Biogas Upgrading Using Zeolite Membranes

Kanadevia has developed a zeolite membrane that selectively separates water from organic compounds. We provide a range of users with membrane dehydration equipment that recycles organic solvents or upgrades bioethanol. Recently, we also developed biogas upgrading units to separate carbon dioxide (CO_2) from biogas as a new application of zeolite membrane and completed demonstration tests overseas. Kanadevia's biogas upgrading units selectively remove CO_2 with minimal methane losses, thereby contributing to the reduction of greenhouse gas (GHG) emissions and achieving high biomethane recovery.

Key Words

Zeolite membrane, Biogas upgrading, GHG reduction

■ Background

Zeolite is a crystalline oxide mainly composed of silicon and aluminum, and has micropores, less than 1 nm wide, throughout its structure. A membrane made from this zeolite is called a zeolite membrane, and separation is achieved by molecular sieving through these pores.

Kanadevia has been rolling out its membrane separation business since 2005, and designs and produces separation and purification units that include proprietary zeolite membrane elements (**Figure 1** (L), 16 mm diameter, 1130 mm length) developed by our company. **Figure 1** (R) shows a schematic representation of the separation. The substance to be separated (biogas in this illustration) is supplied to the outside of the membrane, and the chemical potential difference (pressure difference, concentration difference) between the inside and outside of the membrane is used to make the substance to be removed (CO_2 in this illustration) pass through the membrane. To date, we have delivered many zeolite membrane dehydration units aimed at regenerating organic solvents and upgrading bioethanol. Separation using zeolite membranes is a technology that contributes to the reduction of energy used in separation processes, which are mainly based on distillation, in

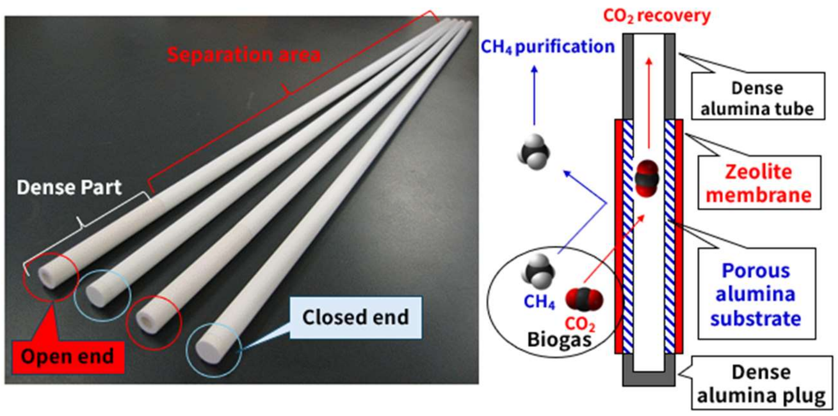

Figure 1 Zeolite membrane element (L) and schematic illustration of separation process (R)

chemical plants, thereby helping reduce GHG emissions, and contribute to achieving a carbon neutral society. To further expand the membrane separation business, we focused on biogas purification as a new application for zeolite membranes.

When organic waste is directly disposed of in landfills, methane is generated and released into atmosphere. Although methane can serve as a fuel, it is a GHG with a global warming potential 28 times that of CO_2. For this reason, countries around the world are studying the appropriate treatment of organic waste, such as anaerobic digestion or composting, with the aim of making effective use of methane and reducing emissions. Among these methods, anaerobic digestion is a technology in which anaerobic microorganisms generate methane from organic waste, enabling appropriate treatment of it and producing carbon-neutral energy.

Biogas is generated using this anaerobic digestion, and it normally contains about 60% methane and 40% CO_2. Due to the high CO_2 content, the calorific value of biogas is lower than that of city gas, and its utilization for power generation requires dedicated biogas combustion equipment. To achieve higher usability, enrichment of methane (biogas upgrading) is required. By purifying biogas, biomethane can be obtained as a refined gas with a calorific value equivalent to city gas 12A. It is widely utilized in Europe and the United States as fuel for power generation, in households, and for automobiles.

A number of methods already exist for biogas upgrading, such as absorption, adsorption, and polymer membrane processes. Based on the idea that zeolite membranes, which separate gas components by molecular sieving, can enable higher-precision biogas upgrading and offer processes with high methane recovery rates while suppressing methane emissions, we began development.

■Biogas upgrading unit

1. Zeolite membrane

In developing a biogas upgrading unit, we first developed a zeolite membrane specifically designed for CO_2 separation. The kinetic diameter of methane is 0.38 nm, while that of CO_2 is 0.33 nm. Therefore, to achieve a molecular sieving effect, a zeolite with pore sizes between these two molecular diameters is required. However, the zeolite membrane that we had already commercialized for dehydration has a pore size of 0.4 nm, so it could not separate methane and CO_2 by molecular sieving.

The zeolite membrane we developed has pores with a diameter of 0.38 nm, so it will selectively allow only the CO_2 of biogas containing both methane and CO_2 to pass through, thereby upgrading the methane. The permeance of CO_2, which is a key performance index for separation membranes, is 1.7 x 10^{-6} mol/($m^2 \cdot s \cdot Pa$), and the ratio of the permeance for CO_2 and methane is over 100[1)]. This is a higher separation performance than that of the polymer membranes previously used for biogas upgrading.

