(2)]

It is said that, if a large amount of CO_2 can be economically supplied to oil fields, EOR using CO_2 will be widely carried out as a means of contributing significantly to raising oil yields. When an oil field is located close to a large scale CO_2 producing source such as a thermal power station, CO_2 recovered from boiler flue gas can be economically supplied to the oil field in large amounts. MHI has entered negotiations to develop a flue gas CO_2 recovery project based on the concept shown in **Fig. 1**.

In addition to EOR, it is believed that CO_2 is usable for ECBMR (Enhanced Coal Bed Methane Recovery) systems capable of effectively recovering methane gas absorbed in coal by injecting CO_2 into deep coal layers that are difficult to mine coal. A pilot test based on this concept is being carried out at the San Juan Basin on the boundary between New Mexico and Colorado in the U.S. It is believed that coal beds have a higher possibility than oil reservoirs as places for sequestrating CO_2 because they are more widely distributed than oil reservoirs.

Because CO_2 has characteristics that are favorable to the effective recovery of oil and natural gas as mentioned above, it should be used as far as possible in the recovery of oil and natural gas, taking into consideration the goal of preventing global warming, as well.

3. CO_2 recovery technology and MHI flue gas CO_2 recovery system

(1) CO_2 recovery system from natural gas, synthetic gas, and combustion exhaust gas

The separation and recovery of CO_2 have been widely performed already for several decades in the production of natural and synthetic gas. CO_2 contained in natural gas reduces the caloric level of natural gas, while dry ice, that is, solidified CO_2, causes problems in LNG plants and ethane recovery plants. Therefore, CO_2 must be removed to prevent these difficulties.

In plants producing hydrogen by reforming natural gas or naphtha, CO that is produced together with hydrogen in synthetic gas is once converted into CO_2, which is separated later. In the process of producing ammonia and urea, CO_2 is separated from the mixture of hydrogen, nitrogen, and CO_2, after which the urea is then produced from the CO_2 recovered from the mixture and the ammonia synthesized from the hydrogen and nitrogen that remain in the mixture.

On the other hand, the needs to recover CO_2 from combustion flue gas have not been large up to now, except small amounts of CO_2 used to produce food and dry ice. Separation of CO_2 from natural and synthetic

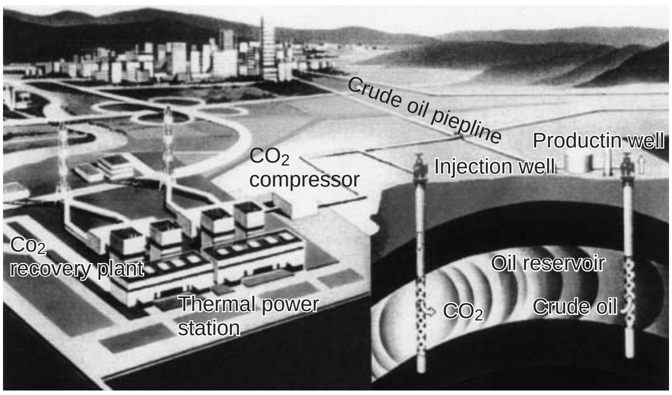

Fig. 1 Conceptualization of EOR using CO_2 recovered from exhaust gas of power station

gas is easy because the original gases have high pressures. However, there are many technical difficulties that need to be overcome in separating CO_2 from exhaust gas, because exhaust gas is low in pressure and contains oxygen, SO_x, NO_x and dust.

(2) Necessity of CO_2 recovery from fixed emission sources

Most fossil fuels (such as petroleum, natural gas, coal) are used as fuel for boilers, gas turbines, and internal combustion engines. These engines, in turn, emit CO_2 into the atmosphere as part of the combustion exhaust gas generated by them. As a result, it is believed that the increased concentrations of CO_2 in the atmosphere are causing global warming. Therefore, unless the amount of CO_2 emitted into the atmosphere is reduced, it will not be possible to prevent global warming. However, there are many difficulties in recovering and sequestrating CO_2 from mobile sources such as cars and ships. Consequently, CO_2 from fixed sources such as boilers and gas turbines is naturally easier to be recovered.

