

# Methanol Synthesis Technology Using CO<sub>2</sub> from Steelworks

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## Abstract:

*To reduce CO<sub>2</sub> emissions from steelworks, a methanol synthesis process using CO<sub>2</sub> from blast furnaces is under development. Since methanol synthesis reactors using CO<sub>2</sub> with existing technologies are expected to be expensive due to lower reaction efficiency and water production, a membrane reactor that can improve reaction efficiency and separate methanol from water is a promising candidate. The separation membrane which influences the performance of the membrane reactor was examined on heat resistance, separation selectivity and durability in high temperature and high pressure of the methanol synthesis reaction, and a promising separation membrane was developed. It was demonstrated that the methanol yield using the membrane reactor was more than double that using the conventional reactor in the reaction test. Further simulations were carried out based on the experimental results for scaling up.*

## 1. Introduction

The response to climate change is an urgent issue that requires reduction of greenhouse gases (GHG), beginning with CO<sub>2</sub>, which are considered to be its cause. Because the steel industry accounts for approximately 14% of total CO<sub>2</sub> emissions in Japan<sup>1)</sup>, development of technologies that contribute to reducing CO<sub>2</sub> emissions by the steel industry, on its own initiative, has an extremely large significance. However, the blast furnace process is the main source of CO<sub>2</sub> emissions in the steel industry, and the technical hurdles to the develop-

ment of a carbon neutral substitute process are high. Even though the Japanese government has set a goal of achieving carbon neutrality (CN) by 2050<sup>2)</sup>, a trial calculation<sup>3)</sup> has shown that the iron and steel-making process will continue to remain as a source of CO<sub>2</sub> emissions even in 2050, suggesting that it will be necessary to use carbon capture and storage (CCS) and carbon capture and utilization (CCU) are required.

Because steelworks exhaust gas has a higher CO<sub>2</sub> concentration than combustion gas from power plants and boilers, and the scale of CO<sub>2</sub> emissions is also larger, it is considered to be a promising CO<sub>2</sub> source for CCU. JFE Steel is conducting multitrack technology development from this viewpoint with the aim of achieving CN in 2050, and is devoting great effort not only to realizing CN in the steelmaking process, but also to the development of CCU technologies<sup>4)</sup>.

To effectively utilize CO<sub>2</sub>, it must be converted to valuable chemicals for which demand exists. Therefore, as one effective utilization technology for CO<sub>2</sub>, JFE Steel is developing a technology for methanol synthesis from CO<sub>2</sub> emitted from steelworks. Methanol is a basic chemical with increasing global demand year by year<sup>5)</sup>, and is also a promising alternative to petroleum-derived chemical feedstocks and fuels. Stable demand is foreseen in the future, even after various CN technologies reach maturity, and the expandability of technology development is also very large.

This paper reports on the development of a membrane reactor which is capable of high efficiency methanol synthesis from CO<sub>2</sub> as a methanol synthesis tech-

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nology for reducing CO<sub>2</sub> emissions from steelworks.

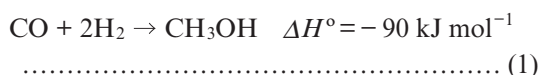
## 2. Chemistry of Methanol

### 2.1 What is Methanol?

Methanol is a colorless, transparent liquid at normal temperature and pressure and is the simplest alcohol, which is expressed by the chemical formula CH<sub>3</sub>OH. Since various organic compounds such as ethylene and propylene as feedstocks for plastics, aromatic hydrocarbons including pharmaceuticals as feedstocks for high performance chemicals, and gasoline, *etc.* can be synthesized from methanol, it is one of the central compounds in C1 chemistry, which is a technological system for conversion of compounds that contain one carbon atom. If CO<sub>2</sub> discharged from steelworks and green hydrogen can be substituted for the conventional fossil resources used as feedstocks for methanol synthesis, it will be possible to reduce emissions of fossil resource-derived CO<sub>2</sub>.

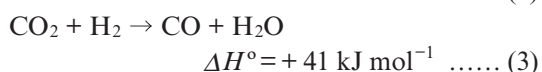
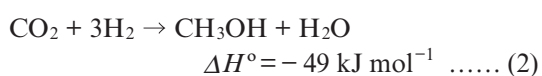
### 2.2 Methanol Synthesis

At present, methanol is mainly produced by converting syngas (mixed gas of H<sub>2</sub>/CO) obtained by steam reforming of natural gas to methanol using a Cu-Zn based catalyst<sup>6)</sup>. The reaction formula is shown in Eq. (1).



