2009 Grand Prize of Minister of Economy, Trade and Industry

Development of Highly Efficient Operation Method for Ultra Low Sulfur Gas Oil

Idemitsu Kosan Company Limited, Aichi Oil Refinery

1. Background and Needs

(1) Company Outline

Idemitsu Kosan's basic businesses are to refine and sell oil, and manufacture and sell oil chemical products. The company also develops and manufactures resources, agrochemicals, and electronic function materials represented by organic EL. As business establishments, the company has four oil refineries and two oil chemical plants in Japan, and 18 domestic branches and 36 overseas offices.

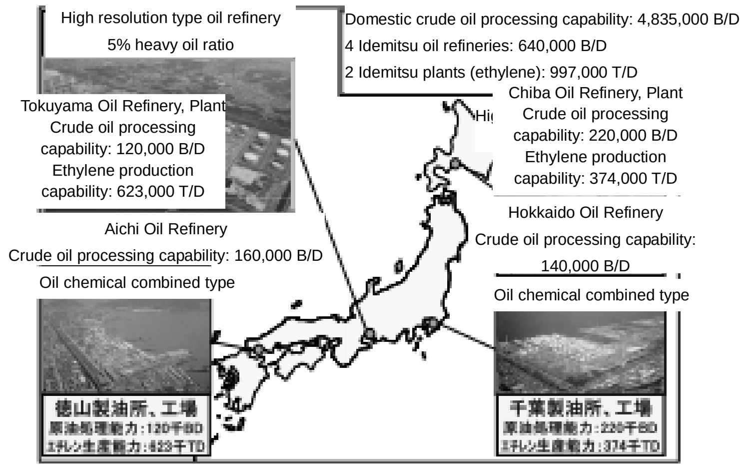

Fig.1 Business Establishments of Idemitsu Kosan

Aichi Oil Refinery is characteristic of the high-resolution type oil refinery that produces low portion of heavy oil. In addition to the equipment that distills imported crude oil and the equipment that removes sulfur from distillate, there is equipment that reforms and dissolves distillates.

(2) Introduction to Energy Management System/Mechanism

In order to contribute to the prevention of global warming, Aichi Oil Refinery is engaged in effective energy use with the target of more than a one percent reduction in yearly energy use. In the refinery, the production management committee, whose chairman is the director of the refinery and the sub-chairman is the deputy director, supervises energy management and energy-saving promotion. Daily operation control and periodical management method are being reviewed under the supervision of an energy management expert. Also, improvement issues are being promoted by a directive from the energy-saving leader in the Management Section. To realize the effective activities, the energy-saving leader consults the energy-saving project team, which is a head office agent, and energy-saving leaders of other business establishments, solicits technical support from expert departments, and horizontally develops the good practices of other business establishments.

