

# Development of 5Nm<sup>3</sup>/hr of steam reformer for PEMFC and the experimental and numerical evaluation for the performance of it

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**Abstract** : We made very small size of steam reformer which can produce 5Nm<sup>3</sup>/hr of hydrogen for PEMFC(Proton Exchange Membrane Fuel Cell). The size of the reformer is about 22L including two stage steam reforming reactor unit and two stage water-gas shift (high temperature shift and low temperature shift). The steam reforming process always brings very strong endothermic reaction at the front of steam reforming catalyst, therefore it is important to concentrate much heat there. In this reason, we considered the location and direction of burner, the arrangement of steam reforming catalyst and the flow path of hot combustion gas for optimal temperature distribution. We made an effort to design the reformer compactly in order to increase heat exchange and heat usage inside. As a result, we could get high heat efficiency and low temperature exhaust gas without extra external heat exchanger. We also carried out various numerical simulations about temperature change, heat distribution, chemical reactants concentration, and the mole fraction of product gas. This paper shows the results of experimental and numerical evaluation for the performance of developed reformer.

## 1. Introduction

Increased pollution due to carbon dioxide emissions from fossil fuel is emerging as a serious problem and based on the policy change for green growth and etc. by the government, many investment and research for alternative energy are in progress. Out of the type of alternative energy, hydrogen has the characteristic of having high density energy without creating pollutants. In particular, the fuel cell that uses this hydrogen as fuel is expected to receive the spotlight as an important energy conversion device regarding hydrogen economics.<sup>1)</sup>

For the commercialization of the supply of fuel cell development system, the most important problem is the establishment of the infrastructure to reliably supply hydrogen. It is expected that a hydrogen production technology through water decomposition will ultimately be established but in the current transitional period, it is determined that the hydrocarbon fuel's reforming reactions will be the core technology in manufacturing hydrogen.

The methods of reforming hydrocarbon fuel are classified as steam reforming, partial oxidation reforming, and autothermal reforming<sup>2)</sup> and within these classifications, steam reforming is a method that supplies both hydrocarbon fuel and steam simultaneously to produce a synthetic gas. This reaction has to supply reaction heat by combusting a portion of the fuel through strong endothermic reaction<sup>3)</sup> so it offsets a portion of hydrogen production efficiency and requires additional equipment, making the reaction large and complex.

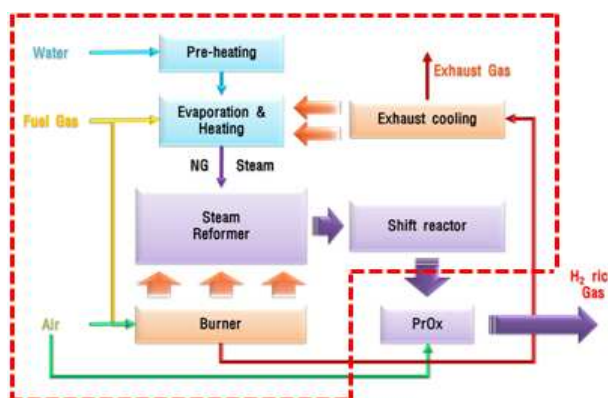


Fig. 1 Schematic of Steam Reformer

It also has the downside of requiring a long initial operating time and has insufficient dynamic properties. However, steam reforming is already commonplace as a gas production process, so a stable hydrogen supply may be possible and compared to other reforming reaction, it has the advantage of having a comparatively larger hydrogen production quantity.

