2008 Prize of Director General of Regional Bureau of Economy, Trade and Industry

"Aiming for Energy Conservation in Hydrogen Manufacturing Equipment"

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Refining Section 1 Project B Group

◎ **Keywords: Rationalization of fuel combustion**

◎ Outline of Theme

In petroleum refining facilities, hydrogen is supplied by hydrogen manufacturing equipment which uses a steam reforming method to create hydrogen as the main product, and by catalytic reforming equipment that manufactures hydrogen as a byproduct of aromatic compounds. In recent years, the increasing shift to sulfur-free petroleum products t has progressed and there is a trend to use increasing amounts of hydrogen, so that the operation of the hydrogen manufacturing equipment, which consumes a huge amount of energy, has been increasing.

Accordingly, by reviewing the hydrogen manufacturing equipment, recovery equipment, and the overall system consumption equipment, together with reducing the operation of hydrogen generating equipment by restoring the performance of the recovery equipment and making effective use of low purity hydrogen, we realized a large energy conservation.

◎ Implementation Period for the said Example

March 2007 – April 2008 (Total of 13 months)

- Project Planning Period March 2007 – January 2008 (Total of 10 months)
- Measures Implementation Period January 2008 – February 2008 (Total of 1 month)
- Measures Effect Confirmation Period February 2008 – April 2008 (Total of 2 months)

◎ Outline of the Business Establishment

- Items Produced LPG, naphtha, gasoline, kerosene, diesel, fuel oil, and lubrication oil
- No. of Employees 565 persons (As of April 1, 2007)

- Annual Energy Usage Amount (Actual results for fiscal year 2006)

  Fuel, etc. (Crude Oil Equivalent) 965,000 kL

  Electric Power 593,859 MWh

◎ Overview of Target Facilities

In the refinery and plant, there are three types of hydrogen, which differ according to the generation equipment, pressure, and purity.

a) 15 kilo Hydrogen: Pressure 1.5MPa, High Purity

General hydrodesulfurizationapplications, polymer applications, etc.

b) 25 kilo Hydrogen: Pressure 2.5MPa, High Purity

Plant hydrodesulfurizationapplications, etc.

c) Reformer Hydrogen: Pressure 2.5MPa, Low Purity

Indirect desulfurization equipment,

Deep desulfurization equipment applications

Each type of hydrogen is linked between the generation equipment and consumption equipment by pipeline. This time, by eliminating the impurities in the low purity reformer hydrogen generated by the Naphtha Catalytic Reforming Equipment (known below as the 2P Equipment), and taking the main target improvement equipment as the Hydrogen Recovery Unit (known below as the HRU Equipment) which recovers hydrogen to high purity 15 kilo hydrogen together with the Hydrodesulfurization Equipment, it was aimed to indirectly reduce the operation of the Hydrogen Manufacturing Equipment (known below as the HY Equipment).

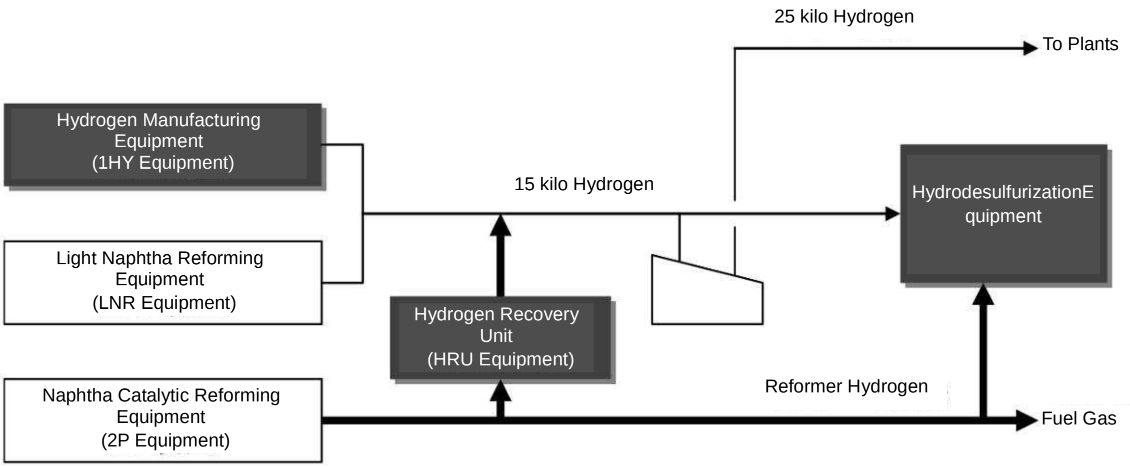


Fig. 1 The Process Chart of the Facility

1. Reasons for Theme Selection

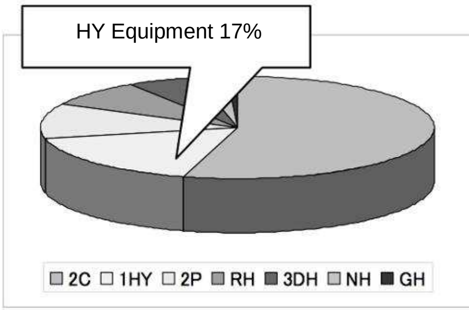


Fig. 2 Percentage of Fuel Amounts Used in this Section

Our section is responsible for comprehensively managing the on-premises balance between the hydrogen generation and consumption. Responding to the hydrogen consumption amount, this section undertakes the role of maintaining the hydrogen balance by carrying out HY equipment operation adjustment and HRU equipment operation adjustment.