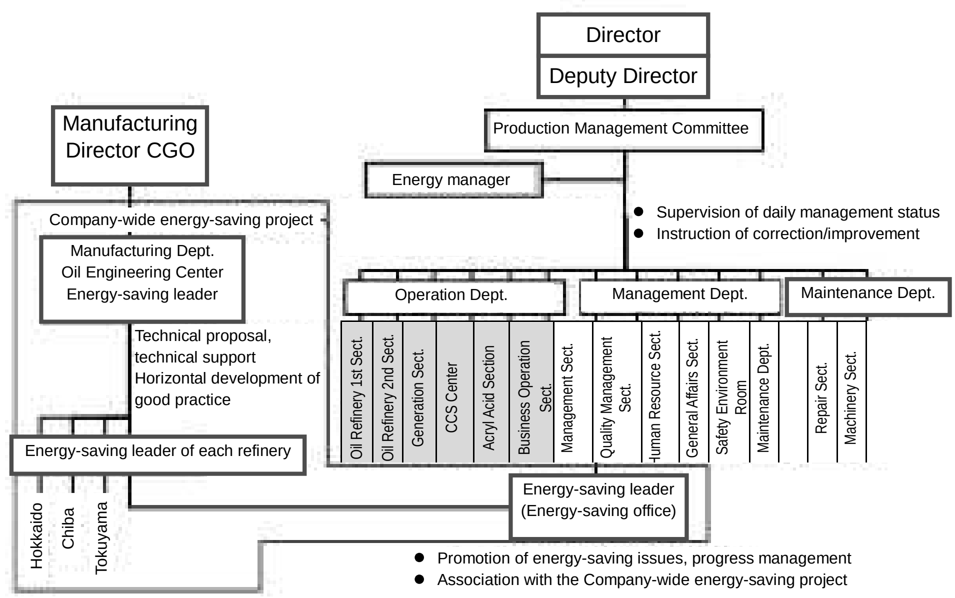

Fig. 2 Energy Management System in Entire Company

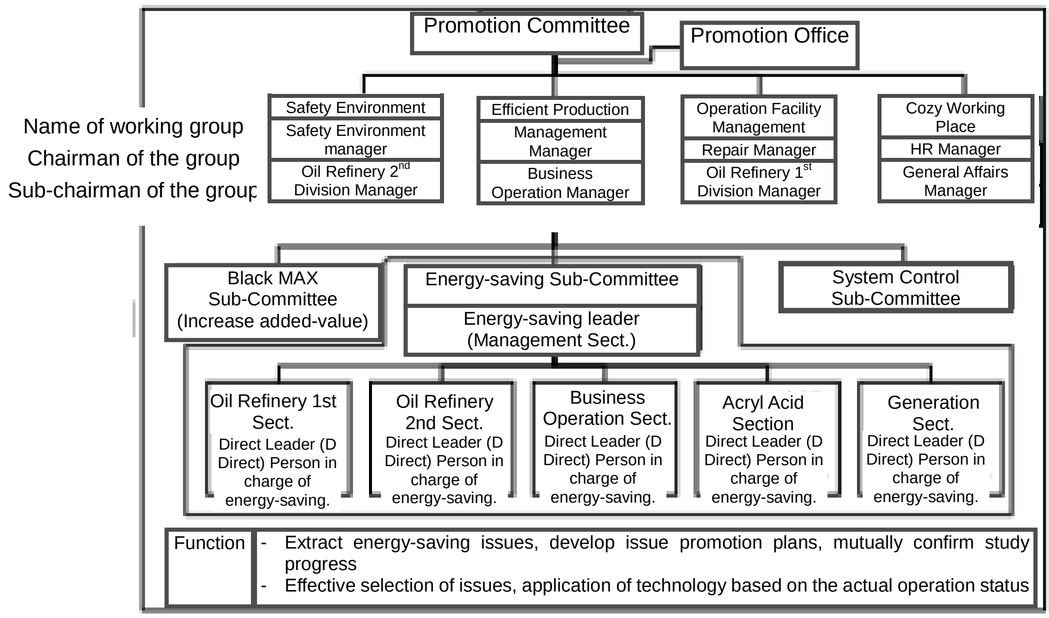

Fig. 3 TPM System in Refinery

As a characteristic of business activities of refineries of Idemitsu Kosan, each refinery introduced the TPM method, established the departmental meeting system that covers sections, and is promoting various issues.

Regarding the energy-saving activities of this refinery, the Energy-saving Branch Meetings are functioning under the Efficient Production Departmental Meeting chaired by Management Section manager. And under the leadership of an Energy-saving leader, members are periodically extracting energy-saving issues, crafting issue promotion plans, and mutually confirming study progress.

Since the leader, who is directly involved in operations, is one of the members, it is possible to effectively select issues and apply the appropriate technology based on the actual operation status.

