R&D on Hydrogen Production by Steam Reforming Method

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1. R&D Objectives

The damage to the environment resulting from large-volume consumption of fossil fuels has been spreading, from the problems of NOx and SOx, which cause regional atmospheric pollution, to the problem of global warming brought about by CO$_2$. Resolving these problems has become one of the foremost issues facing modern society. In addressing these problems, it is considered imperative that the environment be ameliorated through dramatic technological improvements in terms of both fuels and fuel-utilize equipment, plus policy measures to promote the spread of new technologies.

In terms of fuels, attention has focused on new fuel oils as one dramatic approach to a solution. From the standpoint of fuel-utilize equipment, it is believed that the decisive factor will be the fuel cell (cogeneration) system. Viewed from the perspective of fuel suppliers, one of the most important technologies in fuel cell development is high-efficiency hydrogen production technology. Against this backdrop, the present R&D is aimed at promoting the spread of new fuel oils through the development of high-efficiency hydrogen production technology.

Under development at the Shinnen Sodegaura No. 1 laboratory is a fuel reforming treatment technology of the steam-reforming method that has captured attention as a high-efficiency hydrogen production technology. More specifically, with respect to desulfurization technology for adsorption and removal of sulfur compounds from fuel without hydrogen, as well as steam reforming technology that enables hydrogen production at high concentrations, high-performance desulfurizing agent and reforming catalyst are being developed. In addition, research is being conducted to elucidate the mechanisms involved when desulfurizing agent or reforming catalyst has been used, as well as optimization of conditions. Findings necessary for the design of new fuel oils appropriate for target technologies are also being collected.

2. R&D Contents

(1) Targets

Taking fuel oil equivalent to kerosene as the subject, the following targets have been established.

a) Development of elemental technology for fuel reforming

From evaluations of acceleration tests, simulations, etc., the following indices of catalyst performance have been obtained.

- Adsorption desulfurizing agent: Performance demonstrating service life of one year or longer
Steam reforming catalyst: Performance demonstrating service life of two years or longer

b) Development of a hydrogen production system incorporating elemental technology

c) Investigation of the quality of liquid fuel fractions equivalent to naphtha - kerosene and of reforming characteristics

(2) Program

The present R&D will take place over a 5-year period from JFY2000 to 2004, and by the third year, evaluations will be made of a hydrogen production system. From the fourth year onward, applications to fuel cell system will be investigated.

In JFY 2001, developments implemented in JFY 2000 for adsorption desulfurizing agent and steam reforming catalyst were further advanced; a 1 kW hydrogen production system filled with the developed desulfurizing agent and reforming catalyst was fabricated, and data were collected. Meanwhile, steam reforming characteristics were investigated using model substances (pure test agent) for determining the reforming characteristics of each type of hydrocarbon.

3. R&D Results

3.1 Development of Adsorption Desulfurizing Agent

In JFY 2000, an adsorption desulfurizing Ni based agent was discovered that exhibits high performance in desulfurizing JIS No. 1 kerosene without hydrogen addition (hereinafter referred to as "Ni desulfurizing agent"). In JFY 2001, large-scale production of this Ni desulfurizing agent was investigated, pretreatment conditions were optimized and service life was evaluated. The impact of kerosene quality on the agent’s desulfurizing performance was also studied.

(1) Large-scale production

In order to have a method established for producing Ni desulfurizing agent in large, stable quantities, manufacturing consignments to catalyst makers were explored. Trial production was carried out on a scale of 2 kg/batch in accordance with laboratory-scale (300 g/batch) production conditions. It was found that the items trial-produced by catalyst makers exhibited performance equal to or greater than that of laboratory-scale products.

(2) Pretreatment conditions

For activation of Ni desulfurizing agent, hydrogen reduction is required. In order to have sulfur compounds in fuel absorbed on reduced metallic Ni and desulfurized, it is ideal to have more metallic Ni dispersed over the surface area of the desulfurizing agent after reduction. In the present study, therefore, reduction temperature and reduction time period were investigated in detail in order to discover the optimum conditions of reduction for producing metallic Ni in highly dispersed fashion.
a) Impact of reduction temperature

Firstly, the relationship between reduction level and hydrogen adsorption volume was investigated by holding the reduction time period constant and varying the reduction temperature. It was found that the volume of hydrogen adsorption can not be increased simply by elevating the reduction temperature and the reduction level. This can be attributed to the sintering of Ni further at high temperatures.