The on-premises hydrogen balance continues to become tighter due to the recent increase in hydrogen-consuming applications in petroleum refining and the chemical industry. Regarding the periods where the adjoining plants' regular maintenance coincides with the hydrogen generation equipment's regular maintenance periods, the receiving of hydrogen becomes extremely restricted, and the influence on operations is becoming larger.

Additionally, this large fuel-consumption equipment taking up 17% of the section's fuel consumption is also equipment that emits very large amounts of carbon dioxide, and so it is desirable to restrict its operation as far as possible.

However, the supply of hydrogen is one of the most important elements for the stable operation of the refinery and plants, and in view of our mission of providing a stable supply the positive implementation of energy conservation activities is also a difficult issue.

Accordingly, rather than just considering the HY equipment by itself, we considered the entire hydrogen supply system, and as one part of the performance-maintaining activities implemented throughout all the facilities we tackled the reduction in fuel consumption of the HY equipment by devising various measures to allow reduction of the HY equipment operation.

2. Understanding and Analysis of Current Situation

(1) Understanding of Current Situation

1) Hydrogen balance in the refinery and plant

As the hydrogen generating sources, there are the following three main types of equipment.

① Hydrogen manufacturing equipment

This equipment uses the steam reforming method to manufacture hydrogen as the main product, using naphtha, methane and butane as fuels. It generates (a) 15 kilo high purity hydrogen.

② **Light naphtha reforming equipment**

This equipment reforms light naphtha to manufacture benzene, creating (a) 15 kilo high purity hydrogen as a byproduct.

③ **Naphtha catalytic reforming equipment**

This reforms heavy naphtha to manufacture BTX, creating (c) 25 kilo low purity hydrogen as a byproduct. The amount of hydrogen generated as a byproduct from the light naphtha manufacturing equipment (known below as LNR equipment) is roughly constant throughout the year.

While most of the (a) 15 kilo hydrogen is supplied to the refinery desulfurization equipment, a part has its pressure raised using a compressor in order to cover for insufficiencies in the 25 kilo hydrogen.

The (c) 25 kilo low purity hydrogen has limitations in its usage destinations due to purity restrictions. Accordingly, it is being recovered as 15 kilo hydrogen by increasing the purity using the HRU equipment. However, the part of the low purity hydrogen that cannot be processed due to exceeding the processing capacity can only be utilized as fuel gas. In addition, from the point of view of controlling the hydrogen pressure, there was a situation where part of the hydrogen could only be used as fuel gas.

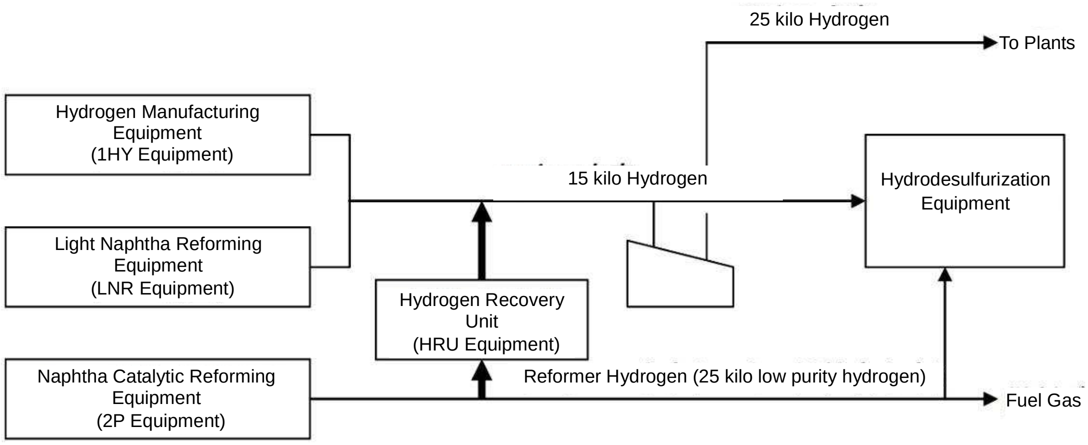


Fig. 3 Hydrogen Balance in the Refinery and Plant

2) HY equipment operation

In the HY equipment, water and hydrocarbons are reacted, reforming them to hydrogen and carbon dioxide. This reaction is an endothermic reaction that uses a large amount of fuel. The HY equipment fuel intensities gradually decrease with the operation rate increase (Fig. 4), reaching maximum efficiency at the maximum operation rate.

On the other hand, the fuel usage amount rises proportionally to the operation rate (Fig. 5). Because the fuel usage amount becomes 160 COE-L for each 1 kNm^3 of hydrogen generated, the reduction of this equipment's operation will be linked with a large energy conservation effect.

Since this equipment is used for absorbing variations in hydrogen supply throughout the entire refinery, it is desirable also from the point of view of stable supply that a surplus should be maintained in the operation to cover the range of stable operation. The current operation rate is reaching an average of 82%, and it was desired from the points of view both of fuel usage and also of stable operation for the operation rate to be reduced.

