

Development of PSA Gas Separation Technology to Reduce Greenhouse Effect

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“Pressure Swing Adsorption” is playing a role of one of the Gas Separation Technologies to save energy consumption instead of Absorption or Distillation in the field of chemical industry. Especially this technology should be focused on “Saving Energy” which will contribute to the reduction of CO₂ emission to cause Greenhouse Effect. Sumitomo Seika has improved this technology to expand its application field to promote “Saving Energy”: In this paper, “Simultaneous N₂/O₂ Production Process” to save energy consumption is described and “Methanol Steam Reforming Hydrogen Generator” to produce lower cost hydrogen is introduced.

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Introduction

As a result of Russia’s signing the Kyoto Protocol Ratification Bill on November 4, 2004, all the requirements for enactment of the protocol were fulfilled. Subsequently, the Kyoto Protocol was enacted on February 16, 2005. During the year 2004, abnormal weather events, such as floods, heat waves, droughts and hurricanes, were observed throughout the world. Japan experienced intense heat, and several powerful typhoons, which attacked the country day after day and brought us tremendous damage. Although it is hard to determine whether such abnormal weather events are directly connected to global warming, if global warming continues in the future, it is expected that weather-related catastrophes will continue to occur around the world.

However, Japan’s greenhouse gas discharge has already exceeded that of the base year. Therefore there is a demand for additional measures and policies. Especially, it is urgent that we make a rapid transition from a society that allows or even promotes global warming to a society that never allows or prohibits global warming. Specifically, the Japanese government is promoting a comprehensive energy-conservation plan in which heat and electricity conservation measures have been integrated, in a revision of the Energy Conservation Law. This plan is intended to assist in regulating factories and office buildings so that more thorough

energy management can be implemented.

Under such circumstances, Sumitomo Seika Chemicals is conducting development and improvement of PSA (Pressure Swing Adsorption) gas-separation technology as one of the energy-conservation technologies. This paper focuses upon the utilization of PSA technology in the separation of nitrogen, oxygen and hydrogen gases.

PSA Gas-Separation Technology

1. Classification of PSA Systems

Table 1¹⁾ shows the classification of industrial uses of PSA systems in accordance with the types of gas to be separated. Depending upon the operating pressure, PSA systems can be classified into one of three types: PSA; VSA or PVSA. In the PSA system, the raw material gas is compressed by a compressor. The adsorption pressure operates at high pressure, while desorption pressure operates at atmospheric pressure. The product gas to be separated in this system is typically water (for the purpose of drying), nitrogen, oxygen or hydrogen. In a VSA system, the pressure of the raw material gas is raised by a turbo blower which blows it into the adsorber. Subsequently, this gas pressure is reduced by a vacuum pump to regenerate the adsorbent. In a VSA system, the specific power consumption is smaller than that of a PSA system because the operating pressure of a VSA system is closer to atmospheric pres-

Table 1 Classified PSA¹⁾

Product Gas	Operating Pressure			Adsorbent	Product Gas		
	Adsorption Pressure	Desorption Pressure	System		Purity	Product	Application
Water (Drying)	0.5-1 MpaG	1 atm	PSA	Alumina, ZMS	H ₂ O < 180PPM	Non-Adsorption Gas	Dryer, Instrument Air
N ₂	0.5-1 MpaG	1 atm	PSA	MSC	Max.99.999%	Non-Adsorption Gas	Heat Treatment Sealing
O ₂	0.2-0.4 MpaG	1 atm	PSA	ZMS	Max.95%	Non-Adsorption Gas	Mini-Mill, Incinerator, Ozoneizer, Glass Making, Medical Use
	1 atm	Vacuum	VSA	ZMS			
	0.01-0.05 MpaG	Vacuum	PVSA	ZM			
H ₂	over 0.5 MpaG	1 atm	PSA	Activated Carbon, MSC, ZMS	Max.99.999%	Non-Adsorption Gas	Semiconductor Manufacturing, Fuel Cell, Glass Making, Heat Treatment
CO ₂	1 atm	Vacuum	VSA	MSC, ZMS	Max.99%	Adsorption Gas	Food Additives, Dry Ice, Welding
CO	1 atm	Vacuum	VSA	Complex	Max.99%	Adsorption Gas	Chemicals
Ar	1 atm	Vacuum	VSA	ZMS	Max.99.9%	Non-Adsorption Gas	Steel Making, Silicon Wafer Manufacturing
CH ₄	0.2-1 MpaG	Vacuum	PSA	MSC	Max.99%	Non-Adsorption Gas	Fuel
	0.01-0.05 MpaG	Vacuum	PVSA	MSC			