Because this is an exothermic reaction which reduces the amount of the substance, higher pressures and lower temperatures are more advantageous in terms of equilibrium constraints, but considering the kinetic advantage, the reaction is conducted under high pressure and high temperature conditions of approximately 5 to 20 MPa and 200 to 280°C.

On the other hand, methanol synthesis from CO<sub>2</sub> is also being studied from the viewpoint of reducing CO<sub>2</sub> emissions, and a small-scale methanol production plant has been in commercial operation in Iceland since 2012<sup>6)</sup>. The chemical formulas for the main reaction and side reaction of CO<sub>2</sub>-based methanol synthesis are shown in Eqs. (2) and (3), respectively.



When CO<sub>2</sub> is used as the feedstock, methanol can also be synthesized by using a Cu-Zn catalyst in the

same manner as with CO feedstocks, but because the equilibrium constraints are stricter than when using a CO feedstock, lower temperature and higher pressure conditions must be used to obtain a methanol yield on the same level. Although a high temperature is kinetically desirable, it is disadvantageous in terms of equilibrium due to the exothermic reaction, and the endothermic reaction shown by the Eq. (3) will also proceed more easily. Moreover, the H<sub>2</sub>O that forms stoichiometrically must be separated from the methanol formed by this reaction, and H<sub>2</sub>O is also a cause of catalyst deactivation<sup>6)</sup>. Thus, if CO<sub>2</sub> is to be used as the feedstock, a decrease in reaction efficiency and an increase in the separation load are in principle unavoidable, and commercial production of methanol from CO<sub>2</sub> is extremely limited from the viewpoint of cost competitiveness. To address this issue, energetic development of catalysts and reactors that contribute to cost reduction is underway.

## 3. Study on Application of Membrane Reactor to Methanol Synthesis

### 3.1 Membrane Reactor

A membrane reactor is a reactor in which reaction and separation can be performed simultaneously by using a membrane with a separation function, i.e., a separation membrane. Membrane reactors can be classified into 3 types, the Extractor type, in which a designated substance is separated from the reaction field, the Distributor type, in which the designated substance is supplied to the reaction field, and the Active contactor type, in which the interior of the separation membrane is used as the reaction field<sup>7)</sup>. The extractor type is an effective reactor for methanol synthesis, which is an equilibrium reaction. If it is possible to separate only the target product in the reaction field, the reaction can be accelerated by Le Chatelier's principle and the separation process in the following stage can be simplified, which means that process simplification, reduced energy consumption and, in turn, cost reduction can be expected. **Figure 1** shows the membrane reactors being

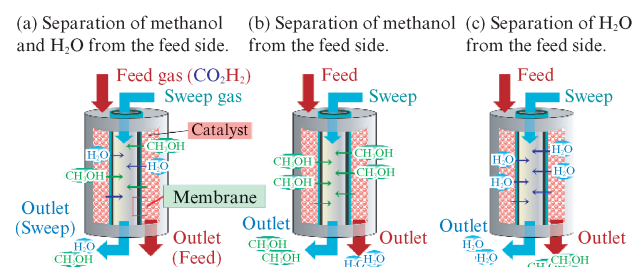


Fig. 1 Concept of membrane reactors for methanol synthesis

studied for application to methanol synthesis from CO<sub>2</sub> for each type of separation membrane. The product separation type<sup>8)</sup> shown in (a) separates methanol and H<sub>2</sub>O from the reaction field, the methanol separation type<sup>9)</sup> in (b) separates only methanol, and the H<sub>2</sub>O separation type<sup>10)</sup> in (c) separates only H<sub>2</sub>O. In all three types of membranes, a zeolite membrane is formed on a porous ceramic tube, and permeation selectivity is controlled by the properties manifested by the structure and composition of the zeolite. The Product separation type in (a) has a large effect in accelerating the equilibrium reaction because all the products are separated from the reaction field, but it is necessary to separate the methanol and H<sub>2</sub>O in the following stage. The Methanol separation type in (b) can simplify product separation in the following stage, but the above-mentioned catalyst deactivation is a concern because H<sub>2</sub>O remains in the reaction field. Regarding the H<sub>2</sub>O separation type in (c), the membrane itself has been applied practically, but there are no examples of practical application to vapor permeation, and the durability of the membrane at a high temperature is a potential problem. Because JFE Steel is developing a methanol synthesis process using the (c) H<sub>2</sub>O separation type separation membrane and membrane reactor, looking at the utilization of the separated steam, which is conducted jointly with the Research Institute of Innovative Technology for the Earth (RITE).

