Technology

Development of Technology for Removing Water in Ammonia Mixed Gases Using Separation Membranes

TSUCHIHASHI Yuta*　　NAKAYAMA Yoshiki*

1. Introduction

Ammonia is produced by the Haber-Bosch process, which uses nitrogen and hydrogen as raw materials and reacts them under high temperature and high pressure, and has long been used for various applications including fertilizer and raw materials for chemical fibers. Also in the semiconductor manufacturing process, high-purity ammonia is used as a material gas, and its water content, which especially affects semiconductor device characteristics, is required to be as low as the ppm to ppb order. A general method for purifying industrial ammonia gas containing tens to hundreds of parts per million of water using a physical adsorbent and supplying it has been established, and we have also commercialized an ammonia purification system that removes trace amounts of water [1].

In recent years, new ammonia synthesis methods using nitrogen in the air and water vapor as raw materials have been researched for environmental friendliness [2, 3]. The ammonia produced by these methods is estimated to contain a large amount of water, and thus inquiries to us regarding purification and water removal of ammonia are increasing.

The use of adsorption purification in order to remove water from ammonia gas containing near-saturated water vapor (water content > 1 vol%) poses the following issues.

- The amount of adsorbent required and the size of adsorption cylinder increases as a large amount of steam is dealt with, and the energy required to remove water from the adsorbent during the regeneration process increases.
- Since ammonia is also coadsorbed on the adsorbent along with water, the amount of ammonia exhausted and lost in the regeneration process increases as the amount of adsorbent required increases.

So, we have developed a water removal technology that combines conventional adsorption purification with membrane separation purification to downsize the adsorption purification section and reduce the energy required for the regeneration process and the ammonia loss. This report describes the purification method and its evaluation results.

2. Overview of the purification process

Membrane separation purification is a method of purification based on the difference in membrane permeation rate caused by the difference in molecular size and the interaction between the membrane and molecules. In this development, we selected a straw-shaped hollow membrane with one side closed as the separation membrane and made a module by inserting the membrane inside the metal housing shown in Figure 1. Gas supplied from the inlet flows around the outside of the membrane, and selectively permeates the membrane, whose inside is kept at a low pressure by a vacuum pump, due to the pressure difference. The ammonia purification and water removal process selectively allows the water to permeate the membrane inward, and obtains the water-removed ammonia from the membrane-impermeable gas outlet. By returning the vacuum pump exhaust to the upstream side of the process as shown in Figure 2, the ammonia purification and water removal can be performed without loss of ammonia even if it is mixed in with the membrane-permeated gas.

We evaluated the membrane separation purification process with the aim of using it as a preliminary step for adsorption purification to reduce the water load there and the amount of adsorbent used, thereby reducing the energy required for the regeneration process and the ammonia loss.