b) Impact of reduction time period

Next, the reduction temperature was fixed and the impact of prolongation of the reduction time period was studied. Figure 1 shows the relationship between reduction level and hydrogen adsorption volume when the reduction time period has been prolonged with the reduction temperature held at 300°C. As shown in the figure, the volume of hydrogen adsorption increases with increasing in the reduction level. After 50 hours of reduction, the reduction level rose roughly twofold over the level after 3 hours of reduction, and the hydrogen adsorption volume increased 2.5 times. A look at the crystallite diameter of Ni in desulfurizing agent after reduction disclosed that when the reduction time period has been prolonged, Ni condensation becomes difficult to produce.

The relationship between hydrogen adsorption volume and desulfurization performance is depicted in Figure 2. Desulfurization performance improved as the volume of hydrogen adsorption increased. By prolonging the reduction time period as indicated above, the reduction level could be elevated while curtailing Ni condensation, and a desulfurizing agent with a large quantity of metallic Ni on its surface could be obtained.
(3) Evaluation of desulfurization life

Using developed Ni desulfurizing agent produced in large volume, the service life of kerosene on the market having a sulfur concentration of 48 ppm was evaluated with the optimum reduction conditions taken as 300°C and 50 hours. The conditions of service life evaluation were atmospheric pressure and 180°C. The evaluation was undertaken under conditions of ninefold acceleration, with the throughput oil volume nine times greater than the standard. The conversion time was the actual evaluation time period times 9. For comparison, service life was also evaluated after reduction took place for 3 hours at 300°C. The results appear in Figure 3. With reduction for 3 hours at 300°C, the sulfur concentration after 2400 hours (converted) exceeded 0.1 ppm. On the other hand, under conditions of reduction for 50 hours at 300°C, optimized in this investigation, the sulfur concentration was lowered below 0.1 ppm in roughly 5500 hours. Moreover, at up to around 4500 hours, desulfurization to below 0.02 ppm, the analytical measurement limit, could be achieved, and in the vicinity of 5000 hours, the sulfur concentration could be upheld at 0.05 ppm or less. This fact indicated that when the Ni desulfurizing agent developed in the present research is used, and the desulfurizing agent is activated under optimum conditions, it is possible to remove sulfur compounds from kerosene for 4000 hours or longer, that is, for one year or longer, assuming that the fuel cells do not operate at nighttime.

![Figure 3: Evaluation of Accelerated Life of Ni Desulfurizing Agent](image)

(4) Impact of kerosene quality on desulfurization performance

In general, it is believed that the lower the concentration of sulfur in feedstock, the easier it is to achieve desulfurization. Nevertheless, in desulfurization experiments using various types of kerosene, it was found that the sulfur concentration in feedstock kerosene is not the sole factor in determining how easy it is to remove sulfur. In order to clarify the reason(s) for this, an investigation was made of the different types of sulfur compounds included in kerosene and of the impact of polynuclear aromatics that poison the adsorption point.
a) Reactivity of sulfur compounds

Sulfur compounds such as benzothiophene and dibenzothiophene are contained in kerosene, and in order to study the impact of these compounds on desulfurization performance, benzothiophene and dibenzothiophene model oils with 500 ppm sulfur concentration (solvent: n-tridecane) were prepared and their reactivities on the developed Ni desulfurizing agent were evaluated. As seen in Figure 4, it was found that although the bulk of sulfur in benzothiophene is removed, the sulfur concentration in dibenzothiophene can only be reduced to 200 ppm, indicating that benzothiophene can be desulfurized much more easily.

![Figure 4: Impact of Sulfur Compounds on Desulfurization Performance](image)

b) Impact of polycyclic aromatics

The impacts of 2-membered ring and 3-membered ring aromatics included in kerosene were investigated. A 2-membered ring aromatic model oil and 3-membered ring aromatic model oil were prepared (tridecane reagent base containing no sulfur to which methylnaphthalene and 2-membered ring aromatic were added, or to which 3-membered ring aromatic and phenanthrene were added). After oil throughput for 80 hours under the same operating conditions, desulfurization reaction was carried out with regular feedstock kerosene, and the sulfur concentration at the desulfurizing unit outlet was compared with that in cases where the model oil had not been throughput. It was found that both 2-membered ring and 3-membered ring aromatics exhibit a poisonous effect. It was also noted that the poisonous effect is higher from 3-membered ring aromatic than from 2-membered ring.