### 3.2 Separation Membrane

In developing the H<sub>2</sub>O separation type membrane reactor, we focused on membranes formed by LTA type zeolite<sup>11)</sup>, which also have commercialized in dehydration applications involving bioethanol and other alcohols, and prepared a prototype in the laboratory. **Figure 2** shows an SEM image and the principle of the prepared membrane<sup>12)</sup>. The membrane consists of a layer of LTA type zeolite approximately 3  $\mu\text{m}$  in thick-

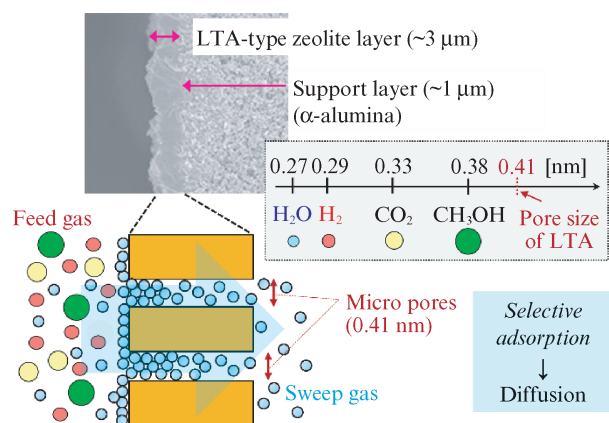


Fig. 2 SEM image and mechanism of separation membranes made of LTA-type zeolite<sup>12)</sup>

ness and its porous support. Although the pore size (0.41 nm) of the LTA type zeolite is larger than any of the molecules related to the methanol synthesis reaction, intrapore diffusion of molecules other than H<sub>2</sub>O is suppressed by selective adsorption of H<sub>2</sub>O on the hydrophilic surface. In other words, permeation selectivity for H<sub>2</sub>O originates from the H<sub>2</sub>O adsorption. However, because the H<sub>2</sub>O adsorption is exothermic, the amount of H<sub>2</sub>O adsorption decreases as the temperature increases, which means permselectivity decreases. Accordingly, whether the high selectivity can be maintained even under a high temperature condition like the methanol synthesis reaction is a key technology.

Permeation tests of a mixed vapor of H<sub>2</sub>O and methanol were carried out with various kinds of membranes formed by the LTA type zeolite. **Figure 3** shows the H<sub>2</sub>O permeance (flux per unit of partial pressure difference) and the selectivity of H<sub>2</sub>O with respect to methanol (permeance ratio: H<sub>2</sub>O/methanol)<sup>12)</sup>. The performance of commercial product A was divided into 4 parts and an evaluation for each part was also plotted as reference. It should be noted that the test does not show the separation performance of commercial product A under its practical application conditions, as this test was different from the standard application of product A. The selectivity of separation membrane ① synthesized based on the literature<sup>13)</sup> was on the same level as that of commercial product A. The hydrophilicity and heat resistance of zeolite generally increase as the Si/Al ratio becomes larger<sup>14)</sup>. Therefore, when studying the synthesis conditions aiming at improved performance under high-temperature conditions, we prepared a new separation membrane ② with a Si/Al ratio increased to 1.5, and found that the selectivity was dramatically improved while maintaining its permeance on the same level as separation membrane ①. As a result, the target performance of the mem-