When the study regarding recent reformer systems are observed, Hong Mei and etc. progressed the study through simultaneous analysis of heat delivery-chemical reaction on the methane steam reformer and a metal monolith catalyst was used on a cylindrical shape to execute a tendency analysis for a performance change based on changes of flow rate, temperature, and composition by altering operating conditions.<sup>4)</sup> Furthermore Wei-Hsin Chen and etc. used the CFD technique to predict the reactions in High Temperature Shift (HTS) and Low Temperature Shift (LTS) and found a reaction rate constant value based on those predictions. They also performed a verification through tendency analysis and experiments with CO conversion rate based on the rate of steam to CO ratio.<sup>5)</sup> J.H Noh and etc. developed a model for predicting the interior temperature, concentration change, and pressure change by using the numerical technique to consider the reformer's heat delivery state, catalyst, and chemical reaction.<sup>6)</sup>

Existing previous studies mostly did not consider the size of the fuel cell or only considered the chemical reaction of one steam reforming or water gas shift and progressed the study focusing on performance change or tendency analysis and etc. based on change in the operating condition or the reformer.

In the current study the 5Nm<sup>3</sup>/hr reformer was chosen as the study subject and a performance evaluation was performed through numerical evaluation and experiments by utilizing a reformer that uses steam reforming for a joint analysis of heat delivery-chemical reaction. The study was performed by using the commercial program Fluent for the analysis of heat and flow, and joint analysis was preformed through a User Defined Function (UDF) for a simulation that is closest to the actual state. Furthermore, reformer interior temperature distribution and exit reformer gas' components were compared with experiment results to increase the reliability of the computational analysis. Additionally, through the join analysis of heat and flow chemical reaction, the 5Nm<sup>3</sup>/hr combustion unit and reformer

interior's chemical reaction and heat delivery state were expressed most closely as the actual state. As this result as a basis, a prototype was developed to perform a study for a performance change based on design variables and performance change based on Anode Off Gas.

## 2. Mathematical formulation and modeling

### 2.1 Governing equation

#### 2.1.1 Thermodynamic aspects

This steady assumes the steady three dimensional state of the combustor and the reactor. The governing equations used for the computational analysis is shown in equations (1)~(4) and there are equations of mass conservation, momentum conservation, and chemical conservation.

Continuity equation

$$\frac{\partial}{\partial x_j} (\rho u_j) = 0 \quad (1)$$

Momentum Balance equation

$$\frac{\partial}{\partial x_j} (\rho u_j u_i - \tau_j) = -\frac{\partial P}{\partial x_i} \quad (2)$$

Energy balance equation

$$\frac{\partial}{\partial x_j} (\rho h u_j + F_{h,j}) = u_j \frac{\partial P}{\partial x_i} + \tau_j \frac{\partial u_i}{\partial x_j} + S_e \quad (3)$$

Species balance equation

$$\frac{\partial}{\partial x_j} (\rho u_j Y_m + F_{m,j}) = S_s \quad (4)$$

#### 2.1.2 Mechanisms and kinetics

5Nm<sup>3</sup>/hr's reformer is composed with a total of three catalysts. For the simulation of the chemical reaction that occurs in each catalyst, the steam reformer reaction (STR) utilized the steam-methane reaction mechanism that was developed by Xu and Froment.<sup>7)</sup> The water gas shift is classified as high heat and low heat and the analysis was performed by utilizing the mechanism researched by Wei and etc.

If the middle process is included for the reformer interior's chemical reaction, there are more than 40 reactions but the reaction mechanism proposed in

**Table. 1** Chemical reactions and the rate equations

Steam reforming				
$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	$\Delta H = +206.1 \text{ KJ/mol}$	$r_1 = \frac{(k_1/p_{\text{H}_2}^{2.5})(p_{\text{CH}_4}p_{\text{H}_2\text{O}} - p_{\text{H}_2}^3p_{\text{CO}}/K_{e_1})}{(\text{Den})^2}$		Kmol/kgcat h
$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	$\Delta H = -41.0 \text{ KJ/mol}$	$r_2 = \frac{(k_2/p_{\text{H}_2})(p_{\text{CO}}p_{\text{H}_2\text{O}} - p_{\text{H}_2}^3p_{\text{CO}_2}/K_{e_2})}{(\text{Den})^2}$		Kmol/kgcat h
$\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$	$\Delta H = +164.0 \text{ KJ/mol}$	$r_3 = \frac{(k_3/p_{\text{H}_2}^{3.5})(p_{\text{CH}_4}p_{\text{H}_2\text{O}}^2 - p_{\text{H}_2}^4p_{\text{CO}_2}/K_{e_3})}{(\text{Den})^2}$		Kmol/kgcat h
Combustion				
$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	$\Delta H = -800.0 \text{ KJ/mol}$	$r = \alpha k \cdot \exp(-E/(R_g T)) c_{\text{CH}_4}$		mol/m <sup>2</sup> s

this study assumed that the most dominant 3 reactions are dominant. The other mechanisms used in steam reforming reaction, water gas shift reaction, and the combustion reaction are displayed in Table 1.