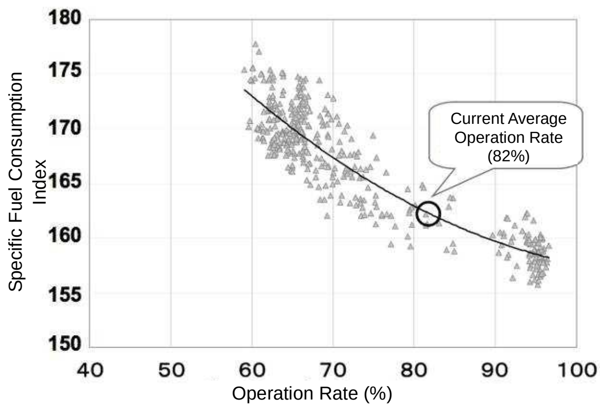


Fig. 4 Operation Rate against Specific Fuel Consumption Index

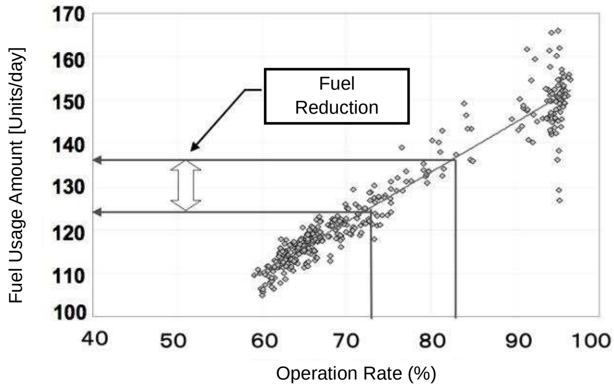


Fig. 5 Operation Rate against Fuel Usage Amount

(2) Analysis of Current Situation

In order to reduce the HY equipment operation, it will be necessary to increase the generation using the equipment that creates hydrogen as a secondary product.

① Increase of byproduct hydrogen due to increased LNR equipment operation

② Increase in usage destinations through direct effective use of byproduct reformer hydrogen or by increasing the purity

The operation of the LNR equipment in ① is roughly constant, and is difficult to increase. Because the usage destinations that can directly utilize the low purity reformer hydrogen generated as a byproduct of the 2P equipment in ② are limited, we understood that it would be essential to increase the capacity of the HRU equipment.

The specific fuel consumptions of the byproduct reformer hydrogen and the hydrogen generated by the HY equipment are as shown below. (Table 1) There is a large difference in the specific fuel consumptionsbetween both pieces of equipment, and it was discovered that even considering a certain amount of investment, increasing the HRU equipment performance would result in large energy conservation.

Since receiving the Minister of Economy, Trade and Industry Award for our case study the previous year, this section had been striving to made efforts to understand and restore the decline in equipment performance, and has been steadily achieving results. Regarding the HRU equipment, too, there had been concern about the decline in performance, but due to the problem of the restoration cost it had been left pending. However, it was judged that restoration would be possible using this intensities difference as the capital, and it was decided to tackle the implementation of the processing performance improvement.

Table 1 Specific Fuel Consumptionfor the Same Hydrogen Generation Amounts

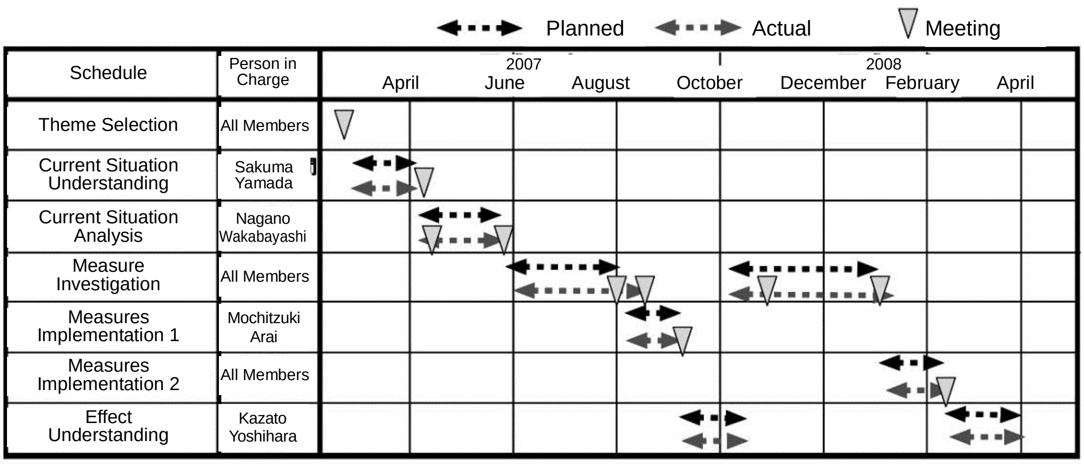
Equipment Name	Specific Fuel Consumption
HY Equipment	160 L
HRU Equipment	1.2 L

3. Progress of Activities

(1) Implementation Structure

Regarding the investigation this time, the groups inside the section appointed persons to be in charge, and activities were implemented. In order that progress would not be delayed, rules were decided for implementing the measures, such as reporting problem points each time they were discovered and holding regular meetings. (Table 2)

Table 2 Implementation Structure and Activity Schedule



(2) Target Settings

By restoring the HRU equipment processing capacity to its initial design performance and recovering the maximum byproduct hydrogen, it was aimed to reduce the HY equipment operations to around 75% and cut the HY equipment energy usage amount by 10%. In consideration of the effect incurred by the energy balance in the refinery, the target was set as 4,000 COE-kL/year.