3.2 Development of Steam Reforming Catalyst

In JFY 2000, Ru-Co/ZrO$_2$ system catalyst developed for naphtha steam reforming was investigated. Improved catalyst 2 (Ru-Co system/high surface area carrier (retaining highly scattered catalyst ingredients)) highly active in kerosene steam reforming was discovered. In JFY 2001, the long-term service life of catalyst was evaluated and catalyst deterioration was examined. Based on the results of these studies, further improvements in catalyst were investigated.
(1) Evaluation of catalyst long-term service life

Catalyst long-term service life was evaluated under the following conditions: S/C = 3, atmospheric pressure, catalytic layer outlet temperature at 730°C, LHSV=0.5h\(^{-1}\). The kerosene conversion rate (gas C1 conversion rate) was calculated by the following equation.

\[
\text{Gas C1 conversion rate} \, (\%) = \frac{(\text{CO} + \text{CO}_2 + \text{CH}_4 \, \text{NL/h})}{(\text{CO} + \text{CO}_2 + \text{CH}_4 + \text{C}_2 - \text{C}_6 \, \text{NL/h})} \times 100
\]

Figure 5 presents the results of an evaluation of service life of improved catalyst 1 (Ru-Co system/high-strength carrier (retaining large volume of catalyst ingredients) developed in JFY 2000. \text{CH}_4 and hydrocarbons of \text{C}_2 or above, such as ethylene, propylene or propane, were increased over time, and it was found that the catalyst deteriorates over time. In approximately 2600 hours, the conversion of kerosene decreased below 100%. At this time, an oil component that had become cloudy was observed in the condensed water. It is said that in the fuel cell system, when the oil component flows out, it has an adverse effect on catalyst downstream and on the fuel cell. This point in time can be considered the final point in the service life. Evaluation of service life was completed in about 3200 hours.

![Figure 5: Evaluation of Service Life of Improved Catalyst 1 (Temporal changes in composition of produced gas)](image)

Evaluation results for service life of improved catalyst 2 are shown in Figure 6. The service life evaluation time period exceeded 12000 hours with the kerosene conversion rate at 100%, and the composition of produced gas remained stable, with virtually no changes recognized in comparison to the early period. Moreover, from forecasts of catalyst deterioration, based on temporal changes in the temperature distribution of the catalyst layer, it was determined that an exceptionally long service life of at least 15000 hours or more can be expected. These findings confirmed that improved catalyst 2 is superior to improved catalyst 1 not only in activity but also in service life.

![Figure 6: Evaluation of Service Life of Improved Catalyst 2 (Temporal changes in composition of produced gas)](image)
In order to determine quantitatively the status of catalyst deterioration, improved catalyst 2 was operated for 3000 hours under the same conditions as when it was evaluated for service life. Then, catalyst was removed from the upper, middle and lower catalytic layers of the reaction pipe. It was then evaluated in terms of physical properties and residual activity. No changes in kerosene conversion rate or in produced gas composition were recognized during 3000 hours of operation. On the other hand, a microreactor was used to evaluate the residual activity of extracted catalyst (hereinafter termed “spent catalyst”), and the ranking of residual activity was as follows: upper layer (0.52) < middle layer (0.66) < lower layer (0.68) < new catalyst (1.00). (Figures in parenthesis denote relative activity.) From this finding it was determined that the percentage of deterioration was the greatest at the catalyst upper layer. Figure 7 presents the results of an evaluation of the physical properties of spent catalyst. At the catalyst upper layer, it was found that because the temperature at this catalyst layer is low, the impact of thermal deterioration (for example, reduced surface area or increased Ru particles) is small, but that the impact of carbon precipitation or sulfur poisoning is large. At the lower layer, on the other hand, it became clear that catalyst layer temperature is high and that the impact of thermal deterioration is large. Catalyst pulverization was also recognized in part of the spent catalyst. This can be attributed to the low catalytic strength of carrier of high surface area, used to increase activity, and to pressure disruption caused by running over a long time period.
Catalyst type & Surface area & Activation point structure & C distribution & C quality & Sulfur \\
New catalyst & & & & & \\
Upper layer WAT 655°C & Surface area decline through sintering & Ru particle diameter increase & & & \\
Middle layer WAT 690°C & & & & & \\
Lower layer WAT 720°C & & & & & \\