sure. The product gas to be separated in this system is typically oxygen, carbon dioxide, carbon monoxide or argon. The PVSA system is occasionally referred to as the VPSA system. In a PVSA system, the pressure of the raw material gas is raised by a roots blower which blows it into the adsorber. Subsequently, desorption and regeneration are performed by the use of a vacuum pump. The operating pressure of a PVSA system is designed at a pressure level in-between that of a PSA system and a VSA system. Its power consumption is as low as that of a VSA system. The amount of adsorbent filled in each system is PSA < PVSA < VSA. The size of the equipment used in each system is proportional to the amount of adsorbent filled in each system. Five types of adsorbents are employed for each system: alumina, active carbon, MSC (molecular sieving carbon), ZMS (zeolite molecular sieve) and complex. Each adsorbent is determined by the kind of product gas and its polarity or hydrophilic properties, which are the important keys that determine the performance of a PSA system.

2. Nitrogen/Oxygen Separation

(1) Nitrogen Separation

Cryogenic processing is one method used to separate and enrich nitrogen from the air. In this method air is cooled down to nearly -180°C , whereupon lique-

fies and is then distilled in order to separate the nitrogen from the oxygen. This process requires high specific power consumption to produce nitrogen. Therefore, in cases where only a small amount of nitrogen needs to be separated and enriched, the PSA system is one of the most useful methods from the perspective of energy conservation. In particular, when the nitrogen supply requirements range from several tens of m^3/H to several thousands of m^3/H , it is most beneficial to employ an onsite PSA system that allows nitrogen to be separated from oxygen at normal temperatures. In addition, an onsite PSA system helps contribute to energy conservation because no subsequent transportation of nitrogen is needed after production.

Gas-separation membrane method is another means of separating and enriching nitrogen onsite. If a relatively high nitrogen purity is required, the nitrogen yield from this method will be less than that from a PSA system. This occurs because the difference in diffusion velocity through the membrane layer, between nitrogen and oxygen, is not as great as that for MSC.

(2) Nitrogen PSA System

A PSA system used to separate and enrich nitrogen from oxygen employs MSC (molecular sieving carbon) for adsorbent. The principle of nitrogen separation by the use of MSC is as follows: As shown in Fig. 1,²⁾ the

micropore diameter distribution of MSC concentrates on around 0.3–0.4 nm, unlike the usual activated carbon. For this reason, as shown in Fig. 2,²⁾ the difference in adsorption velocity between nitrogen and oxygen, both of which possess a molecular size similar to the MSC micropore diameter, becomes greater within nearly one minute. Because this separation method uses the difference in adsorption velocity between nitrogen and oxygen, it is referred to as a Velocity Separation Type PSA system.³⁾ One characteristic of this method of gas separation is that excess moisture contained within the raw material air will decrease the difference in adsorption velocity. Therefore, it is preferable to dehumidify the air prior to PSA operation.

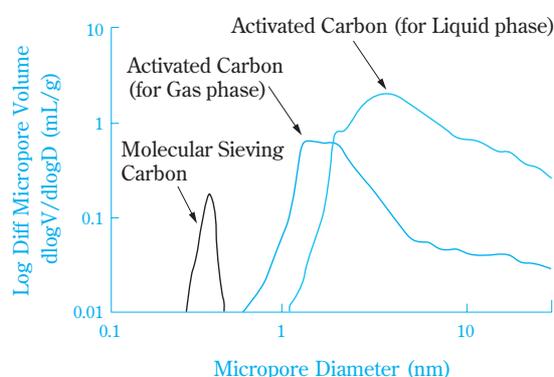


Fig. 1 Micro Pore Distribution Model of Activated Carbon and Molecular Sieving Carbon²⁾