(3) Clarification of the Problem Points

1) Adsorption vessel valve problem

① Outline of equipment

The HRU equipment is equipment that absorbs and eliminates hydrocarbon impurities in the hydrogen using pressure swing adsorption (PSA). The adsorption vessel consists of six vessels. Through repeating the adsorption of impurities during pressure increases and the desorption of impurities during pressure decreases, the impurities will be absorbed, discharged and eliminated to increase the hydrogen purity. (Fig. 6)

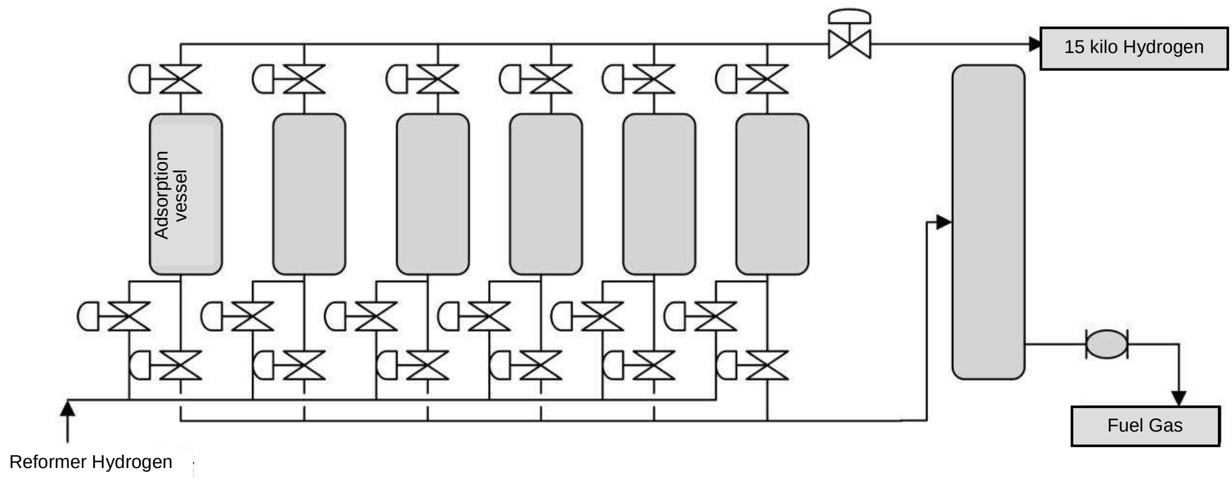


Fig. 6 HRU Equipment

② HRU equipment designed processing performance

Although the HRU equipment's designed processing performance is 170kNm^3/D, the maximum processing performancein actual operation was 110 kNm^3/D, and there was a situation where it was not possible to increase the processing amount due to the adsorption capacity of the adsorptive materials. For this reason, there was a limit of 50-60 kNm^3/D on

the product's hydrogen amount.
Here, the capacity is said to be shown by the ratio of the maximum product hydrogen amount used for raising the pressure in the adsorption vessel to the raw material processing amount. Further, the coefficient that adjusts the increase or decrease in the product hydrogen amount used for raising the pressure is shown as the capacity factor. (Fig. 7)

$$\text{Capacity} = \frac{\dfrac{A}{24 \times \text{A Flow Meter Range}} \times B \times \text{B Flow Meter Range}}{\text{Maximum Product Hydrogen Amount (Constant) for pressure rising}} \times 100$$

A: HRU Loading (Raw Material Processing Amount) B: Product Hydrogen Amount Coefficient (Capacity Factor)

Fig. 7 HRU Capacity Formula

The HRU equipment is a "black box" of advanced technology from the adsorptive materials to the control tuning. Further, although the maximum processing performance in long-period operation has reduced to 110kNm^3/D, the actual improvement measures can not be determined. (Fig. 8) Accordingly, we focused our attentions on clarifying the mechanisms behind the drop in performance, together with establishing measures for recovering the performance.

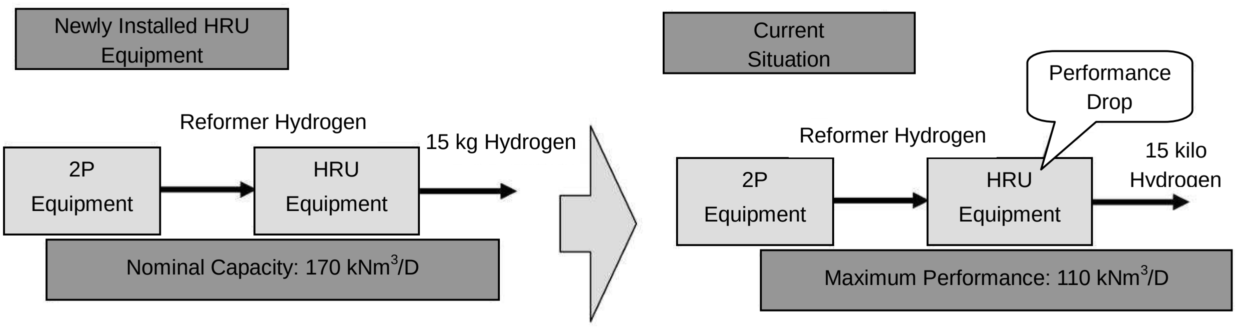


Fig. 8 HRU Equipment Performance Drop

③ Confirming the problem points when adjusting the purity of the product hydrogen (Mechanical point of view)

