

第139回定例研究会(2012WHEC 報告会) 資料5


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「Development of hydrogen production systems with Pd-based alloy membrane」

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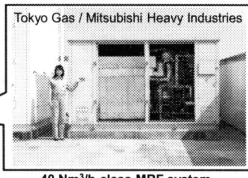
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Introduction


- Membrane Reformer (MRF)
 - * Hydrogen production system with Pd-based H₂ permeable membrane
 - * Simpler, more efficient than conventional hydrogen production system (SMR+PSA)

Membrane reformer enables...

- Improvement of efficiency
- Downsizing the hydrogen production system

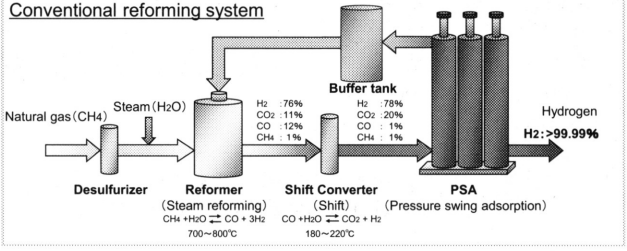
Enhance the advantage of the on-site distributed hydrogen production

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Conventional System and Membrane Reformer System

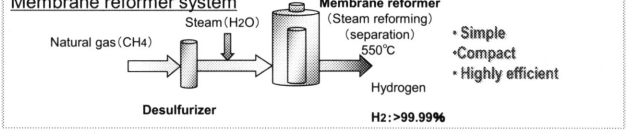
Conventional reforming system



Reformer (Steam reforming): $CH_4 + H_2O \rightleftharpoons CO + 3H_2$ (700~800°C)


Shift Converter (Shift): $CO + H_2O \rightleftharpoons CO_2 + H_2$ (180~220°C)

Membrane reformer system



Membrane reformer (Steam reforming) (separation) (550°C)

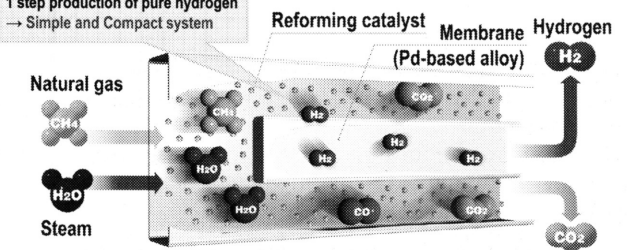
- Simple
- Compact
- Highly efficient

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Principle of the Membrane Reformer

1 step production of pure hydrogen
→ Simple and Compact system



Steam reforming reaction


 $CH_4 + H_2O \rightleftharpoons CO + 3H_2$

Shift reaction

 $CO + H_2O \rightleftharpoons CO_2 + H_2$

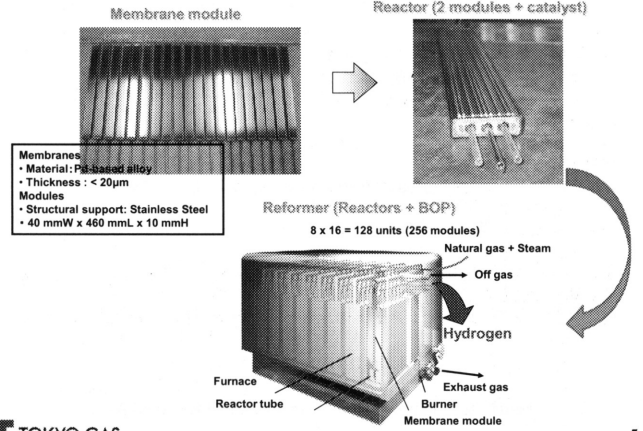
Acceleration of reforming reaction by selective separation of hydrogen → High efficiency

High CO₂ concentration of the off-gas → Energy-efficient CO₂ capture

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Assembly of the membrane module




Membranes

- Material: Pd-based alloy
- Thickness: < 20µm

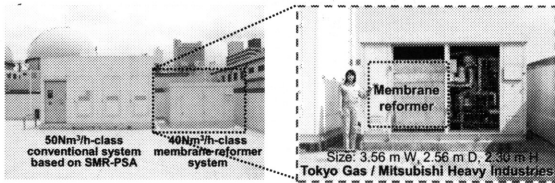
Modules

- Structural support: Stainless Steel
- 40 mmW x 460 mmL x 10 mmH

Reformer (Reactors + BOP)
8 x 16 = 128 units (256 modules)

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40 Nm³/h-class MRF (Membrane Reformer) System



Developed the 40 Nm³/h class MRF system in 2003 and improved the performance in 2007.