Figure 7: Physical Properties of Spent Catalyst

(3) Catalyst improvement

In light of the aforesaid investigation of catalyst deterioration, advances were made in catalyst improvement, taking the following as improvement yardsticks: 1) elevation of coke deposition performance, and 2) selection of carrier of high strength and high surface area. With respect to 1), there were mainly changes in added elements. Respecting 2), selection was made from among carriers that can be obtained industrially. As a result, improved catalyst 3, of higher activity than catalyst 2, was discovered. Figure 8 shows the results of accelerated deterioration test on Ru-Co/ZrO₂ catalyst, improved catalyst 2 and improved catalyst 3. It was determined that the service life of improved catalyst 3 was long because with this catalyst, the drop in kerosene conversion rate (C₁ conversion rate) was later and milder than with the other catalysts. Moreover, after this evaluation, the coke volume of each spent catalyst was measured as follows: 0.6 wt% in Ru-Co/ZrO₂, 3.3 wt% in improved catalyst 2 and 0.9 wt% in improved catalyst 3. It was thus learned that coke production is suppressed in improved catalyst 3. (It is believed that the coke volume of Ru-Co/ZrO₂ was low because of the short evaluation time.)

Improved catalyst 3 was trial produced, based on its specifications, by catalyst makers with the aim of mass production. As opposed to 10 g/batch on a laboratory scale, 5 kg/batch was trial produced. Operations and equipments used in production processes were modeled on industrial manufacturing. Given that there was no problem in operations during production and that the performance of laboratory products could be replicated by the trial-produced catalyst, it was concluded that industrial manufacture of the catalyst is possible.
3.3 Development of Hydrogen Production System

(1) Preliminary investigation of kerosene desulfurization/reforming system

Using process simulation, an investigation was made, in terms of material balance, of the kerosene desulfurization/reforming system in which the developed desulfurizing agent and reforming catalyst had been applied. Figure 9 presents a model of process flow using simulation, together with calculations of the composition of produced gas at each component.

Figure 9: Process Flow of Kerosene Desulfurization/Reforming System and Composition of Gas Produced by Each Component (Calculated Values)
H₂ concentration at the CO converter outlet (hereinafter, “dry base”) was 74.4%. This value is roughly equivalent to 74.7%, the theoretical maximum concentration of H₂ calculated when the kerosene (mean composition: C₁₂.₂ H₂₃.₃) used as the latest calculation base has been completely reformed to CO₂ and H₂. In addition, the H₂ concentration at the CO selective oxidizer outlet was 70.9%. It was thus found that a value could be obtained which is not inferior to the H₂ concentration (about 75%) at CO selective oxidizer outlets in city gas reforming as currently being reported.

(2) Design/Fabrication of practical reforming unit tester

With cooperation from fuel cell makers, a 1 kW kerosene practical reforming unit and its tester were designed. A summary flowchart appears in Figure 10. Here the practical reforming unit refers to reforming unit, CO converter and CO selective oxidizer. For the practical reforming unit, it was assumed that a unit successfully used in reforming of 1 kW of city gas could be applied as is. The reforming unit comes together with a CO converter as a single body, and it has a burner that burns hydrogen returning from the fuel cell stack, thereby adding heat. In addition, this burner can also burn LPG for combustion improvement during startup or when the unit is running. An electric heater is used to heat the reforming unit when it is being started up. A heat-independent design applies, however, when city gas has been used, so that, during routine operation, the unit can run while being heated only through combustion of the city gas introduced and hydrogen returning from fuel cell stack. Since it has been converted as is for use of city gas, the design of the latest reforming unit is not suitable for kerosene. When kerosene is used, thermal independence is difficult to realize. It was decided, therefore, to use an electric heater to bolster the steam line, etc. A vaporizer that uses steam heat was employed for vaporization. It was made possible to supply JIS No. 1 kerosene or pre-desulfurized No. 1 kerosene (desulfurized kerosene) as the feedstock kerosene. A desulfurizing unit was installed on the line supplying No. 1 kerosene. It was arranged so that the desulfurizing unit can be heated with an electric heater. It was also made possible to supply desulfurized kerosene as is to the vaporizer. An external view of the practical reforming unit tester appears in Figure 11. The desulfurizing unit was filled with Ni desulfurizing agent, and the reforming catalyst was filled with improved catalyst 3.
(3) Results of operating practical reforming unit tester (vaporization - reforming operation)

Without using a desulfurizing unit, desulfurized kerosene was supplied directly to vaporizer, and the vaporizer was operated. Hereinafter, this procedure is referred to as the vaporization - reforming operation. The vaporization - reforming operation was carried out with a 100% load in which kerosene equivalent to 1 kW of generated power was circulated. Operating conditions are given below.