For the product hydrogen, the 15 kilo hydrogen purity adjustment is carried out in the adsorption vessel pressure-raising process by returning a part of the product hydrogen as hydrogen for use in raising the pressure. If the amount of hydrogen used for pressure-raising is increased, the pressure will rise, but the recovered amount of hydrogen

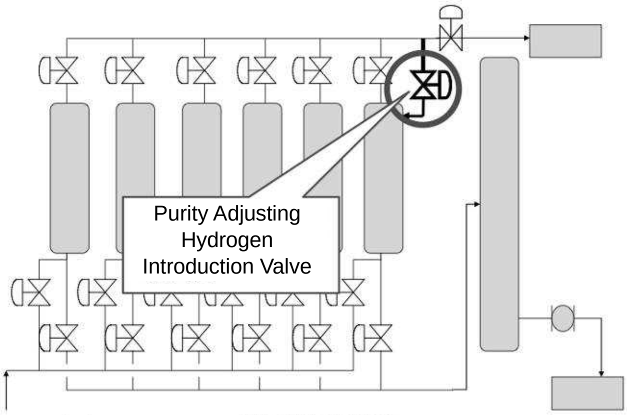


Fig. 9 HRU Equipment Purity Adjustment

will be reduced. Conversely, if there is less hydrogen, the purity will be reduced, but the product hydrogen amount will increase. The pressure in each of the adsorption vessels repeats the adsorption and desorption inside the processes from pressure raising to pressure lowering, comprising 12 processes. In the situation where the product hydrogen purity is to be increased, by operating the adjusting valve shown in the figure at right during the adsorption vessel pressure-raising process, part of the product hydrogen can be introduced to the adsorption vessel to increase the amount. (Fig. 9)

If the hydrogen for pressure-raising is increased, the equipment capacity increases and the HRU equipment processing amount will be reduced. For this reason, the maximum amount of pressure-raising hydrogen is fixed, and in the situation where the target hydrogen purity could not be attained, the only thing that could be done was to reduce the overall loading on the HRU unit (Raw material processing amount).

In particular, the adjusting valve concerned operates 2 million times per year, and in consideration of the number of operations, this valve requires the adjusting valve to be regularly replaced. When there were “Adjusting valve problems” or “Pressure setting problems”, the hydrogen processing amount will be reduced, so investigations were started and a disassembly inspection of the valve was carried out. As a result of the investigation, no problems were found either in the valve or the operation condition. The FTA utilized at that time is shown in Fig. 10.

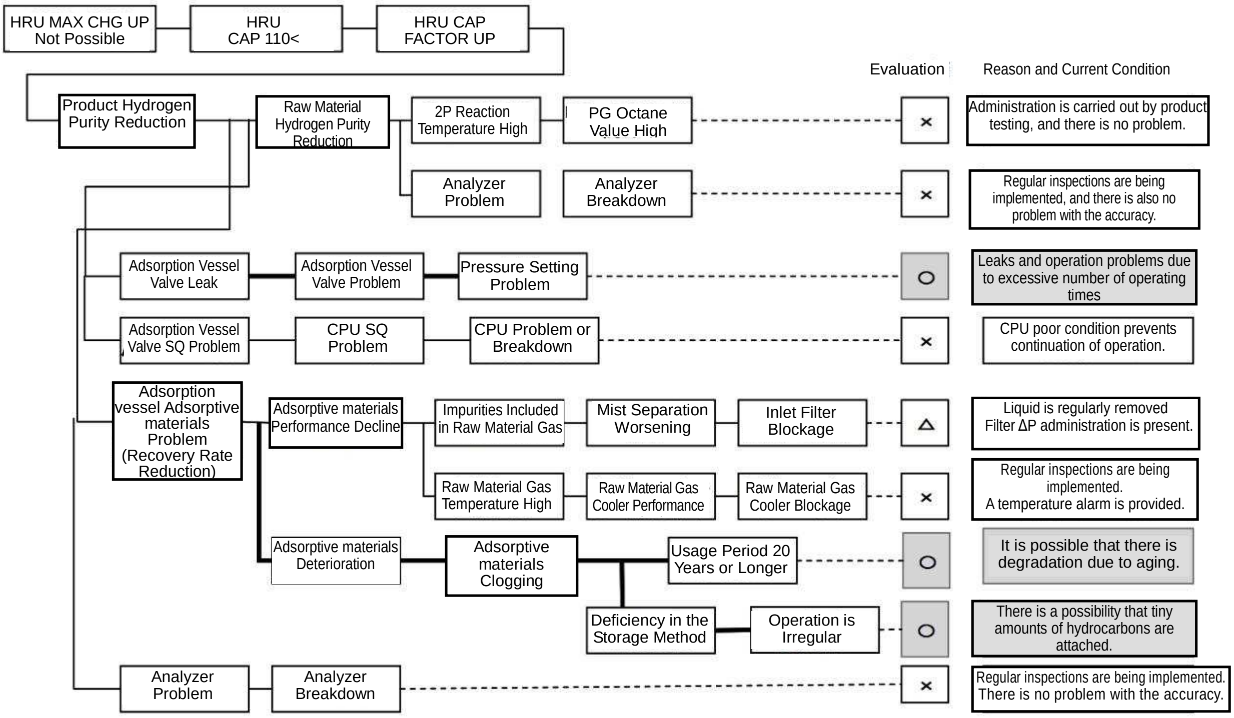


Fig. 10 Performance Reduction FTA

Because we had previously understood that the adsorptive materials could be used semi-permanently, we did not think to consider this so deeply. However, from the above result we thought that deterioration of the adsorptive materials might be occurring through repeated long-period use, or there could be deterioration of the adsorptive materials due to defective storage methods. Accordingly, we investigated the adsorptive materials.