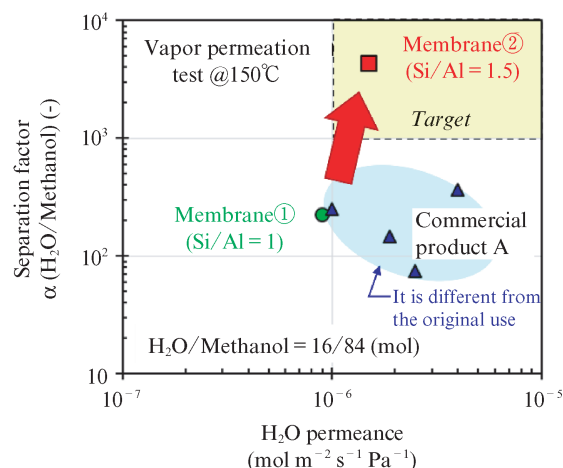
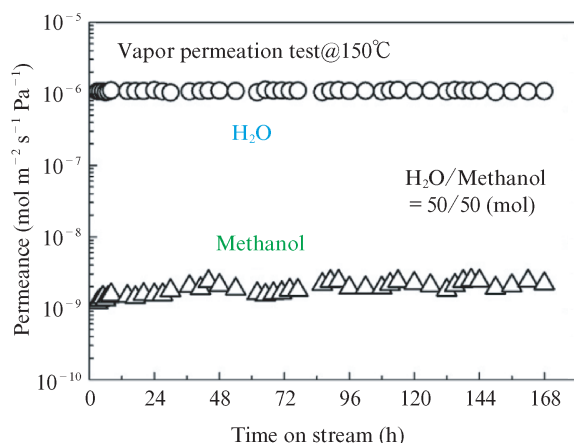


Fig. 3 Separation performance of various membranes made of LTA-type zeolite<sup>12)</sup>

Fig. 4 Durability test of new membrane<sup>12)</sup>

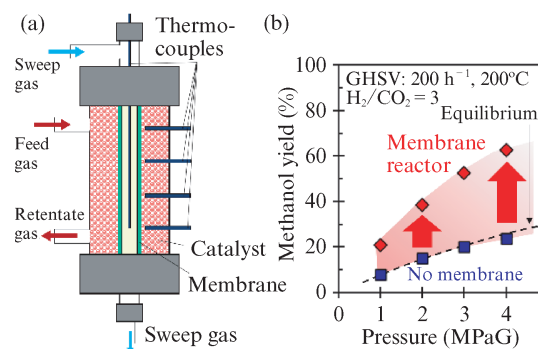
brane reactor (selectivity  $> 10^3$ , H<sub>2</sub>O permeance  $> 10^{-6}$  mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>) was achieved.

Next, a durability test of the new membrane was conducted using the same apparatus as the permeation test described above. Since it is known that LTA type zeolite is unstable in high-temperature environments that include a large amount of water vapor<sup>15)</sup>, an accelerated test was carried out with excess H<sub>2</sub>O (50 mol%). The results are shown in **Figure 4**. The permeance of H<sub>2</sub>O and methanol was steady in continuous operation for 168 h, demonstrating that stable, high separation performance is possible. Based on these results, the new membrane is considered to be a suitable for methanol synthesis.

### 3.3 Methanol Synthesis Test Using New Separation Membrane

A laboratory-scale methanol synthesis test was conducted using the new membrane described in section 3.2. **Figure 5** (a) shows a diagram of the membrane reactor<sup>12)</sup>. The reactor had a double-tube structure consisting of a porous alumina inner tube (effective membrane length: 120 mm), on which the membrane was formed on the outer surface, and a pressure vessel holding the inner tube (diameter: 41 mm). The space between the inner tube and the pressure vessel was filled with a commercially-available Cu-Zn catalyst, and the reaction test was performed by flowing H<sub>2</sub> and CO<sub>2</sub> through the catalyst. For comparison, a reaction test using a non-porous SUS tube with no membrane as the inner tube was also carried out using a non-porous SUS tube with no membrane as the inner tube.

Fig. 5 (b) shows the results of the methanol synthesis test at each reaction pressure<sup>12)</sup>. The Gas Hourly Space Velocity (GHSV), which expresses the feedstock gas flowrate (L h<sup>-1</sup>) per amount of catalyst (L), was set at a constant 200 h<sup>-1</sup>. When the membrane was not used, the methanol yield was substantially the same as

Fig. 5 (a) Apparatus of membrane reactor and (b) result of methanol synthesis tests<sup>12)</sup>

the equilibrium yield. However, when the membrane was used, the methanol yield increased greatly at all reaction pressures, and exceeded 60% at 4 MPaG. When the membrane was not used, the purity of the methanol was  $< 50$  mol%, but purity improved to  $> 95$  mol% when the membrane was used. These results provided experimental clarification that both a remarkable reaction acceleration effect and separation of methanol and H<sub>2</sub>O in the reaction field can be achieved by using the membrane.