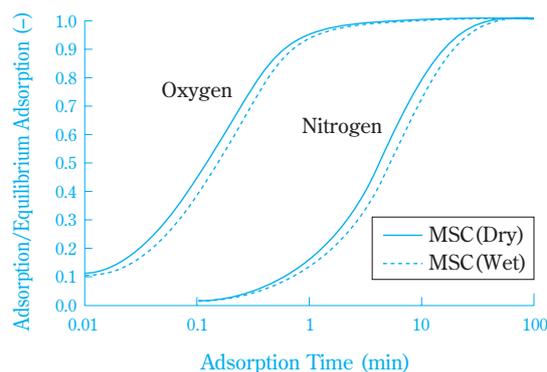


Fig. 2 Influence of Humidity in Adsorption Velocity Curve²⁾

This velocity difference can be changed to a subtle degree by adjusting the size of the MSC micropore diameter. While the adsorption velocity decreases with smaller micropore diameters, the relative velocity difference between nitrogen and oxygen increases. On the contrary, with larger micropore diameters,

although the adsorption velocity is greater, the relative velocity difference between nitrogen and oxygen decreases. Table 2 shows this characteristic qualitatively as it affects PSA performance. In terms of this characteristic, if the N₂ Production Rate is increased, a large quantity of nitrogen can be produced with a small amount of adsorbent (MSC), consequently requiring the use of smaller PSA equipment having a lower manufacturing cost. On the other hand, if the N₂ Recovery Rate is decreased, a larger amount of compressed air is required, resulting in greater specific power consumption. To solve this problem, Sumitomo Seika Chemicals has developed an operating method that increases the nitrogen recovery rate without reducing the nitrogen production rate, through the use of MSC which has a relatively large micropore diameter. Using this method, we have successfully created a compact PSA system that produces 99.9% pure nitrogen at the rate of 35 Nm³/H. This unit is shown in Fig. 3 and its dimensions are: 1.3 m (W) × 2.0 m (L) × 2.4 m (H).

Table 2 Relationship between Micro Pore of MSC and Characteristic of Gas Separation

Smaller	←	Micro Pore	→	Larger
Longer	←	Optimum Adsorption Time	→	Shorter
Less	←	N ₂ Product Rate	→	More
More	←	N ₂ Recovery Rate	→	Less



Fig. 3 N₂ PSA Unit

(3) Oxygen Separation

Cryogenic processing is appropriate for producing large amounts of oxygen and nitrogen. However, for the production of up to approximately 10,000 Nm³/H of

gas, the cost of a PSA system is cheaper than that of cryogenic processing. Moreover, because of the small difference between the boiling points of oxygen and argon, oxygen is not easily separated via distillation in a cryogenic plant. The PSA system also shares a similar characteristic. Since the adsorption capacity of oxygen is close to that of argon, when ZMS (zeolite molecular sieve) is employed, argon is also enriched in a similar proportion to oxygen, thus preventing oxygen enrichment over about 95%O₂.

(4) Oxygen PSA System

As shown in Table 1, there are three types of PSA systems for producing oxygen: PSA systems, which uses air compressors; and VSA and PVSA systems, both of which use air blowers along with vacuum pumps. However, recently there has emerged a new VSA system that operates at pressures less than atmospheric pressure without an air blower. Because the specific power consumption tends to increase as adsorption and desorption pressures deviate far from atmospheric pressure, less power will be consumed in cases where adsorption and desorption pressures are well-balanced and near atmospheric pressure. For instance, when the above two pressures are set at +0.05 MpaG and -0.05 MpaG, far from atmospheric pressure, the specific power consumption is expected to be less than 0.34 kw/Nm³ O₂. On the contrary, when oxygen is produced by a cryogenic plant, the specific power consumption is said to be nearly 0.44 kw/Nm³ O₂. This gives testament to the fact that although the purity of oxygen produced by a PSA system is less than 95%, this system is rated highly for energy savings. **Fig. 4** and **5** show an oxygen PVSA system that generates 1,600 Nm³/HO₂ × 3 plants. Fig. 4 shows the inside of the machine room, while Fig. 5 shows the outside of the machine room where the adsorbers and silencers are located.