Also, the IT system called XHQ (neXt generation, HeadQuarters) is being used at all oil refineries. This system collects in real time operation information on all oil refineries and plants and fabricates and displays it as administrative information. Thus, this system enables everyone, from top management to on-site operators, to simultaneously share problems and issues, to make timely decisions, and to plan countermeasures. In energy-saving activities as well, as top management and staff can monitor intensity status of each equipment, they can promptly take action from detection of abnormalities to improvements. Furthermore, as it is possible to see and compare improvement issues and the status of progress for each business establishment, employees can accelerate horizontal development and increase rivalries. Also, as the result of each activity is shared by the entire department, employees are motivated for improvements.

(3) Reasons for Theme Selection

As the breakdown of the fuel consumed by this refinery, in addition to some 28% used by the supply facility that supplies steam and electricity, each desulfurization equipment consumes around 19% and the hydrogen producing equipment that produces hydrogen used for desulfurization reaction uses 19%, totaling approximately 38% (Fig. 4).

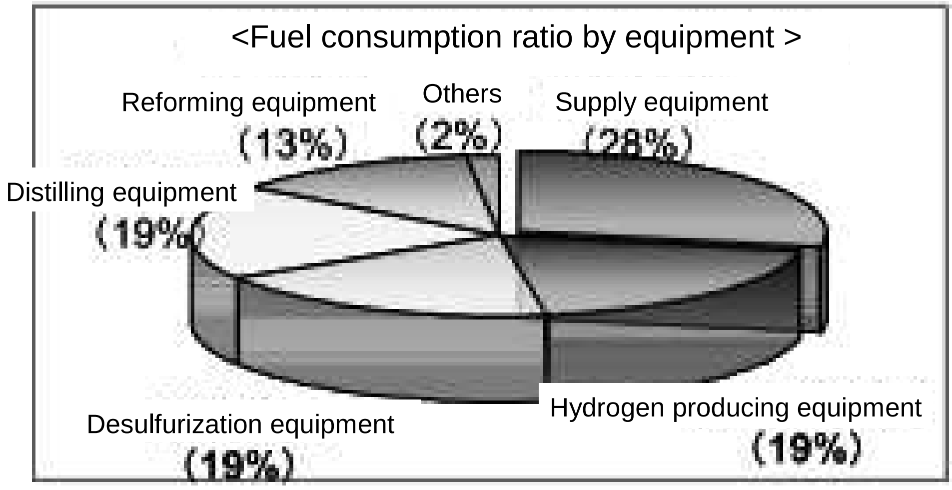

Fig. 4 Energy consumption ratio by equipment

Desulfurization equipment uses a catalyst to remove impurities like sulfur in gasoline, gas oil, and heavy oil by reacting with hydrogen (Fig. 5).

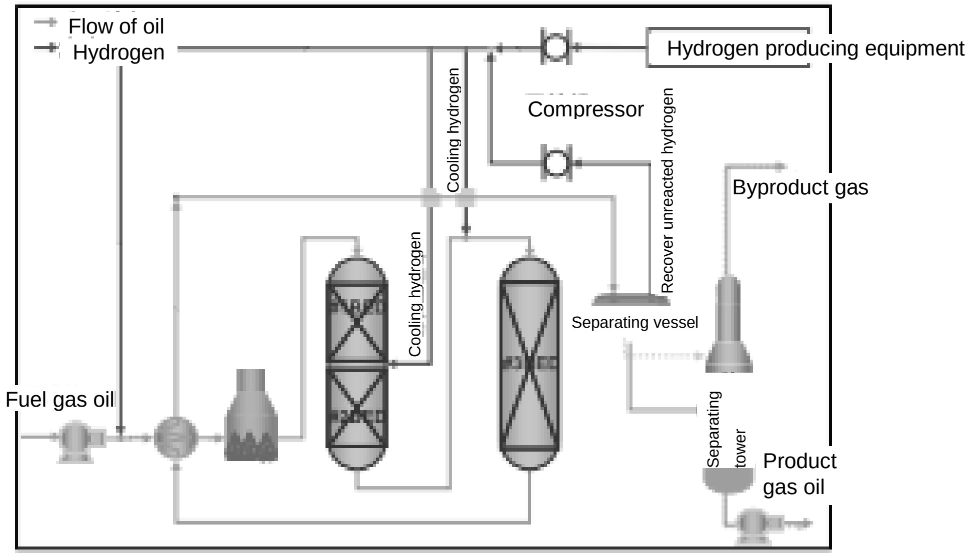

Fig. 5 Flow of gas oil hydrodesulfurization equipment

Hydrogen producing equipment works to reform materials like light carbon hydrogen and steam into hydrogen and carbon dioxide at high temperature to produce hydrogen used for desulfurization (Fig. 6).