2. Biogas upgrading process

Figure 2 shows the biogas upgrading process used by Kanadevia. The biogas upgrading process can be divided into the pre-treatment process and the membrane separation process. The pre-treatment process is used to eliminate volatile organic compounds (VOC), moisture, hydrogen sulfide, and other impurities. The permissible concentrations of these impurities are regulated in various countries or regions as standards for biogas use, so must be eliminated. In this process, scrubbers and activated carbon remove VOCs and hydrogen sulfide, while separators and dryers remove moisture.

The membrane separation process is used to remove CO_2 and concentrate the methane. The biogas, from which the impurities were removed in the pre-treatment process, is compressed by a compressor and fed to the separation membrane. The demonstration testing (discussed later) used the membrane module shown in the summary column. It adopted a two-stage separation flow, with the permeable gas in the first stage off-gassed,

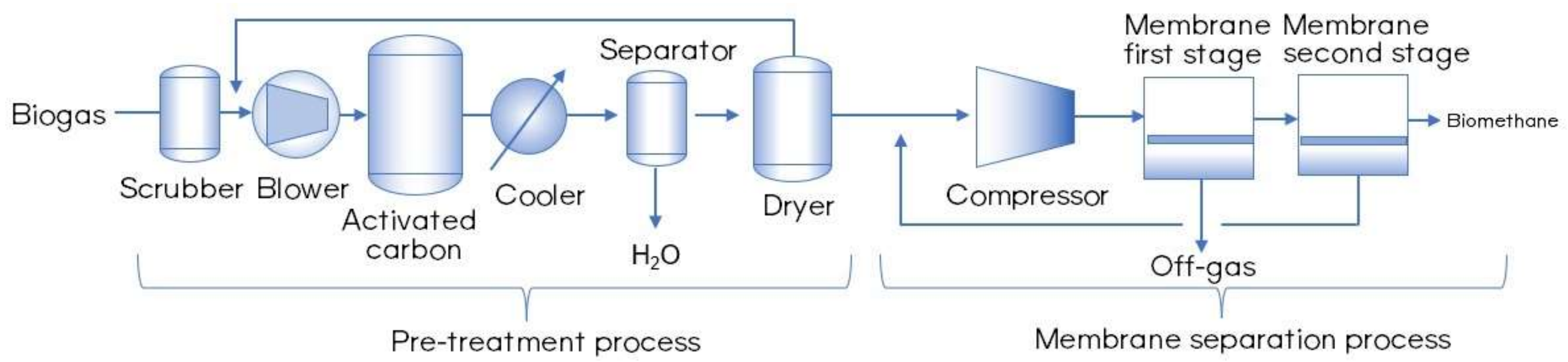

Figure 2 Biogas upgrading process

and the permeable gas in the second stage recycled, thus improving the methane recovery rate.

■Demonstration testing of biogas upgrading unit

We conducted a demonstration test of biogas upgrading overseas using actual biogas made from cow dung and other materials. The performance targets for this demonstration test were set at a CO_2 concentration of 4% or less within the biomethane and a methane loss of 2% or less. The changes in CO_2 concentration in the biomethane during the demonstration testing are shown in **Figure 3**. The CO_2 concentration and methane loss during rated operation held steady at not more than 4% and not more than 2%, respectively.

Based on the demonstration test results, the zeolite membrane performance showed no deterioration during the test period. In addition, analysis of the zeolite membrane used in the demonstration test revealed no changes compared with its condition before testing.

These results suggest that high-purity biomethane can be obtained stably with a high recovery rate.

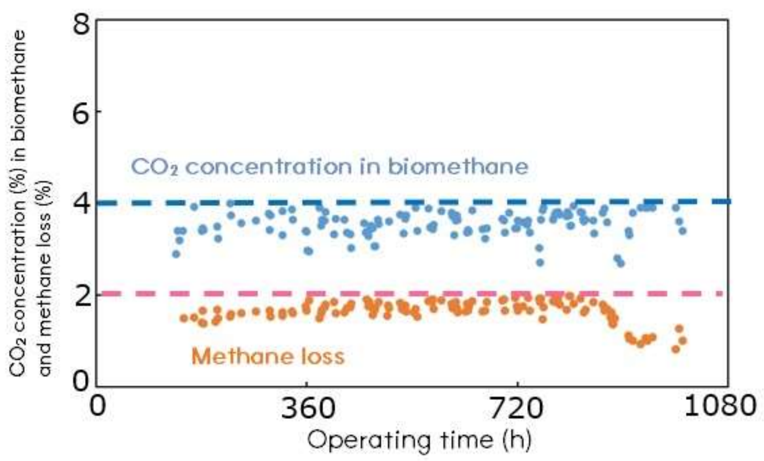

Figure 3　Changes in CO_2 concentration in biomethane and methane loss during demonstration testing

■ Conclusion

To further expand our membrane separation business, we developed a zeolite membrane specialized in the separation of methane and CO_2 and a biogas upgrading unit. We have completed demonstration testing overseas and are moving towards commercialization. At the same time, we are also moving ahead with studies on developing a process that will improve methane recovery rates still further, and find ways to use the separated CO_2. In the future we aim to apply zeolite membranes not only to biogas but also to applications such as flare gas recovery in the natural gas sector, thereby contributing to the reduction of greenhouse gas emissions.

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References

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