## 4. Scaling-Up the Membrane Reactor

### 4.1 Design Based on Material Properties

As described above, the superiority of the membrane reactor was clarified at the laboratory scale. However, for practical application, it is necessary to scale-up the membrane reactor to increase CO<sub>2</sub> throughput. A simulation was carried out to establish the design policy and identify problems in scaling-up. A model incorporating the rate formula of the methanol synthesis reaction<sup>16)</sup> and the rate formula of membrane permeation was prepared, and after adjustment based on the test results in Figure 5, a 1-dimensional isothermal simulation was carried out with GHSV fixed at 2 000 h<sup>-1</sup>. Assuming use of 7 membrane tubes with a membrane length of 1 m and an outer diameter of 12 mm in the membrane reactor, the effect of the amount of catalyst at a constant membrane surface area was studied. Although the amount of catalyst is increased by enlarging the reactor inner diameter  $d_1$ , the evaluation was carried out at a constant GHSV by simultaneously increasing the feedstock gas flowrate. The simulation results are shown in **Figure 6**. The results showed that the maximum methanol yield occurred when  $d_1=70$  mm, indicating that an appropriate ratio of the membrane surface area and the amount of catalyst exists. As the reason for this, it is thought that the membrane, which ideally should allow perme-



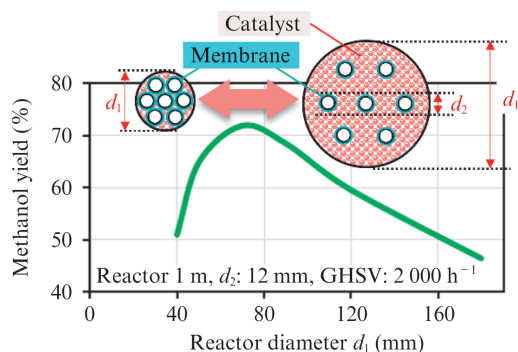


Fig. 6 Effect of reactor diameter on methanol yield

ation of only H<sub>2</sub>O, also allows permeation of some H<sub>2</sub>, which has a small molecular diameter. When  $d_1 < 70$  mm, the membrane surface area is relatively large in comparison with the feedstock gas flowrate, and it is thought that the methanol synthesis reaction is suppressed by a significant drop in the partial pressure of H<sub>2</sub> in the feedstock gas due to H<sub>2</sub> permeation of the membrane. On the other hand, when  $d_1 > 70$  mm, the membrane surface area is relatively small in comparison with the feedstock gas flowrate, and H<sub>2</sub>O permeation of the membrane becomes insufficient, suppressing the equilibrium shift effect. In other words, an optimum design exists, depending on the respective performances of the membrane and catalysts and the setting of GHSV.

For actual operation of a reactor, factors such the structure of the connecting parts and the maintenance method must also be considered. For example, it is possible to insert 7 membrane tubes with outer diameters of 12 mm if the inner diameter of the reactor is larger than  $d_1 = 36$  mm, but if  $d_1$  of the reactor is too small, it will be physically impossible to fix the membrane tubes and fill the catalyst because the tubes will be too close to each other. This means that it is necessary to set a practically possible value of  $d_1$ . In addition, if the membrane tubes are fixed at both the top and bottom of the reactor, as illustrated in Figure 5 (a), there is an increased possibility that the tubes may crack due to the difference in the thermal expansion coefficients of the metal pressure vessel and the ceramic membrane tubes as the length of the tubes becomes longer. **Figure 7** shows a schematic diagram of a membrane reactor of 1 meter scale, considering these kinds of operational problems and material properties.

Considering the difference in the thermal expansion coefficients of the materials, a cantilever design supported at the bottom was adopted for the membrane tubes, and an opening was provided at the top of the reactor to allow catalyst filling. To ensure workability when inserting and fixing the membrane tubes,  $d_1 > 70$  mm was adopted as the reactor inner diameter,