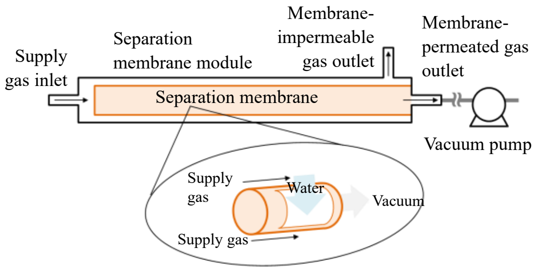

Figure 1 Water removal with separation membrane

* Chemical Synthesis Department, Tsukuba Development Center, R&D Unit

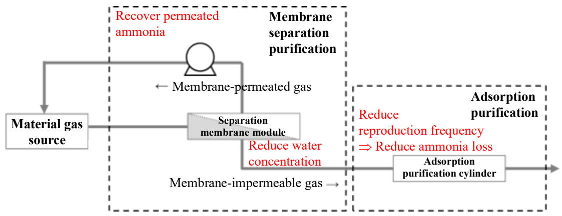

Figure 2 Overview of purification process

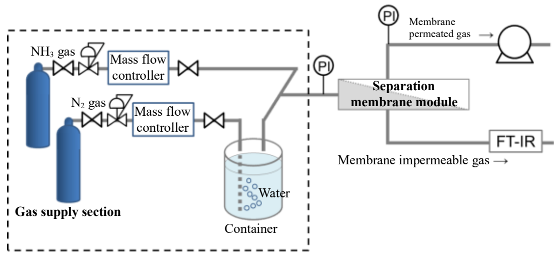

Figure 3. Flow of basic evaluation equipment

3. Basic evaluation of membrane separation purification

3.1. Membrane used for evaluation

It is known that the separation performance of separation membranes varies greatly depending on the material that constitutes the membrane (hereinafter referred to as “membrane material”). In this evaluation, we selected zeolite separation membranes, whose practical example[4)] in water removal from organic solvents is known. The gas permeation rate through the membrane varies depending on the chemical affinity between the gas molecules and the membrane material (such as Si/Al ratio) and the compatibility between the size and shape of the gas molecules and the membrane structure (such as pore size) [5)] Therefore, we selected three types of separation membranes with different Si/Al ratios and pore sizes as shown in Table 1 for evaluation.

Table 1. Membrane used for evaluation

Separation membrane	Si/Al ratio	Pore size [nm]
A	Low	0.40
B	Medium	0.38
C	High	0.38

3.2 Evaluation equipment and method

Figure 3 shows the flow of the basic evaluation equipment. The equipment consisted of a gas supply section, a separation membrane module housing a separation membrane, a vacuum pump, and an analyzer (FT-IR). In the gas supply section, nitrogen gas was bubbled into water to generate gas containing saturated water vapor, which was then mixed with ammonia gas. The resulting nitrogen-based ammonia gas mixture (water concentration of about 1 vol% and ammonia concentration of 8 vol%) was supplied to the separation membrane module at atmospheric pressure and then purified with the inside of the membrane kept at a low pressure of about 300 PaA by the vacuum pump. Then, the water and ammonia concentrations of the membrane-impermeable gas were measured using FT-IR.

Two indices were used for the evaluation: water removal rate and ammonia yield, as shown in Equation 1 and Equation 2. The higher the ammonia yield, the less ammonia permeated the membrane, meaning that the water removal was highly selective.

$$\text{Water removal ratio (\%)} = \frac{\text{(Water concentration in supply gas)} - \text{(Water concentration in membrane-impermeable gas)}}{\text{Water concentration in supply gas}} \times 100 \quad (1)$$

$$\text{Ammonia yield (\%)} = \frac{\text{Ammonia concentration in membrane-impermeable gas}}{\text{Ammonia concentration in supply gas}} \times 100 \quad (2)$$

3.3 Evaluation results

Table 2 shows the evaluation results for each separation membrane. Under conditions where the contact time between the supply gas and the separation membrane was short, the water removal rate was only about 50%, but the ammonia yield exceeded 90%, confirming selective water removal (Entry 1 to Entry 3). This selectivity is presumably due to the fact that condensable gases such as water vapor generally have a higher affinity for zeolite pores.

Next, when the contact time was extended, the separation membrane A exhibited an improvement in water removal rate while maintaining the selectivity (Entry 4), while the separation membranes B and C exhibited a significant decrease in selectivity (Entry 5 and Entry 6) although the water removal rate improved. In general, the lower its Si/Al ratio, the more hydrophilic the zeolite tends to be. The separation membrane A is considered to have the strongest interaction between the membrane and water molecules, thus presumably leading to the high water selectivity.

Finally, we selected the separation membrane A and optimized the contact time, so that more than 90% in both the water removal rate and the ammonia yield was achieved.