2) Degradation of the adsorptive materials over time (Chemical point of view)

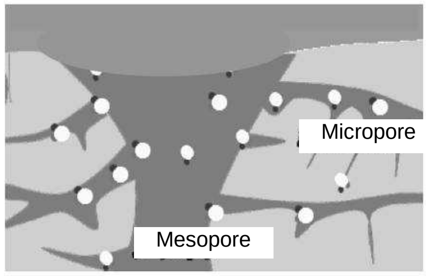
① Adsorption mechanism of the adsorptive materials

The adsorptive materials used in the HRU equipment consist of a molecular sieve, activated alumina, and activated charcoal. Depending on the molecular structure, the molecular sieve effect of the adsorptive materials can selectively adsorb the hydrocarbons that make up the impurities.

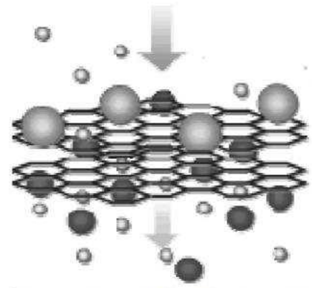
For example, inside the activated charcoal there are small holes called micropores surrounding the molecules, large holes called macropores that allow gas to pass in and out, and intermediate size mesopores. The adsorption capacity will be determined by the good condition of these pores.

In molecular sieves, by trapping the molecules in a zeolite framework matching the molecule size, it is possible to select a molecular sieve that can selectively absorb the required types of impurities.

Regarding the causes of impediments to the adsorption and desorption effects of the adsorptive materials, the following items can be suggested.



Structure of Activated Charcoal


Zeolite Selective Permeation Image

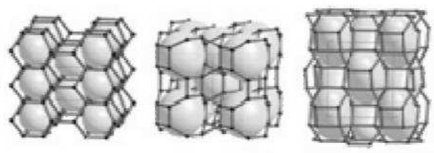

Various Zeolite Structures (Cage)

Fig. 11 AdsorptionMechanisms

② Causes of degradation

(a) Pore reductions due to heavy hydrocarbons and gums

(b) Change in properties of the adsorptive materials (Changes in acidity, etc.)

(c) Pore reduction due to adsorptive materials wear

(d) Reduction of fine pores due to adsorptive materials wear, and blockages of fine pores or rises in pressure due to various kinds of fine particles in the zeolite structure (cage).

Because hydrogen systems are comparatively clean systems, the causes of degradation are few, although the effects of wear and hydrocarbons can be considered. In the past, there was a period when the HRU equipment stopped due to the relationship with the hydrogen balance when there was a hydrogen surplus. At this time, the results of an investigation found that the reformer hydrogen atmosphere was maintaining a slight pressure.

When storing the absorbing agent, it is undesirable to store it in a condition with the hydrocarbons still attached. (Currently, the hydrocarbons are displaced using an inert gas before storage.) The reformer hydrogen includes hydrocarbons in the order of several %,

and storing the absorbing agent with these hydrocarbons still attached was believed to be a cause of the performance reduction.
Accordingly, an actual test run was carried out to confirm the degree of absorbing agent degradation.

(4) Investigations

1) Adsorptive materials degradation

① Hydrogen recovery rate confirmation test run

The hydrogen recovery rate is shown by the following formula.
Hydrogen Recovery Rate = Product Hydrogen Amount/(Raw Material Hydrogen Amount x Raw Material Hydrogen Purity/100) x 100
While maintaining the same product hydrogen purity, we changed the raw material hydrogen purity, raw material processing amount, and product hydrogen amount. When we confirmed the hydrogen recovery rate, we found the results in the table below.
Although the current hydrogen recovery rate was designed to be around 93%, it was found that the actual rate was around 87%. Because the hydrogen recovery rate did not change even when the conditions were changed, we could confirm that degradation of the adsorptive materials was occurring.

HRU Charge (Raw Material Processing Amount)	Raw Material Hydrogen Purity	Product Hydrogen Purity	Product Hydrogen Amount	Hydrogen Recovery Rate
101 kNm^3/D	60%	98.50%	53 kNm^3/D	87.50%
103 kNm^3/D	70%	98.50%	62 kNm^3/D	86.50%

② Adsorptive materials replacement

Replacement of the entire amount of adsorptive materials in the six adsorption vessels was carried out. When test operation was implemented, the designed performance processing amount of 170 kNm^3/D was secured, and a surplus was created in the adsorption capacity. The hydrogen recovery rate was restored to the initial designed amount of 93%, and the product hydrogen amount increased from 50 kNm^3/D before the adsorptive materials was replaced to 100 kNm^3/D after the replacement.
This enabled a 5% reduction in the HY equipment loading. However, only implementing this measure was not sufficient to achieve the target reduction rate. Accordingly, obtaining advice from surrounding persons, we focused our attention on the new issue of increasing

the usage destinations of the low purity reformer hydrogen.