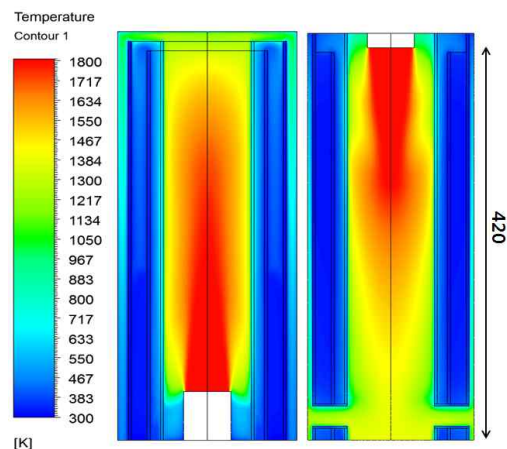
## 2.2 Modeling of Reformer

### 2.2.1 Burner Direction

Existing developed reformers had burners which mostly had the shape of bottom-up direction. Furthermore in the case of the catalysts, the catalyst layer is heated through the burner's heat so it is stationed around the burner and the heat is delivered in this shape as the heat energy flows through the outer wall of the catalyst. The reformer gas is injected from the bottom to the top of the catalyst through the interior wall and after it is pre-heated with the burner's heat, it is injected through the top of the catalyst to start the reforming in this region. The height of the catalyst layer is fixed based on the required catalyst capacity of the reformer, so if the height becomes higher the reformer capacity increases. If the catalyst layer is shaped up high in these bottom-up burners, a state occurs where the heat created by the burner starts to concentrate in the top of the reformer. While the top is excessively heated because of the concentrated heat on the top, a state occurs where the bottom portion does not receive enough heat for reforming. Therefore the burner was substituted to be a top-down shape so that the reformate gas will be heated and the burner's exhausted gas' path would effectively heat the top and bottom portion of the reformer. As a result, the effect of simultaneously heating the top and bottom of the reformer was achieved, as shown on Fig. 2.