Table 2. Basic evaluation results

Entry	Separation membrane	Contact time with separation membrane [s]	Water removal ratio	Ammonia yield
1	A	0.0020	52.5%	97.0%
2	B	0.0020	51.9%	93.5%
3	C	0.0020	43.3%	95.0%
4	**A**	**0.049**	**84.5%**	**96.4%**
5	B	0.049	91.0%	42.8%
6	C	0.049	91.4%	51.6%
Optimum conditions	A	0.073	90.9%	92.6%

4. Demonstrative evaluation of combination with adsorption purification

4.1 Evaluation equipment and method

Figure 4 shows the flow of the demonstrative evaluation equipment. The equipment was configured according to the concept shown in Figure 2: The membrane separation purification section was connected to the material gas source, membrane-impermeable gas was introduced into the adsorption purification cylinder, and the adsorption purification cylinder was connected to the FT-IR. Table 3 shows the conditions for membrane separation and adsorption.

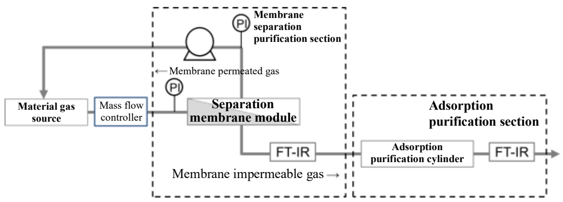

Figure 4 Flow of demonstrative evaluation equipment

Table 3 Demonstrative evaluation conditions

Item		Condition
Membrane separation	Contact time with separation membrane [s]	A 0.073
Adsorption separation	Adsorbent LV [cm/s] SV [h^{-1}]	Molecular sieve - 3A 1.22 64.0

4.2. Evaluation results

Table 4 shows the results. The ammonia yield and water removal rate in the membrane separation purification section almost reproduced the results of the basic evaluation. The actually measured amount of the coadsorbed ammonia was 1.42 kg. It was confirmed that the membrane separation purification followed by adsorption purification removed water to the ppm order (< 2 ppm, below the detection limit).

Table 4 Demonstrative evaluation results

Item		Result
After membrane separation purification	Ammonia yield Water removal ratio	93.9% 88.7%
After adsorption purification	Water content	< 2 ppm

Based on these results, the water load on the adsorbent and the ammonia process yield were estimated and compared for each of the cases: “membrane separation purification + adsorption purification” and “adsorption purification only”. Figures 5-1 and 5-2 show flow diagrams with the conditions of the calculations indicated in red. The amount of water that can be adsorbed by the adsorption cylinder is estimated to be 2.80 kg when the water concentration in the gas is 0.11 vol% and 3.50 kg when the water concentration is 1.0 vol%, based on the results of a water adsorption test conducted beforehand using the adsorption cylinder alone.

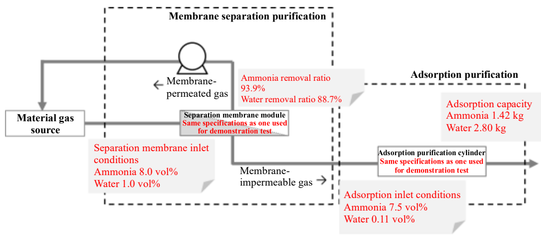

Figure 5-1 Estimation condition “membrane separation purification + adsorption purification”

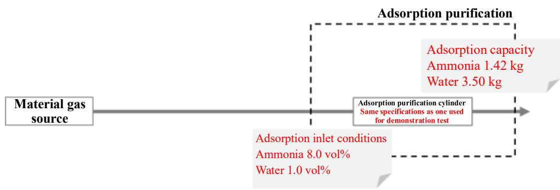

Figure 5-2 Estimation condition “adsorption purification only”

Table 5 shows the results of the estimations. In the case of “adsorption purification only”, 3.50 kg of water is adsorbed and the adsorbent breaks when 435 m^3 of gas is supplied into the adsorption cylinder. On the other hand, in the case of “membrane separation purification + adsorption purification”, the amount of adsorbed water is 0.31 kg when 435 m^3 of gas is supplied into the adsorption cylinder, which is 3.19 kg less than the case of “adsorption purification only”. The water loading ratio in this case is 11% (= 0.31 kg adsorbed / 2.80 kg adsorption capacity), which means that the amount of adsorbent and adsorption cylinder size can be reduced by 89%. It is expected that the reduction in the amount of adsorbent will also reduce the heating energy used in the regeneration process.