2) Effective usage of surplus reformer hydrogen

Because the usage destinations for the low purity reformer hydrogen are limited, the surplus portion is adjusted by expending it as fuel gas. Even after restoring the performance of the HRU equipment, there was a condition where approximately 30-40 kNm^3/D of reformer hydrogen was being supplied as fuel gas. The only piece of equipment among our equipment capable of using this hydrogen was the kerosene and diesel deep hydrodesulfurization equipment (known below as the 3DH equipment), and the hydrogen was used mixed with the 15 kilo hydrogen. The 3DH equipment continuously used 50 kNm^3/D (Fig. 13), and an investigation was carried out to determine whether it would be possible to increase this usage amount further.

① Relationship between pressure and hydrogen purity on the desulfurizing reaction

The 3DH equipment is hydrogenated desulfurization equipment which adds hydrogen to raw oil and heats it, using a desulfurizing catalyst to eliminate the sulfur portion. In the hydrogenation reaction, in general if the hydrogen partial pressure reduces, there will be a greater chance to have lowering of the desulfurization rate and disposition of carbon (coking) on the catalyst, causing an adverse affect on the reaction and catalyst lifetimes.

As the causes of the reduction on the hydrogen partial pressure, there is the hydrogen purity reduction and the reaction pressure reduction. If the low purity hydrogen usage amount is increased, the hydrogen partial pressure due to the hydrogenation reaction in the 3DH equipment will be reduced. Accordingly, an investigation was made into the influence of the catalyst on the hydrogen partial pressure lower limit from the point of view of the reaction and catalyst performance.

② Alleviation of 3DH equipment operation hydrogen partial pressure

In the 3DH equipment hydrogen partial pressure, in the current situation a value 0.5MPa below the operating value will be the minimum value. Accordingly, we confirmed this with the specialist division, and had them carry out a simulation of the influence of the hydrogen partial pressure reduction on the catalyst lifetime. As a result, the effect on the catalyst lifetime was found to be negligible, and it could be confirmed that there would be no influence on the catalyst replacement periods. It was found that if the hydrogen partial pressure could be lowered to the minimum value, the reformer hydrogen would be able to use an additional 40 kNm^3/D, so that all of the fuel gas supply portion could be introduced.

③ **Improvement of the pressure control method**

The adjusting valve for the reformer hydrogen intake has a large capacity large valve and a small capacity small valve to match the flow amount. Because the expending of the reformer hydrogen as fuel gas is combined with a pressure adjustment, system changes were made so that the small valve could be used for pressure adjustmentto allow minute pressure adjustments to be made. By doing so, all of the hydrogen supplied as fuel gas could be recovered, and at the same time the hydrogen pressure adjusting sensitivity could also be improved. (Fig. 13)