(3) Characteristics and superiority of CO_2 recovery system from exhaust gas

MHI and the Kansai Electric Power Co., Ltd. began to cooperate on a joint research and development project on a CO_2 recovery system based on exhaust gas of thermal power stations in 1990, with the major aim of preventing global warming. At first, the conventional absorption process using monoethanolamine (MEA) absorbent, which had been evaluated as a CO_2 recovery process most superior in terms of energy-savings at that time, was reviewed. As the result of this review, showed that there are difficulties in applying the MEA-based process to a large scale plant for preventing global warming because of problems such as large amounts of energy consumed in recovering CO_2 and the rapid deterioration of the absorbent with its large loss. Accordingly, both companies began the current project, in order to find a new absorbent as a first step in basic research. As a result, they have developed a new energy-saving absorbent that has lower levels of both deterioration and loss. The new absorbent has been already used in a commercial plant that produces urea in Malaysia.

The cooperation of the two companies not only led to the development of the new absorbent but also to the application of new devices and improvements in their developed CO_2 recovery system. In addition, new packing materials capable of remarkably reducing the pressure loss of the exhaust gas system and devices capable of significantly reducing absorbent loss have been also developed.

Furthermore, cooperation between the two companies has led to the development of a new steam system that effectively uses energy in both power station and CO_2 recovery system.

MHI is proceeding with expansion of its business activities using the CO_2 recovery system based on combustion exhaust gas as a core technology and taking advantage of the great superiority of the total system.

4. Technology for effective utilization of CO_2

The applications of the technology for utilization of CO_2 can be broadly classified into the following four areas.

4.1 General use

A very common use of CO_2 is in beverages and dry ice. CO_2 for these purposes is distributed to the market as liquefied carbon dioxide and domestic consumption in Japan is about 800 000 tons/year. Welding, coolant, dry ice, and beverage (cola and beer) are classified as the general use of CO_2.

4.2 Chemical industry

CO_2 is used in the production of a wide range of chemical products such as urea, methanol, DME (dimethylether), GTL (abbreviation of “Gas to Liquid”), soda ash and baking soda (sodium bicarbonate), as well as oxo-gas and CO.

(1) Urea

Urea is currently produced by the synthesis of ammonia synthesized mainly from low cost natural gas and CO_2 recovered from the offgas of the ammonia-synthesizing process. However, when urea is synthesized using natural gas as a feed stock through steam reforming, there is a shortage in the balance of CO_2 to ammonia. Accordingly, in order to improve the balance of CO_2 to ammonia, CO_2 recovered from the offgas of a steam reformer producing hydrogen and CO from natural gas is fed into the urea synthesis process so that the volume of urea produced is maximized. The urea plant of the Petronas Fertilizer Co. in Malaysia delivered by MHI was designed based on this process.

(2) Methanol

At present, methanol is also produced primarily from natural gas. Hydrogen and CO are produced in a ratio of 3:1 by steam-reforming of the natural gas. However, since the optimum ratio of hydrogen and CO is 2:1 when synthesizing methanol, CO_2 recovered from the gas in the steam-reforming process of natural gas is recycled to the up stream of the same process as a supplement of carbon in order to maximize the production of methanol. In order to increase the production capacity of methanol plant in Saudi Arabia, delivered by MHI, plans are currently being made to modify the production process by injecting CO_2 recoverd from flue gases.

Fig. 2 shows a system in which CO_2 recovered from the flue gas of a steam reformer is recycled to optimize the ratio between hydrogen and CO in order to increase the volume of methanol produced, in the process of producing methanol using natural gas as a feed stock.

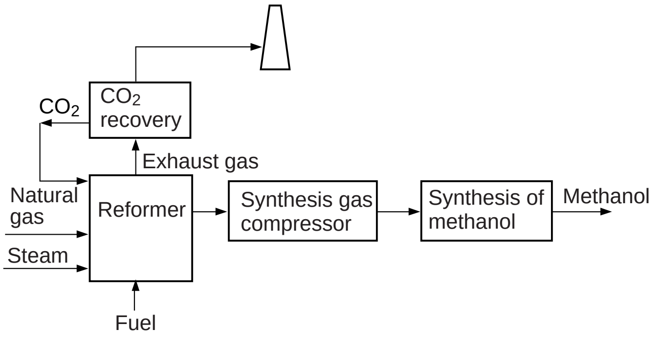

Fig. 2 System for increasing methanol production by CO_2 recovered from offgas in methanol plant

(3) DME

DME is synthesized through methanol, using the same system as that used in the preceding method to produce methanol.