Table 5 Water loading ratio evaluation results

Item	Membrane separation purification + Adsorption purification	Adsorption purification only
Weight of adsorbed water [kg] [a]	0.31	3.50
Water loading ratio [b]	11%	100% (broken)

[a] Weight of adsorbed water when 435 m^3 of gas is supplied into adsorption cylinder

[b] Calculated by (Amount of adsorbed water) / (Adsorption capacity) × 100

Next, the ammonia yield improvement effect of reducing the amount of adsorbent by 89% in the case of “membrane separation purification + adsorption purification” was estimated. Figure 6 shows a flow diagram with the conditions of the estimation indicated in red. By reducing the amount of adsorbent, the amount of coadsorbed ammonia is also reduced by 89% to 0.16 kg.

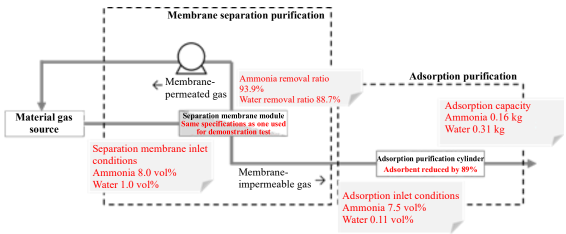

Figure 6 Estimation condition “membrane separation purification + adsorption purification”

Table 6 shows the results of the estimations. The weight of ammonia product obtained when 435 m^3 of gas is supplied into the adsorption cylinder was calculated to be 24.6 kg. The overall process yield by weight after the amount of coadsorbed ammonia was subtracted was 99.4%. When the same calculation is performed for “adsorption purification only,” the yield is 94.6%, indicating that the combination of membrane separation purification and adsorption purification can improve the ammonia yield of the process by about 5%.

Table 6 Ammonia process yield calculation results

Item	Membrane separation purification + Adsorption purification with reduced adsorbent	Adsorption purification only
Weight of coadsorbed ammonia [kg]	0.156	1.42
Weight of obtained ammonia[kg] [a]	24.6	25.0
Ammonia process yield [b]	99.4%	94.6%

[a] Weight of obtained ammonia when 435 m^3 of gas is supplied into adsorption cylinder

[b] Calculated by (Weight of obtained ammonia) / {(Weight of obtained ammonia) + (Weight of coadsorbed ammonia)} × 100

5. Conclusion

We conducted a basic evaluation of water removal by membrane separation and found conditions under which both high selectivity and water removal rate can be achieved. In addition, we conducted a demonstrative evaluation of the combination of membrane separation purification and adsorption purification, and achieved water removal to the ppm order from an ammonia gas mixture containing approximately 1 vol% water. The obtained results show that membrane separation purification reduces the water load on the adsorbent, that the amount of adsorbent required can be reduced by 89%, and that the ammonia yield in the process is improved by about 5% compared to the case of adsorption purification only.

In the future, we will improve the analytical method and measure the ppb level of water content to more accurately evaluate the water removal capability, and will also check the durability of the separation membrane and optimize the adsorption cylinder size through long-term evaluation.

Reference

1) Toshiyuki Abe, Kenetsu Uemori, Eiji Kurita, Takashi Yoneda, Taiyo Nippon Sanso Technical Report, **2004**, *23*, 86
2) Ashida, Y.; Arashiba, K.; Nakajima, K.; Nishibayashi, Y. *Nature*, **2019**, *568*, 536.
3) Lan, R.; Irvine, J. T. S.; Tao, S. *Scientific Reports*, **2013**, *3*, 1145.
4) Division of Separation Processes, The Society of Chemical Engineers, Japan, Recent Chemical Engineering 63: Latest Advanced Membrane Separation Processes - From Fundamentals to Applications, Sankeisha, **2014**, p110-111.
5) Hiroshi Sagara, “Separation Technology” - Chemistry you want to know about, The Nikkan Kogyo Shimbun, Ltd., **2008,** p164.