The adsorbent used in oxygen PSA systems is ZMS (zeolite molecular sieve), which is described by the following general chemical formula: M₂/nO · Al₂O₃ · xSiO₂ · yH₂O (where n represents the valence of positive ion M, x represents a number equivalent to or greater than 2, and y represents a number equivalent to or greater than 0). ZMS is a kind of agent in which metal ions are replaced in the vicinity of the Al. ZMS agents are classified as Na type, Ca type or Li type, depending upon the particular metal ion. The relative nitrogen adsorption capacities of these different types



Fig. 4 Inside of Machine Room of O₂ PVSA Plant



Fig. 5 Outside of Machine Room of O₂ PVSA Plant

can be expressed as follows: Na type < Ca type < Li type. When an Li type is employed, the amount of adsorbent can be reduced due to the greater adsorption capacity, thus resulting in an oxygen plant of smaller size. For this reason Li type ZMS has been more popular in recent years. Additionally, because Li type ZMS has the highest adsorption capacity ratio of nitrogen to oxygen among all ZMS types, it requires the least energy consumption to enrich oxygen. The aforementioned specific power consumption, which is less than 0.34 kw/Nm³O₂, is the value achieved by an Li type ZMS.

(5) Simultaneous Production of Nitrogen and Oxygen

When nitrogen is separated from air by a nitrogen PSA system, a higher enriched concentration of oxygen can be recovered from the desorption gas. For instance, when 99%N₂ is produced, the measured oxygen content in the desorption gas changes, as shown in **Fig. 6**.

In **Fig. 6**, it can be observed that oxygen content increased to nearly 60% almost 10 seconds after the start-up of the desorption step.

This phenomenon occurs because oxygen is diffused and desorbed faster than nitrogen through the

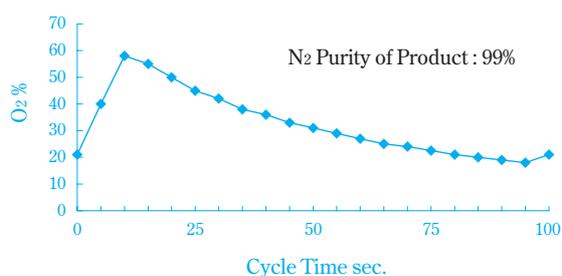


Fig. 6 O₂% of Desorption Gas of N₂ PSA

MSC micropores during the desorption step, just after being diffused and adsorbed faster than nitrogen. Once this gas is recovered and averaged so as not to interfere in the regeneration of adsorbent, nearly 32%O₂ desorption gas, which is nearly twice as great a concentration as the nitrogen product gas, is obtained.⁴⁾ Finally the compressed air may be efficiently utilized for the consumption of 99%N₂ in gas sealing and the dilute 32%O₂ can be used for aeration during wastewater treatment, incineration or oxidation reaction in chemical processing.

Next, in the course of oxygen production by an oxygen PSA system, highly enriched nitrogen can be recovered from its desorption gas.⁵⁾ For instance, as shown in Fig. 7, when 90%O₂ is generated by an oxygen PVSA plant, its desorption gas volume and oxygen content changes in response to the desorption pressure pattern. Although the mean oxygen content of this gas is approximately 11%, if its desorption gas is recovered during approximately 10 seconds of the final stage of the desorption step, its oxygen content will be less than 5% and the volume of recovered nitrogen will be

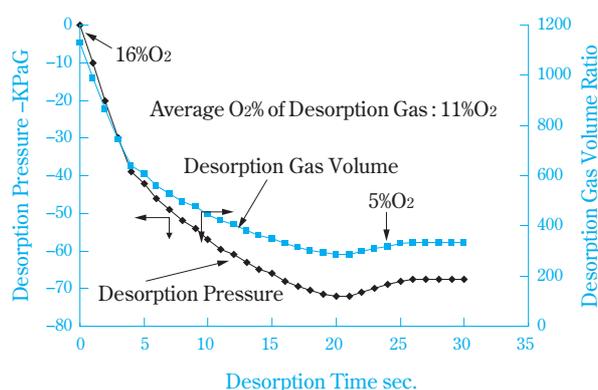


Fig. 7 O₂% and Desorption Gas Volume of O₂ PVSA

about 95%N₂, approximately 1.6 times as much as that of the PVSA oxygen product gas. Because this nitrogen is the desorption gas generated as a result of adsorption by ZMS, it contains approximately 3,000 PPM carbon dioxide. The moisture content of this nitrogen is approximately DP-20°C. When nitrogen concentrations greater than 99% are required, carbon dioxide and moisture should be removed from the gas by the use of a gas separation membrane. This can reduce the concentration of carbon dioxide to 300 PPM or less and decrease the moisture content to approximately DP-40°C.