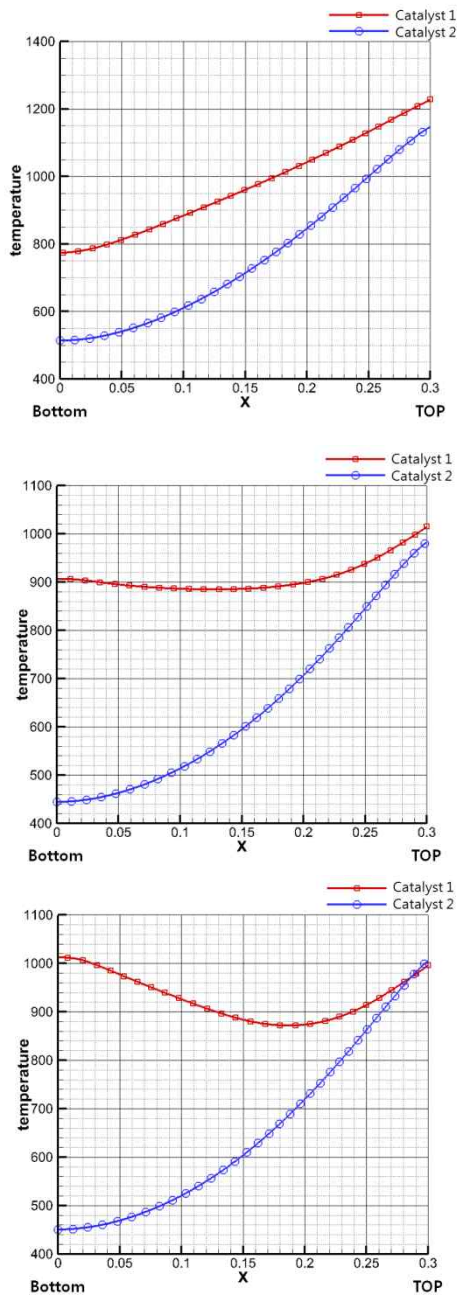
### 2.2.2 Burner Depth

The initial burner depth is 50mm. To investigate the level of catalyst heating based on the burner depth, the burner location in the 50% and 75% depth from the top of the catalyst was selected to perform a computational analysis. In this case, the initial STR reaction begins in the front lower end of the catalyst layer and to decrease the initial operation time the heat is concentrated in this area to adjust the conditions so that the strongest endothermic reactions will occur. As shown on the picture, as the burner depth becomes deeper it is visible that the heat becomes concentrated on the lower front end. However an excessively high heat concentration may lower the durability of the catalyst and since heat wasn't sufficiently delivered to the rear of the catalyst, a height setting is required so that heat is concentrated on the front lower end in the initial phase and then the heat energy is evenly transmitted to the rear of the catalyst. Furthermore, if the burner's flame is directly in contact with the bottom, this too will create negative effects on the reformer that is sus310 material if it is operated for



**Fig. 2** Temperature contour for Burner Direction

an extended period of time.



**Fig. 3** Temperature distributions at the Stream reformer Catalyst

### 2.3 Boundary Conditions

As the set boundary condition displayed on Table 2 for the reaction analysis in this study, the 4.0LMP and 2.4LPM gas are each injected into the combustor and reformer. The general Natural Gas composition was input as Mole Fraction so that the composition of the gas would be the closest simulation.

Each wall inputted the value of 3mm thickness of sus310 material and since the pellet form of the catalyst layer could not be modeled, the porosity

**Table. 2** Inlet boundary conditions

Region	Gas	Flow Rate	Temp.
Combustion	NG	10 L/min	300.15K
	Air	110 L/min	300.15K
Reformer	NG	20 L/min	473.15K
	Water Vapor	55 g/min	473.15K

**Table. 3** Properties of the catalysts

Properties of the Steam Reforming catalyst	
Porosity	0.35
Density	3986 (Kg m <sup>-3</sup> )
Specific Heat	930 (J Kg <sup>-1</sup> K <sup>-1</sup> )
Thermal conductivity	25.08 (W M <sup>-1</sup> K <sup>-1</sup> )
Properties of the High temperature shift catalyst	
Porosity	0.35
Density	7633.65 (Kg m <sup>-3</sup> )
Specific Heat	421.53 (J Kg <sup>-1</sup> K <sup>-1</sup> )
Thermal conductivity	80.38 (W M <sup>-1</sup> K <sup>-1</sup> )
Properties of the Low temperature shift catalyst	
Porosity	0.35
Density	6877.2 (Kg m <sup>-3</sup> )
Specific Heat	475.32 (J Kg <sup>-1</sup> K <sup>-1</sup> )
Thermal conductivity	183.25 (W M <sup>-1</sup> K <sup>-1</sup> )

was calculated and the effect was input to perform the calculation. Furthermore, the utilized catalyst's properties were displayed on Table 3 for the heat energy analysis that is transmitted to the catalyst layer,