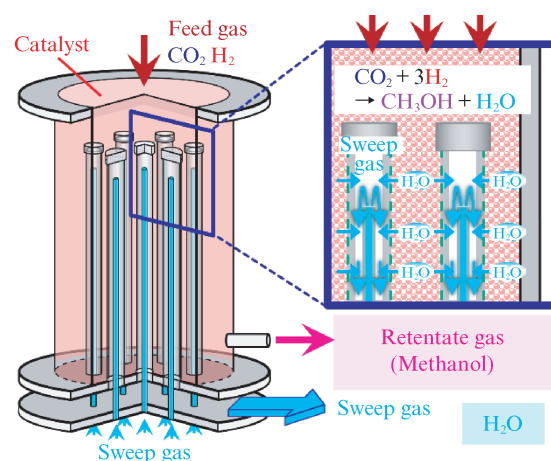


Fig. 7 Schematic diagram of a 1 m-scale membrane reactor

and uniform spacing was provided between the tubes. Moreover, in order to accelerate removal of H<sub>2</sub>O and heat from inside the reactor, as the structural design adopted for this reactor, the sweep gas is circulated from inner tubes inside the membrane tubes, and after changing directions and returning from the tip of the membrane tubes, the sweep gas is discharged from the reactor bottom together with H<sub>2</sub>O.

#### 4.2 3-Dimensional CFD Simulation

Based on the 1-dimensional model and design concept in section 4.1, two types of CFD simulation models were constructed to study the influence of reaction heat and the effect of the membrane, and an analysis was conducted. Type (i) was a packed bed reactor without H<sub>2</sub>O permeation, and type (ii) was a membrane reactor with H<sub>2</sub>O permeation. The lengths of both reactors were 1.2 m (length of permeable part of membrane: 1 m), and heat medium oil for cooling was circulated from the bottom to the top of the outer periphery of the reactor. The feedstock gas (H<sub>2</sub>/CO<sub>2</sub> = 3, 40 NL min<sup>-1</sup>, 5 MPaG, 200°C) introduced from the top, while the sweep gas (Ar, 40 NL min<sup>-1</sup>, 0 MPaG, 25°C) was introduced from the inner tubes inside the membrane tubes. The reactor was designed so that the membrane tubes occupied the space from the bottom to a height of 1.1 m, and a space containing only the catalyst, without membrane tubes, existed 0.1 m in the upper part. The results of a temperature distribution analysis of the reactor are shown in **Figure 8** (a). In both (i) packed bed reactor and (ii) membrane reactor, heat was generated at the height range of 1.0 to 1.2 m, and the temperature reached approximately 240°C. In the height range from 0 to 1.0 m, heat generation did not occur in (i), but temperature reaching about 230°C occurred in (ii).

Figure 8 (b) shows the methanol yield at each height (0.2 m increments) in the two reactors. No difference

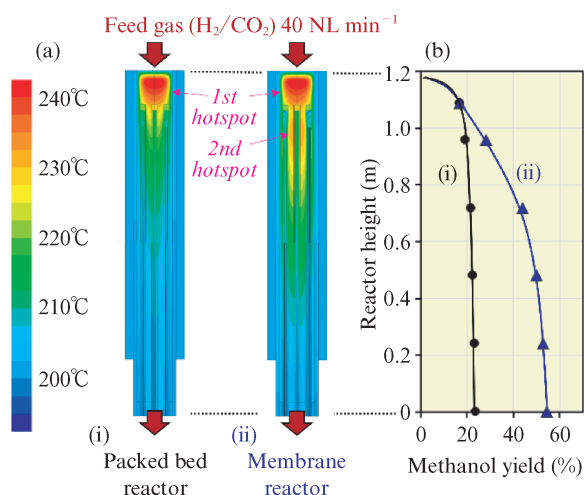


Fig. 8 (a) Temperature distribution and (b) methanol yield of each reactor

between the two reactors can be seen at heights from 1.0 to 1.2 m, and the methanol yield was about 20%. On the other hand, in the height range from 0 to 1.0 m, the methanol yield remained about 20% in (i) due to equilibrium constraints, while in (ii), the reaction was accelerated remarkably by H<sub>2</sub>O separation, and the methanol yield increased to 55%. The heat generation in the height range of 0 to 1.0 m in (ii) occurred due to acceleration of the methanol synthesis reaction by the membrane. As can be seen in Fig. 8 (a), it was found that hotspots occurred around two areas in the membrane reactor, that is, in the vicinity of the inlet and at the membrane.