Table 3 shows a cost comparison between individual PSA gas production and simultaneous N₂/O₂ production: an oxygen PVSA plant producing 90%O₂ at a rate of 340 Nm³/H to supply 90%O₂ and dilute 36%O₂ to a melting furnace, as well as a nitrogen PSA plant producing 95%N₂ at a rate of 135 Nm³/H for gas sealing.

Table 3 Cost Comparison between N₂ PSA/O₂ PVSA Production and Simultaneous N₂/O₂ Production

	N ₂ PSA/O ₂ PVSA Production		Simultaneous N ₂ /O ₂ Production			
	O ₂ PVSA	N ₂ PSA	O ₂ Recovery from Desorption Gas of N ₂ PSA		N ₂ Recovery from Desorption Gas of O ₂ PVSA	
			O ₂ PVSA	N ₂ PSA	O ₂ PVSA	N ₂ Compressor
Product Gas Purity	90%O ₂	95% N ₂ CO ₂ < 1PPM DP : -60°C	90% O ₂	95% N ₂ CO ₂ < 1PPM DP : -60°C	90% O ₂	95% N ₂ CO ₂ : Approx.0.3% DP : -20°C
Product Gas Flow Rate	340Nm ³ /H	135Nm ³ /H	310Nm ³ /H	135Nm ³ /H	340Nm ³ /H	135Nm ³ /H
Specific Power Consumption	0.34kw/Nm ³	0.24kw/Nm ³	equivalent to 0.31kw/Nm ³	0.24kw/Nm ³	0.34kw/Nm ³	0.168kw/Nm ³
Gas Cost						
Fixed Cost	6.4 Yen /Nm ³	1.8 Yen/Nm ³	6.0 Yen/Nm ³	1.8 Yen/Nm ³	6.4 Yen/Nm ³	0.9 Yen/Nm ³
Variable Cost	3.4 Yen/Nm ³	2.4 Yen/Nm ³	3.1 Yen/Nm ³	2.4 Yen/Nm ³	3.4 Yen/Nm ³	1.7 Yen/Nm ³
Total	9.8 Yen/Nm ³	4.2 Yen/Nm ³	9.1 Yen/Nm ³	4.2 Yen/Nm ³	9.8 Yen/Nm ³	2.6 Yen/Nm ³
Annual Gas Cost	26,656,000 Yen	4,536,000 Yen	22,568,000 Yen	4,536,000 Yen	26,656,000 Yen	2,808,000 Yen
Annual Saving Gas Cost		—		4,088,000 Yen		1,728,000 Yen

Table 4 Raw Material Gas of H₂ PSA

Raw Material Gas Component	Methane (Natural Gas) Steam Reforming Gas	Methanol Steam Reforming Gas	Cokes Oven Gas
H ₂	77.0%	74.9%	56.0%
CO	2.6%	0.8%	6.8%
CO ₂	18.0%	24.2%	2.5%
N ₂	80ppm	50ppm	6.0%
CH ₄	2.5%	1ppm	26.5%
O ₂	5ppm	1ppm	0.4%
CH ₃ OH	—	0.1%	—
CmHn	—	1ppm	2.5%
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H ₂ Product Purity	5N	5N	5N
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H ₂ Recovery Rate	78%	83%	67%

(2) Hydrogen Generator

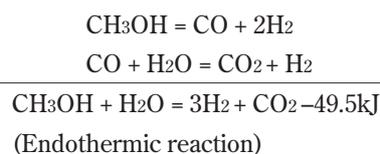
In recent years, several onsite hydrogen generators incorporating integrated hydrogen PSA systems and reforming units, have been installed as hydrogen stations for fuel cell vehicles. For example, WE-NET has installed 2 stations in the Kansai district. Additionally, one JHFC project has been the installation of 10 hydrogen stations in the Kanto district. These stations employ PSA systems to separate and refine hydrogen from reformed fuels, which include methanol, natural gas, LPG, naphtha, gasoline and kerosene. Furthermore PSA systems are also used to separate and recover hydrogen from the COGs discharged from coke ovens in steel mills.