## 3. Experiment

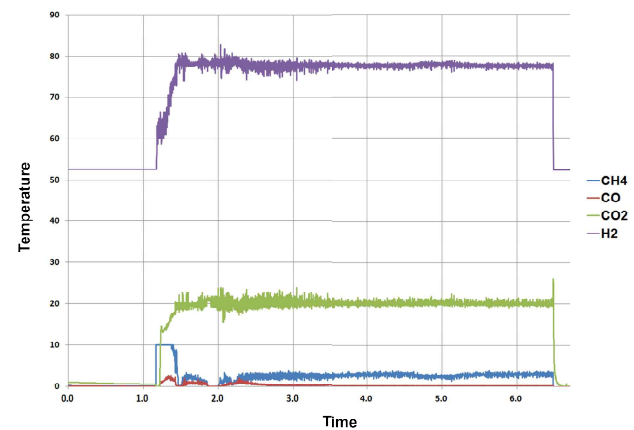
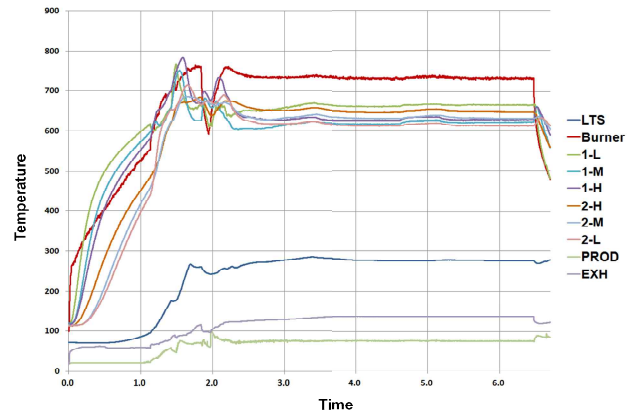
### 3.1 Experimental device configuration

Based on the computational analysis performed previously, the experiment through the Anode Off Gas and operating conditions was performed after the 5Nm<sup>3</sup>/hr reformer was produced.

The reason for the AOG experiment is to inject the past 25% of the H<sub>2</sub> in the fuel cell system stack back into the reformer. The purpose of this is to increase the reformer efficiency by reducing part of 10LPM's burner fuel. In this study it was verified if the H<sub>2</sub> produced by the corresponding reforming of NG heat that is supplied by the burner showed the same tendencies when it was injected into the burner. The experiment device produced for the experiment are



**Fig. 4** Reformer Design and Manufactured reformer



**Fig. 6** Experimental result for temperature distribution and gas analyzer by NG



**Fig. 5** Test station of 5Nm<sup>3</sup>/hr Reformer

displayed on Fig.5 and Fig.6. The experiment device injects the desired flow of gas into the reformer based on the input set point value on the computer control program. Based on each condition, the temperature is measured in a total of 9~10 Thermo Couple and in the process of venting, a portion of the gas was taken to analyze the reformed gas properties through the Gas Analyzer.

## 4. Result and discussion

### 4.1 Burner Natural Gas Experiment

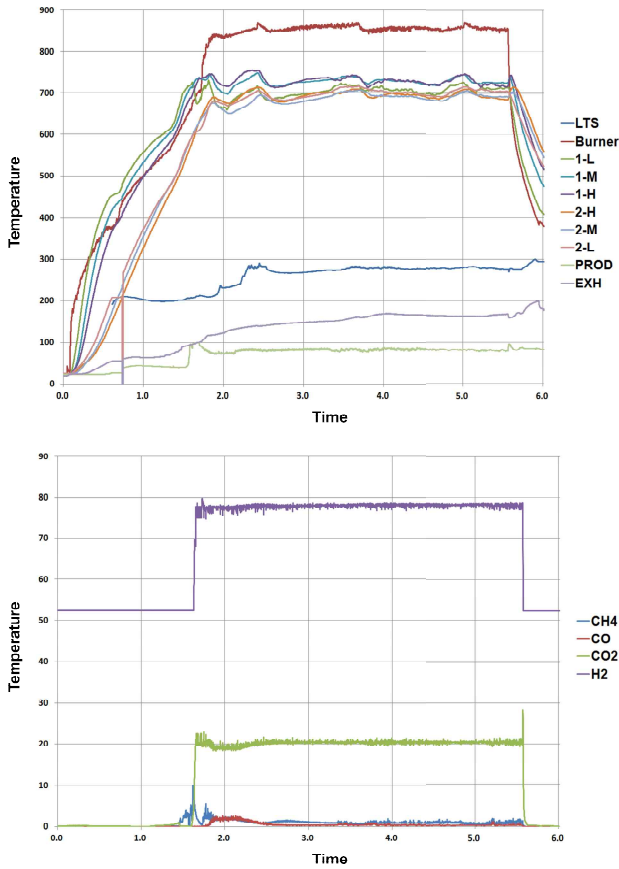
The reformer experiment was performed with the 5Nm<sup>3</sup>/hr which was produced based on simulation results. In a regular operation the Air/Fuel ratio is 1.1. Therefore 10LPM is injected for the NG in the combustor and 110LPM is injected for the Air. In picture 7, as the burner's heat increases the heat transmits to the catalyst layer and it is verified that all catalyst layer's temperature is increasing. 10:34 minutes after the picture, the decrease in the heat of the catalyst layer means that the reformed gas and steam is injecting into the catalyst layer interior to start the SR reaction which is the endothermic