- Kerosene flow volume: 3.5 g/min
- S/C ratio = 3.0, Reforming catalyst outlet temperature: 700°C
- O₂/CO ratio of CO selective oxidizer = 1.5 (Calculated in advance to determine required air volume)
- H₂ imitation gas returned from fuel cell stack: Composition and flow volume on assumption of 80% hydrogen utility rate
- Presence/absence of combustion improvement by burner: Improved combustion implemented with LPG (Amount required for control of reforming catalyst layer outlet temperature)

The startup time (time until kerosene is supplied to 100% load) under these conditions was approximately 1 hour. Presented in Table 1 are the kerosene conversion rate and the composition and flow volume of reforming gas at the CO selective oxidizer outlet. Given the fact that the kerosene conversion rate determined from produced gas composition and flow volume was 100%, plus the fact that kerosene component was not detected from water in the drain tank at the CO selective oxidizer outlet, it could be confirmed that the kerosene was reformed almost completely. As for produced gas composition (dry), H₂ concentration was 71.3%, closely matching 71%, the value calculated from simulations. The concentrations of CH₄ and other ingredients also matched well with the aforesaid calculated values. These findings indicate that the reforming catalyst applied exhibits outstanding reforming performance also within a practical reforming system. CO concentration was 0 ppm (below the lower measurement limit). The flow volume of H₂ in produced gas was 1000 NL/h. This is roughly equivalent to the amount of H₂ required for generating 1 kW of electric power. These results confirmed that in vaporization - reforming operation, by supplying kerosene equivalent to 100% load, catalyst at each location exhibits prescribed performance, and hydrogen equivalent to 1 kW of generated electric power can be produced as indicated by calculations from simulations.

<table>
<thead>
<tr>
<th>Kerosene conversion rate</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Produced gas flow volume</td>
<td>1485 NL/h</td>
</tr>
<tr>
<td>H₂ production volume</td>
<td>1007 NL/h</td>
</tr>
<tr>
<td>H₂</td>
<td>71.3%</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.4%</td>
</tr>
<tr>
<td>CO</td>
<td>0 ppm</td>
</tr>
<tr>
<td>CO₂</td>
<td>24.3%</td>
</tr>
<tr>
<td>N₂</td>
<td>4.0%</td>
</tr>
<tr>
<td>C₂+</td>
<td>0.0%</td>
</tr>
</tbody>
</table>

Reforming unit efficiency based on operational results was calculated at 77% (HHV). The definition of reforming unit efficiency is given in Figure 12. In this operation, an electric heater must be used to heat the steam line, so thermal independence is not attained, but the aforesaid values have been given for reference.
Figure 12: Definition of Reforming Unit Efficiency

Reforming unit efficiency \( \varepsilon_{FP} = \frac{\text{Calorific value of } \text{H}_2 \text{ discharged from reforming unit } \times 0.8^*}{\text{Calorific value of kerosene supplied to reforming unit} + \text{Calorific value of } \text{LPG} \text{ supplied to burner for combustion improver}} \)

* The rate of hydrogen utility by fuel cell stack is assumed to be 80%. The remaining 20% is used by reforming unit burner.

In order to investigate the impact of load reduction on operation, kerosene was circulated in amounts equivalent to 25% load, 50% load and 75% load, and vaporization - reforming operation was implemented. The composition of produced gas at the reforming unit outlet is presented in Figure 13. It was found that the composition of each ingredient roughly matches at any load. Moreover, these values were roughly equivalent to equilibrium calculations.

![Gas Composition at Reforming Unit Outlet with Each Load](image)

Figure 13: Gas Composition at Reforming Unit Outlet with Each Load

3.4 Liquid Fuel Quality versus Steam Reforming Characteristics

Using improved catalyst 3, the steam reforming reactivity of each model substance (n-paraffin, iso-paraffin, naphthene, olefin, aroma) was evaluated. The conditions of evaluation were: S/C = 3, atmospheric pressure, reaction temperature at 350 - 500°C, LHSV = 2h\(^{-1}\).