(4) GTL

GTL is a process of synthesizing kerosene and gas oil from natural gas through Fischer-Tropsch (FT) synthesis. In this GTL synthesis, it is necessary to adjust the ratio of hydrogen and CO to be 2:1 in the same way as in methanol production. Therefore, CO_2 recovered from the offgas of a steam reformer is recycled to the synthesis process line, so that the ratio of hydrogen and CO can be adjusted, accordingly.

From the standpoint of total system design, this process adopts a system in which CO_2 that is not used to contribute to the FT synthesis reaction is recycled to the upper stream of the steam reformer.

4.3 Utilization of CO_2 for EOR

Of the several methods with the potential to increase the yield of crude oil, an EOR system using CO_2 is a system that theoretically can make oil recovery to the maximum. CO_2 has properties such as low critical pressure, low critical temperature, heavy specific gravity, and large solubility in oil, which is favorable to the EOR. The EOR system using CO_2 improves oil recovery and makes oil production economically feasible, because CO_2 increases the fluidization of crude oil largely in an oil reservoir by making crude oil miscible at lower pressure than natural gas.

Many CO_2-EOR projects have been commercialized mainly in the U.S. since the 1970s, and currently about 200,000 barrels of crude oil is additionally produced each day through the use of such systems. In addition to the U.S., the systems have also been used in Canada, Turkey, and Hungary. In fact, among the CO_2 applications in use, CO_2 consumption is greatest in EOR.

In the U.S., CO_2 is supplied from CO_2 gas fields through pipe lines. On the other hand, the MHI flue gas CO_2 recovery system installed in a power station makes it possible to conduct EOR in an oil field close to the power station, because CO_2 recovered from the exhaust gas of the power station can be supplied directly to the oil field. The preceding Fig. 1 shows an outline of this concept. In order that the CO_2 - EOR is economically feasible, a large amount of crude oil must be additionally produced through the injection of CO_2, which in turn requires that a large amount of CO_2 be available at low cost. According to one feasible study, it has been verified that the MHI flue gas CO_2 recovery system installed in a power station close to an oil field makes EOR highly feasible. The MHI system not only can improve oil recovery but can also contribute to the prevention of global warming by reducing the level of CO_2 emissions.

4.4 Utilization of CO_2 for recovery of coal bed methane

The systems used in the recovery of methane from coal beds and CO_2 from combustion exhaust gas as a measure for sequestrating CO_2 have already been explained in Item (3) of Section 2 above.

5. Sequestration method of CO_2

The sequestration of CO_2 has been well studied both with respect to geological and ocean sequestrations, with the former already having been applied in commercial projects.

Geological sequestration includes the EOR systems already noted above, as well as coal bed methane recovery performed together with coal bed seam sequestration of CO_2. There are three methods of sequestration that are used strictly in the sequestration of CO_2: those in aquifers in abandoned oil reservoirs, and abandoned gas reservoirs.

Underground aquifers are widely distributed in areas where there are sedimentary layers in the earth. In Japan, however, sedimentary layers are small in scale with the result that aquifers are few in number. Despite such negative conditions, studies are being carried out to explore the possibilities for extending the opportunities to sequestrate CO_2.

There are voids in underground beds that are filled with water (usually salty water). CO_2 can be sequestrated in these voids, with the water being replaced by the injection of CO_2. **Fig. 3** shows a conceptual schematic of the sequestration of CO_2, that has already been carried out in Norway. In Japan, it is thought that the