Achievements

Efficiency: 81.4% (HHV)
Capacity: 40.5 Nm³/h
Purity: 99.999% (5N)

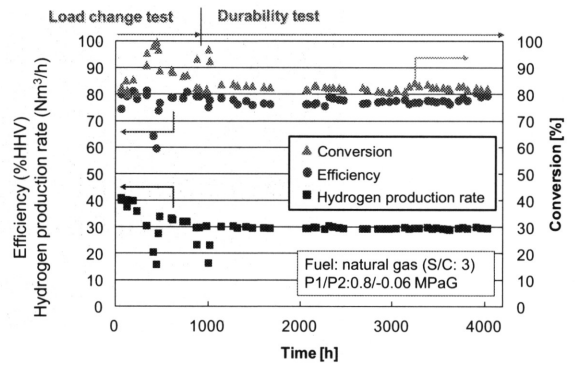
The efficiency of the MRF was improved by...

- Increase the membrane area
- Improve heat recovery
- Use more efficient auxiliaries

The efficiency of the 2nd MRF is over 80% and higher than the conventional hydrogen production system with PSA.



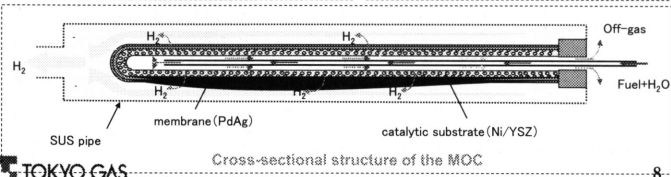
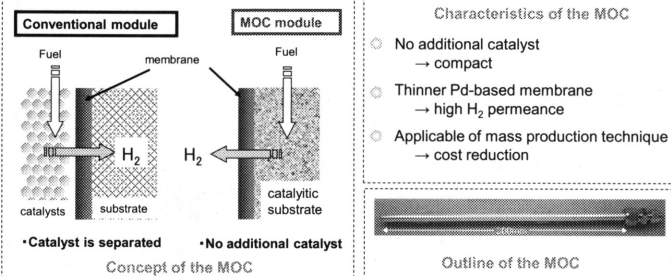
Long term operation test for the 40 Nm³/h MRF



- Conversion, efficiency, and production rate are stable in the operation.
- For the mounted improved modules, no significant leakage has been detected.



Membrane on Catalysts (MOC) module



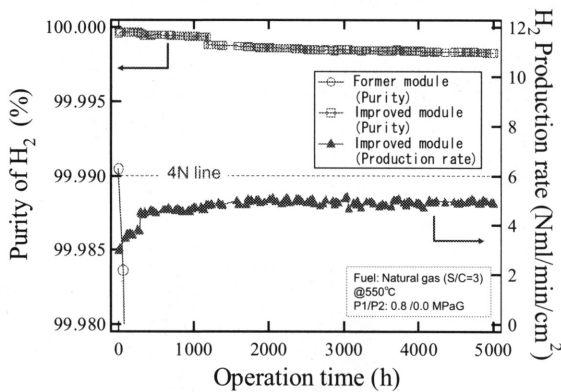
Some causes of the leak on the MOC

Leaking points are determined under a leak test in water.

Leak point			
causes	<circumstances problems> • Some impurity particles coming from the vessel react with Pd-membrane and make micro pores.	<production problems> • Imperfection of the plating process makes voids in the membrane.	<connection problems> • Mismatch of the materials at the connection part causes some leak under thermal cycles.
measures	• Coating a blocking material on the inner surface of the stainless vessel.	• Achieving perfect plating technique.	• Applying a glass-seal technique to the connection part between the module and the stainless pipe.



Long term operation for the MOC module



- Modification improved the durability of the MOC module.



Acknowledgement

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