On the assumption that the reforming reaction is a pseudo primary reaction for each model substance, an Arrhenius curve was plotted for each hydrocarbon type, from which the activation energy was then calculated. The activation energy sequence is as follows.

n-paraffin, naphthene, olefin, aroma > iso-paraffin
In addition, reaction speed was calculated from Arrhenius curve under fixed reaction conditions (450°C, S/C = 3, atmospheric pressure), and the reaction speeds of each model substance were compared with that of n-octane (carbon number = 8). The results appear in Figure 14. A look at the relative activity of n-paraffin reveals that when there has been an increase to two carbon chains, reforming performance drops by about one half. This trend is the same regardless of the type of hydrocarbon. The sequence of reforming performance by hydrocarbon type can be arranged as follows.

Reforming reaction sequence: iso-paraffin > n-paraffin, naphthene>> aroma, olefin.

Catalyst IKC-03, 450°C, S/C = 3, Atmospheric pressure

![Figure 14: Reforming Reactivity of Model Substances](image)

The coke volume produced on catalyst by means of model substance reforming reaction was investigated and the relationship between relative reactivity of each hydrocarbon and produced coke volume was plotted (Figure 15). We can see that when hydrocarbon types of low reactivity, such as aroma or olefin, or heavy hydrocarbons of large carbon number, have been used as feedstock, the volumes of coke produced become greater. It is suspected that in feedstock of low reactivity, following adsorption onto catalyst surface, the substances remain stagnant for a long time without converting to CO or H₂, and eventually turn into coke.
4. Synopsis

(1) Development of adsorption desulfurizing agent

a) Service life evaluation

The pretreatment (reduction) conditions of Ni desulfurizing agent were investigated and the reduction conditions for maximizing the surface Ni volume, important for sulfur adsorption, were discovered. After pretreatment under these reduction conditions, kerosene on the market with 48 ppm sulfur concentration was used to evaluate service life. It was confirmed that a desulfurization could be maintained at 0.05 ppm or below for longer than 5000 hours.

b) Impact of kerosene quality on desulfurization performance

Desulfurization performance depended on the types of sulfur compounds included in the kerosene. Benzothiophene was easy to desulfurize, but desulfurization of dibenzothiophene was difficult. What is more, polynuclear aromatic compounds in kerosene poisoned the desulfurizing agent and lower desulfurization performance.

(2) Development of steam reforming catalyst

a) Evaluation of catalyst service life

The newly-developed improved catalyst 2 maintained 100% kerosene conversion even after 12,000 hours of operation, and the outlet gas composition remained stable from the initial period. Judging from the conditions of endothermic peak movement, service life would be forecast to be even longer. This catalyst could be of high practical value.
b) Catalyst improvement

Through an investigation of changes in added elements and of carriers of high strength level and high surface area, it was discovered that improved catalyst 3 exhibits higher performance and longer service life than improved catalyst 2. Improved catalyst 3 was trial produced in imitation of industrial manufacture. It was found that this catalyst can be produced by operating industrial manufacturing equipment and that it can reproduce laboratory-scale performance.

(3) Investigation of hydrogen production system

A kerosene desulfurization/reforming system was designed and fabricated using newly-developed desulfurizing agent and reforming catalyst, and research on system operation was begun.

a) Design/fabrication of practical reforming unit tester

A kerosene reforming unit and its tester were designed and fabricated by converting a practical reforming unit (including reformer, CO converter, and CO selective oxidizer) which had been successfully used to reform city gas of 1 kW class.

b) Results of operating reforming unit tester (vaporization - reforming operation)

Vaporization - reforming operation was carried out by supplying desulfurized kerosene directly to an atomizer without using a desulfurizing unit. Kerosene equivalent to 100% load (1 kW) was supplied, and operation was performed with S/C = 3.0 and the temperature of the reforming catalyst layer outlet at 700°C. It was confirmed that $\text{H}_2$ was produced in accordance with values calculated in simulations and that catalyst at each location exhibits prescribed performance also in the hydrogen production system.

(4) Liquid fuel quality versus steam reforming characteristics

The steam reforming reactivity of model substances, which were pure test agents, was evaluated and the following results were obtained.

- Reforming reaction sequence: iso paraffin $>$ n-paraffin, naphthene $>>$ aroma, olefin
- With all the hydrocarbons, reforming reactivity drops as the carbon number becomes larger.
- The lower the reactivity of the model substance, the easier it is for coke to precipitate on the catalyst.