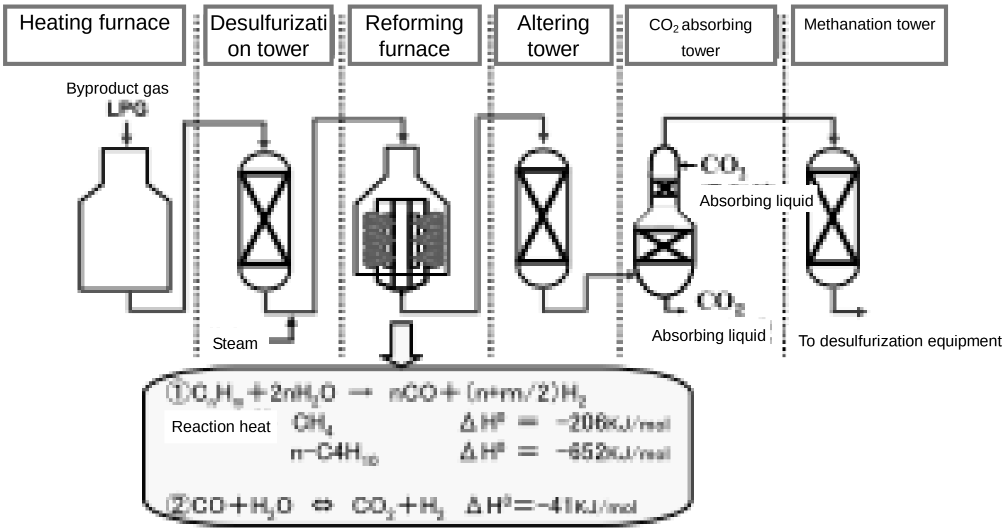

Fig. 6 Flow of hydrogen producing equipment

Since this reforming reaction is a heat absorbing reaction, it occurs at a high temperature of 900℃, requiring an enormous amount of heat. You can see that desulfurization of oil products requires lots of energy. On the other hand, when we look at domestic environment protection measures, as sulfur in gas oil transforms to sulfuric oxide by combustion, causing acid rain and degradation of exhaust gas filter of diesel cars, sulfur was reduced to the extremely low level of 50 ppm in 2003 and 10 ppm in 2007 as the environmental regulation of product gas oil.

As a result, the volume of hydrogen needed for desulfurization is constantly on the rise. Therefore, the operation rate of hydrogen producing equipment is increasing, causing the rise in fuel volume consumed by the hydrogen producing equipment and increasing the volume of CO_2 emitted as exhaust gas. This trend conflicts with the activities to protect the environment. (See Fig. 7 and Fig. 8.)