In addition to compact size, hydrogen stations also require hydrogen generation of greater efficiency ((retained energy of hydrogen gas contained in a hydrogen product tank/total energy input into a hydrogen station) × 100%). However, the costs of generating hydrogen by reforming and charging tanks at high pressure is estimated to be 110–120 yen/Nm³.⁶⁾ Under the current situation in which these costs must be reduced down to 70 yen/Nm³ by the year 2020, the process must be further improved and simplified in order to achieve costs that are less than one-half of the cost of conventional equipment.

In 2003, Sumitomo Seika Chemicals developed a high-yield, 3-adsorber type of PSA system. As a result of this development, we have successfully reduced the size of adsorbers to one-sixth the size of conventional units. Because the size of reforming units was previously several times larger than that of PSA units, an urgent need arose to reduce the size of reforming units as well. In response to this demand, Sumitomo Seika

Chemicals—together with Mitsubishi Gas Chemicals Company, Inc.—developed a compact hydrogen generator that employed steam reformation of methanol.

As shown in the following chemical formulae, steam reformation of methanol is comprised of methanol cracking and the degeneration of carbon monoxide, which both occur almost simultaneously on the same catalyst. Therefore, one feature of this process is that it produces less carbon monoxide than that produced by the steam reformation of natural gas. Because methanol steam reformation is endothermic, the methanol solution must be heated outside of the reforming unit through the use of an electric heater or combustor. This system achieves greater hydrogen generation efficiency than that from the steam reformation of natural gas or propane, which progresses at over 750°C, because less heat is released from the reforming unit and the reaction start up and shut down times are shorter, due to the lower reforming temperature.



An MH type hydrogen generator is created through the integration of a reforming unit and a hydrogen PSA unit. Fig. 10 shows a flow diagram for this generator. Because the MH type hydrogen generator utilizes a methanol solution of less than 60 wt% as its raw material, the methanol solution is not treated as a hazardous material. Moreover, since this generator operates at pressures lower than 0.1 MPa., it is not subject to the High Pressure Gas Safety Law. The special features of the MH type hydrogen generator are as follows: PSA desorption gas is employed as fuel for the methanol solution vaporizer. Methanol cracking and degeneration of carbon monoxide are performed in a single reactor. Furthermore, the size of the reformer can be minimized due to the greater heat transfer efficiency of the vaporizer. In addition, the area of heat transfer can also be minimized due to the following reasons: the oil heating medium used for the reactor is vaporized at a pressure of 0.1 MPa or lower and the reactor is heated by the heat of condensation generated from this vaporization process.

In particular, with respect to the use of methanol as a hydrogen source, among all hydrocarbons methanol generates the second smallest amount of carbon diox-