In scaling-up the membrane reactor, a design that minimizes the thermal load on the membrane is extremely important from the viewpoints of durability and separation performance. Therefore, the effect of heat removal from the interior of the reactor by the sweep gas was studied. There are two methods for circulating the sweep gas, the co-current method and the counter-current method. In the co-current method, the sweep gas is supplied from the tip of the membrane tubes using the inner tube as the inlet, and the gas then flows in the same direction as the feedstock gas along the inner wall of the membrane tubes. In the counter-current method, the sweep gas flows along the inner wall of the membrane tubes in the opposite direction from the feedstock gas and is supplied as far as the tip of the membrane tubes; in this case, the inner tube acts as the outlet. **Figure 9** shows the results of an analysis of the temperature distribution in the upper part of the reactor for these two sweep gas flow methods. Focusing on the temperature of the feedstock gas in the area around the membrane tube, the temperature was about 230°C with the co-current flow, but temperature reaching nearly 240°C occurred with the counter-current

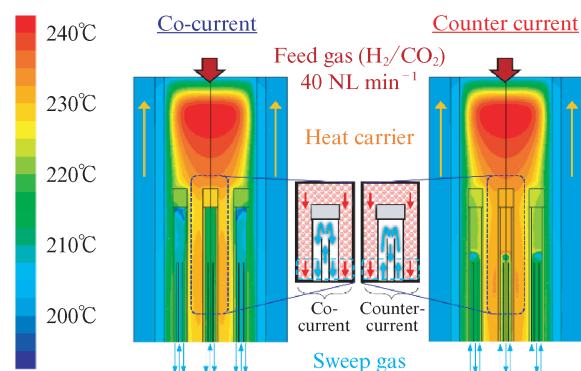


Fig. 9 Effect of flow direction of sweep gas on temperature distribution of membrane reactor

flow. Looking at the temperature inside the membrane tube, the temperature with the co-current flow was generally 220°C or less, and regions where the temperature fell below 200°C also existed. However, with the counter-current flow, the temperature was about 220°C at the outer periphery and approximately 230°C in the central part. Because deterioration of the selectivity at higher temperatures is a concern when the temperature exceeds 200°C<sup>17)</sup>, it was found that the difference in the heat removal effects of the co-current and counter-current flows is an important factor that has a large influence on the performance of the membrane reactor.

### 4.3 Experimental Apparatus of Large-Scale Membrane Reactor

Based on the experimental and simulation studies, the large-scale membrane reactor shown in **Photo 1** was designed and fabricated, and was introduced adjacent to the bench-scale plant for CO<sub>2</sub> capture and separation ASCOA-3<sup>18)</sup> at JFE Steel's West Japan Works (Fukuyama). The specification of the apparatus was based on the schematic diagram in Figure 7 and made

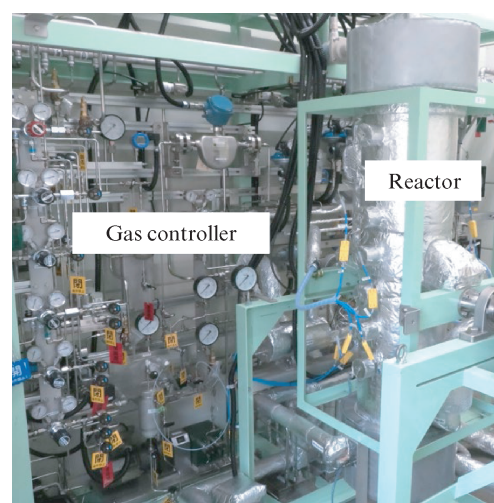


Photo 1 Experimental equipment of 1 m-scale membrane reactor

it possible to insert up to a maximum of 7 membrane tubes, and the co-current sweep gas flow method was adopted, reflecting the results in section 4.2. Heat medium oil was used for heat removal when steady operation was achieved and for heating at the start of the reaction. Using this apparatus, which makes it possible to conduct methanol synthesis reaction tests under various conditions, various technical issues are currently under study with the aim of establishing a practical process. In the future, a demonstration test in which methanol is synthesized from the actual blast furnace gas by sequential operation with the ASCOA-3 is planned.

## 5. Conclusion

As an initiative for carbon neutrality currently being in progress at JFE Steel, this article introduced the development of a technology for methanol synthesis from CO<sub>2</sub> by a membrane reactor. In many cases, examples of research on membrane reactors using a combination of a gas-solid catalytic reaction and a membrane are comparatively small, laboratory-scale projects. Therefore, the authors wish to promote technology development that clarifies the engineering-related issues and leads to solutions through scaling-up, with the aim of practical application.

Part of these results were obtained in commissioned projects (JPNP16002, JPNP20014) of Japan's New Energy and Industrial Technology Development Organization (NEDO).

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