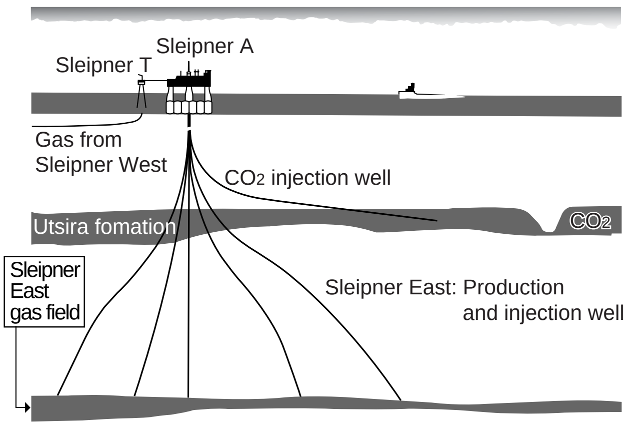

Fig. 3 CO_2 disposal in Norway
In Norway, CO2 recovered from natural gas is disposed of in underground aquifers.

sequestration of CO_2 into aquifers distributed in the continental shelf is the most practical method that can be adopted, in the same way as in Norway[3].

In addition to aquifers, abandoned oil and gas reservoirs that are no longer productive are possible locations where CO_2 can be sequestrated. Both oil and gas reservoirs were created in ancient times with their upper structures preventing oil or gas from leaking into surrounding geological structures. Accordingly, it is thought that such reservoirs are natural locations where it is possible to ensure the safe injection and storage of CO_2.

6. CO_2 emission trade and cost of recovering and sequestrating CO_2

(1) Present trends in CO_2 emission trading prices

CO_2 emission trade began in the U.K. in April 2002. Work is moving ahead to revise applicable laws in other EU nations to permit the region as a whole to start trading of CO_2 by 2005. When CO_2 emission trade begins as whole the EU in 2005, the trading market price is expected to be about 20 to 33 euros/ton of CO_2. The penalty to be imposed when the agreed limits on CO_2 emissions are exceeded is expected to start from 50 euros/ton of CO_2 and rise up to a level of 100 euros/ton of CO_2 in the future[4].

(2) Cost of recovering and compressing CO_2

MHI is endeavoring to reduce the CO_2 recovery costs required to operate a CO_2 recovery system as well as the costs to compress and dehydrate CO_2 required to supply recovered CO_2.

It is presumed that there is a possibility of reducing the CO_2 compressing and dehydration costs to 20 US dollars/ton of CO_2 at locations where a large amount of exhaust gas is available, a large scale CO_2 recovery plant can be installed, and where fuel costs are low. It is expected that the cost of transporting and sequestrating recovered and compressed CO_2 can be reduced to 5 US dollars/ton in the future, although these costs are largely dependent on the distance from the source of CO_2 emission to the location where the CO_2 is sequestrated and the conditions of that location. According to some forecasts, CO_2 recovery and sequestration would become feasible if the total cost could be reduced to 25 US dollars/ton of CO_2.

(3) Condition for ensuring feasibility

In order that a plant recovering CO_2 from combustion exhaust gas can be feasible, CO_2 must be efficiently available and the user of recovered CO_2 must also be ensured of obtaining a sufficient level of profitability. MHI is currently expanding various activities that are mainly focused on realizing the effective use of CO_2 technology, as explained in Section 4.

The recovery cost and price of CO_2 are infinitely variable depending on location. For instance, in the case where energy cost is high and recovery of CO_2 can be performed only in a small scale like Japan, the CO_2 recovery cost is provably around 10 000 yen/ton of CO_2.

On the other hand, where low cost energy is readily available and CO_2 can be recovered on a large scale as is the case in oil-producing countries, total costs, including costs for recovering and compressing CO_2, can probably be reduced to about 20 US dollars/ton of CO_2.

If CO_2 emission trading markets are established worldwide in the future and the CO_2 emission trading price becomes 25 US dollars or higher for each ton of CO_2, projects that are aimed strictly at CO_2 sequestration will become feasible. Then, CO_2 recovery and sequestration will become a widely used means of preventing global warming.

7. Conclusion

As explained in the previous Section, CO_2 recovery from combustion exhaust gas is already feasible at present in some fields (chemical applications and EOR) where CO_2 is effectively utilized.

MHI intends to expand the utilization of the MHI flue gas CO_2 recovery system in such fields, and also work for the early realization of projects recovering and sequestrating CO_2 from the exhaust gas of power stations, with the aim of contributing to the prevention of global warming as a final goal.

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