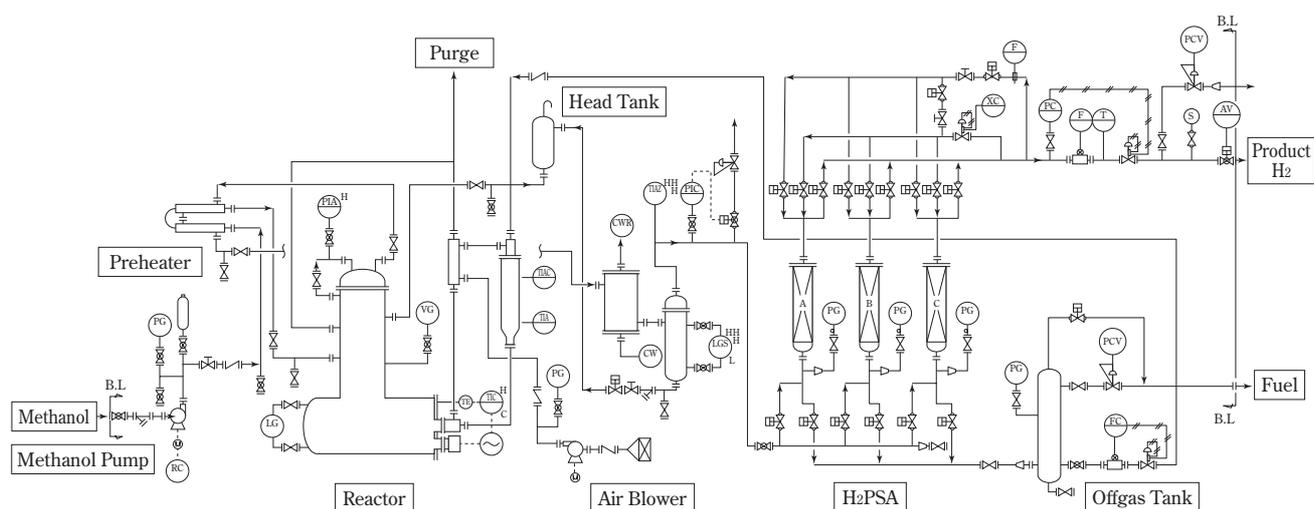


Fig. 10 Flow Diagram of 20MH H₂ Generator

ide (next to methane) per volume of hydrogen produced. As an example, **Table 5** shows the specifications for a 20 MH type methanol steam reforming hydrogen generator that can produce a volume of 20 Nm³/H. The size of this unit has been successfully minimized to 1.8m (W) ×3.2m (L) ×3.0m (H), as shown in **Fig. 11**. Further improvements are currently being undertaken to achieve even more compact dimensions.

Table 5 Specification of 20MH H₂ Generator

Product Gas Flow Rate	20 Nm ³ /H
Product Gas Component	
H ₂	higher than 99.999vol.%
CO	< 1vol ppm
Product Gas Pressure	0.8MpaG
Hydrogen Recovery Rate	83%
Utility Consumption	
Methanol	0.61kg/Nm ³ · H ₂
Power	0.65kw/Nm ³ · H ₂
Cooling Water	30L/Nm ³ · H ₂



Fig. 11 20MH H₂ Generator

From the perspective of energy consumption for hydrogen production, a methanol solution is effective because the operating pressure can be raised to approximately 0.1 MpaG without a gas compressor, merely through the use of a pump. This is possible because a methanol solution is an incompressible fluid. On the contrary, when methane (natural gas) is used, since it is a compressible gas, the hydrogen generation efficiency will inevitably be less as a greater pressure is needed, which requires the use of a gas compressor. The highest efficiency for hydrogen generation, 65.6% (LHV)⁷⁾, was achieved in 2003 by the methanol steam reforming hydrogen station established by the Engineering Advancement Association of Japan in Kawasaki.

Conclusion

When we think about what we can do as we engage in all manner of industrial activities, and consider that global warming is the question most critical for the continuance of human life, we must recognize that the age in which industrial gases, such as oxygen, nitrogen and hydrogen, “can be used simply by opening a valve” has now changed to an age in which such gases “should be produced by ourselves while simultaneously conserving energy.” We would like to conclude this report with the hope that to achieve this goal, the discharge of carbon dioxide will be further reduced through the integration of PSA technology—one of the most efficient energy conservation technologies known—into the production plant.

References

- 1) K. Haruna, *J. Vac.Soc. Jpn. (Vacuum)*, **43** (12), 1088 (2000).
- 2) M. Tsuji, *Plant and Process*, **October in 2002**, 50 (2002).
- 3) T. Kawai, "Pressure Swing Adsorption Technology", Kogyo Gijutsukai (1986) p.4.
- 4) Sumitomo Seika Chemicals, Co. Ltd, Patent 2005-118717 (2005).
- 5) Sumitomo Seika Chemicals, Co., Ltd. Patent 2005-144261 (2005).
- 6) WE-NET Task1, The Institute of Applied Energy, NEDO Report, March 12th, (2003).
- 7) K. Okazaki, "JHFC Report of Hydrogen and Fuel Cell Project in 2004", Test Report of Hydrogen Station Field(2005), p.61.

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