reaction. The experiment results reveal that the STR catalyst layer's temperature in general remains within 100K. This can be seen as a result similar to the simulation results where the heat delivery between catalyst layers are efficiently designed to be seamlessly achieved and hence the temperature between two catalyst layers has decreased.

### 4.2 Anode Off Gas Experiment

AOG experiment results are revealed on the picture. Compared to the result that only injected NG, the burner area interior's temperature increased by around 150K and the catalyst layer's temperature also increased around 50~100K. However it can be observed that the temperature deviation has rather decreased. This is because in the case of a burner where the steady amount of gas is injected, it can be confirmed that there wouldn't be a large temperature variation after stabilization but in the case of AOG, based on the produced hydrogen's quantity, portion of it may be injected into the burner so when the hydrogen's quantity changes momentarily there may be a temperature variation even after stabilization.





**Fig. 7** Experimental result for temperature distribution and gas analyzer by AOG

#### 4.3 Gas Analyzer result

Results when experimented with only injecting NG into the burner and results when only injecting hydrogen gas using AOG is displayed on Table 4. When result value of the two analysis are observed, a difference in CH<sub>4</sub> quantity can be first observed and this result can be seen because the catalyst's interior temperature had the tendency to become slightly higher when experimented with AOG so it was more active when compared with the reforming reaction of NG experiment. Furthermore, through the stored heat in the interior of the reformer, the WGS reaction was also actively generated so the result can be verified where the CO's removal was more smoothly achieved. However, when the catalyst layer's temperature becomes excessively high because of the stored heat, it may pass the active temperature zone so it is required that an appropriate temperature is maintained through efficient heat exchange.

**Table. 4** Comparison between NG and AOG Experimental results for product gas composition

Symbol	Fraction $x_i$ of NG experiment (DRY)	Fraction $x_i$ of AOG experiment (DRY)
[-]	[mol %]	[mol %]
CH <sub>4</sub>	1.58	0.91
H <sub>2</sub>	77.86	78.33
CO	0.64	0.38
CO <sub>2</sub>	19.92	20.38

## 5. Conclusions

Through simulations and experiments a reformer was able to be designed that is more compact than existing reformers

(1) The STR catalyst layers shape was designed to have a more seamless heat delivery compared to existing reformers. Fast and even temperature distribution appeared in all catalyst layer interior and the initial operating time was reduced. Furthermore, by reducing the surface area that is exposed to the exterior, the effect of less heat loss was achieved and it was possible to manage an appropriate temperature in both ends of the catalyst layer through stored heat and heat delivery.

(2) The gas composition that is actually produced in the reformer was confirmed through the experiment and the interior temperature distribution was identified in that state. In comparison to existing reformers even regarding commercial products, a more advanced reformer in heat distribution and gas analysis value was developed.

(3) Other than only using NG to inject to the burner and supplying necessary heat energy, AOG experiment to apply to actual fuel cell system using reformed hydrogen gas was possible. With this as a basis, rather than using the MFC, the BOP should be used for repetitive experimentation to establish a reformer operating condition in the future.

## Acknowledgements

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