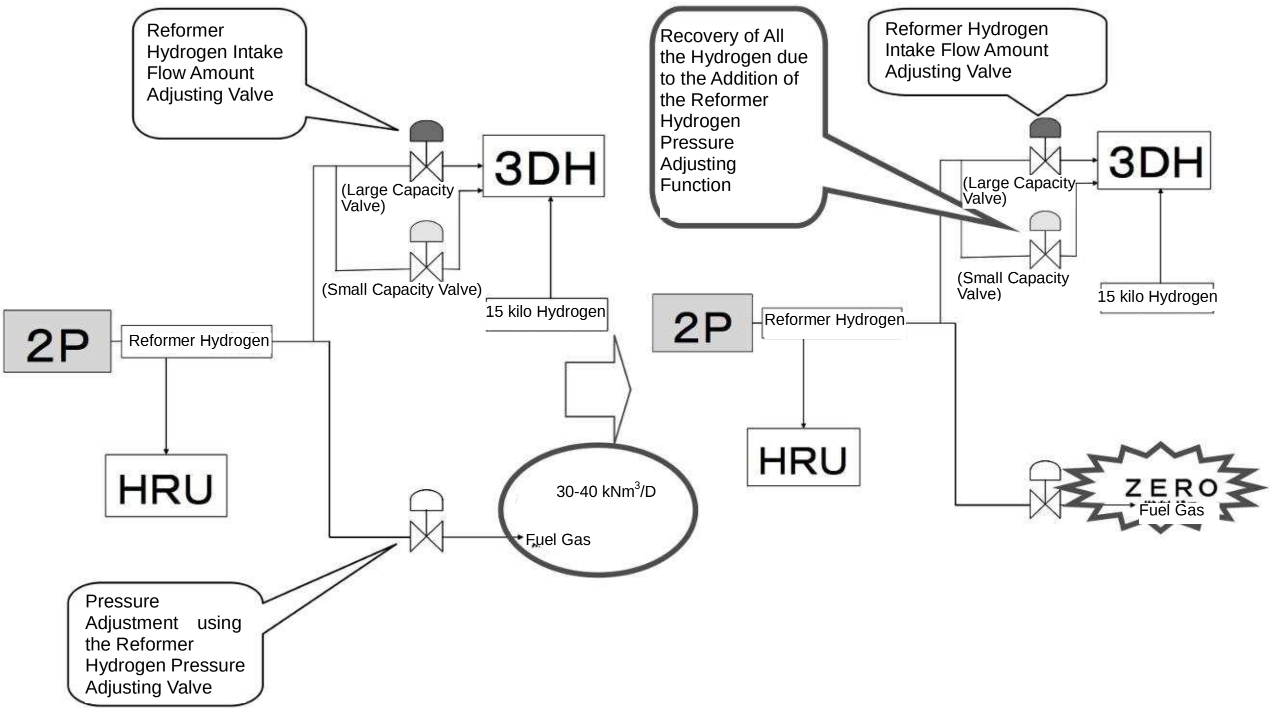


Fig. 13 Reformer Hydrogen Balance

4. Details of Measures

(1) HRU Equipment Adsorptive Materials Replacement

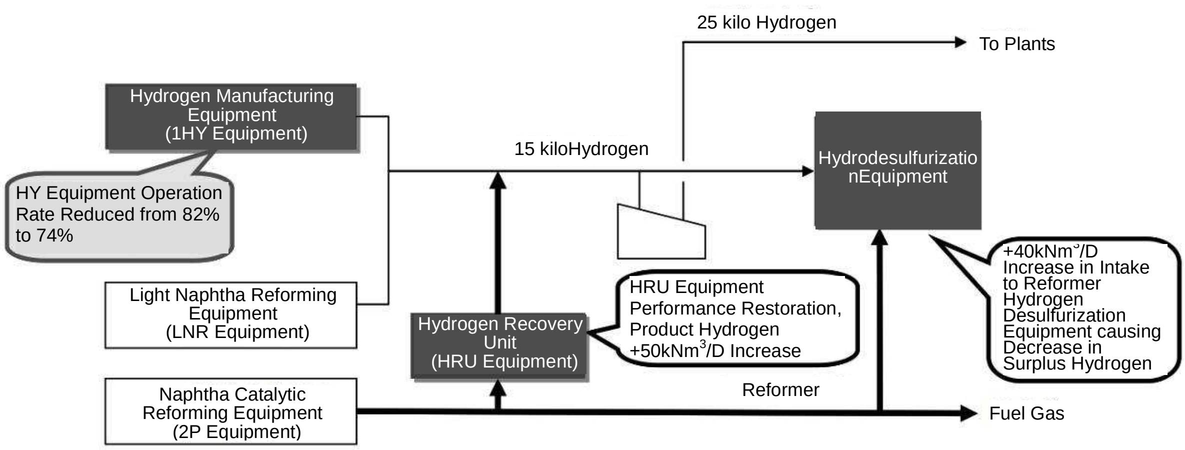
The replacement of the entire amount of adsorptive materials filling up the HRU equipment a desorption vessels (6 vessels) with the latest adsorptive materials was carried out. In addition, by carrying out day-to-day performance administration of the hydrogen recovery rate which indicates the degradation of the hydrogen recovery equipment, we could incorporate this in the system for monitoring the trends in HRU capacity to allow visualization of the situation.

(2) Effective Use of Surplus Reformer Hydrogen in the 3DH Equipment, and Pressure Adjustment Improvement

By reviewing the 3DH equipment operation hydrogen partial pressure and making maximum use of the reformer hydrogen, all of the hydrogen that was previously supplied as fuel gas could be recovered. In addition, the review of the hydrogen pressure adjusting system enabled the extraction of hydrogen as fuel gas to be completely halted.
Due to the above improvements, the HY equipment operation could be reduced, and it was possible to reduce the fuel consumption.

5. Effects Achieved after Implementing Measures

a. Due to the replacement of the HRU equipment adsorptive materials, the product hydrogen was increased from 50kNm^3/D to 100kNm^3/D. As a result, the HY equipment operation rate was reduced from 82% to 77%.
b. In addition, the 3DH equipment reformer hydrogen intake amount was increased from 50kNm^3/D to 90kNm^3/D. In addition, by improving the pressure adjustment of the fuel gas, the final HY equipment operation rate became 74%.



Due to the above improvements, the target of reducing the HY equipment energy use by 10% was achieved, and an energy conservation amount of 4,100 COE-kL/year was realized in the on-premises energy balance.

Item	Amount
Energy Conservation Total Amount	¥350 million/year
Energy Conservation Amount (Crude Oil Equivalent)	4,100 COE-kL/year
CO_2 Reduction Amount	10,800t/year
Adsorptive Materials Replacement Cost	¥55 million

6. Summary

In order to reduce the huge energy consumption amount of the HY equipment, attention was focused on the entire hydrogen system including the HRU equipment and 3DH equipment rather than concentrating only on the HY equipment main unit, and improvements were implemented. The final result allowed a reduction to be achieved in the HY equipment operation.

In the activities this time, a variety of approaches were taken, such as returning to the origins to confirm the design values, and broadening our viewpoint to tackle issue solutions, that allowed us to realize the foregoing results. In the future we intend to continue tackling energy conservation activities while constantly keeping in mind the reduction of global environmental loading based on our experiences this time in returning to the origins.

7. Future Plans

Further proceeding with performance-maintaining activities and visualization activities, we will swiftly rectify equipment problems, together with implementing similar case studies in other locations through carrying out horizontal developments.