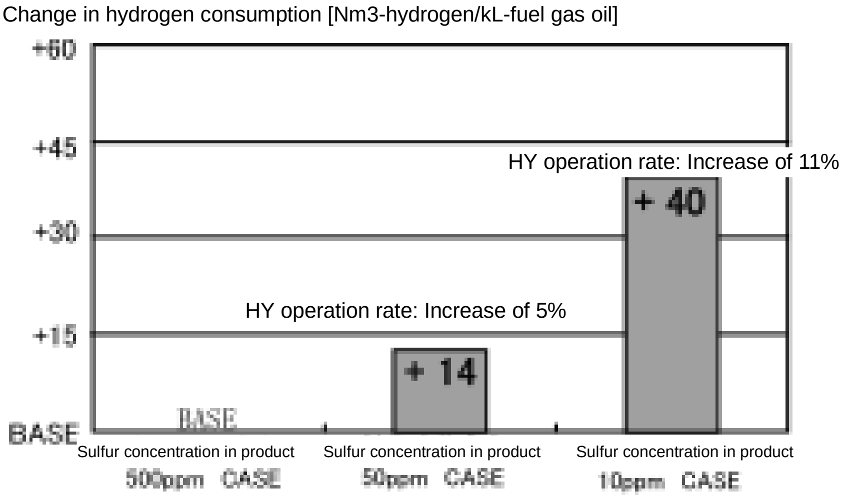

Fig. 7 Increase in hydrogen consumption due to lower sulfur in gas oil

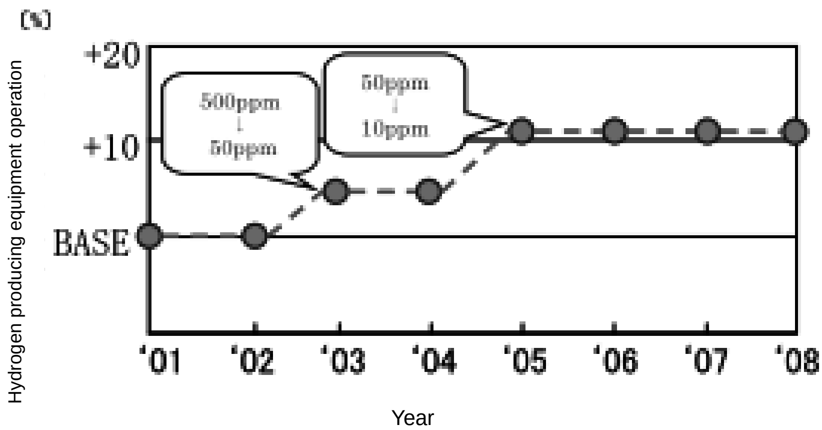

Fig. 8 Trend of hydrogen producing equipment operation rate increase

For these environment protection measures, since 2005, this refinery has been running the operation of 10 ppm of sulfur level in product gas oil prior to the regulation. Thanks to data accumulated from operation results and pilot tests, it is possible to accurately predict sulfur levels in product gas oil.

The following is the simplified reaction formula.

$$K=A \times EXP(-E/RT) \times (PH_2)\,\alpha$$

K: Reaction speed constant, A: Frequency factor, E: Activation energy
R: Gas constant, T: Reaction temperature, PH_2: Hydrogen partial pressure
α : Constant (Value calculated from the measured value)

In consideration of the above background, targeting the 2nd light oil hydrodesulfurization equipment (hereafter 2DH equipment), under the severe operating conditions of ultra-low sulfur level operation of gas oil (under 10 ppm of sulfur in product gas oil), we tackled the issue of reducing energy consumption by slashing hydrogen consumption.

2. Contents of activity

In tackling the issue, we took the following two points as prerequisites.

- ◆ Is it possible to detect through catalyst reaction analysis the lower limit of hydrogen partial pressure that has been traditionally difficult to accurately predict?
- ◆ With the minimum facility investment, is it possible to realize a reduction in energy consumption by choosing proper operating conditions?

This refinery is a high-resolution type refinery having a characteristic of dissolving heavy quality residual oil. As crude oil is of heavy quality, the sulfur level in gas oil fractions tends to be high. Therefore, the hydrogen partial pressure that drives reactions is high for the operation. Under this condition, sulfur and nitrogen in raw material gas oil are transformed into hydrogen sulfide and ammonium, respectively, and are separated from the hydrocarbon compounds, which are the constituent components of gas oil. Under high pressure, in addition to the desulfurization reaction, hydrogen is used for other functions, such as saturation of olefin and aromatic hydrocarbons, and the hydrogenation dissolution that severs carbon chains (See Fig. 9).

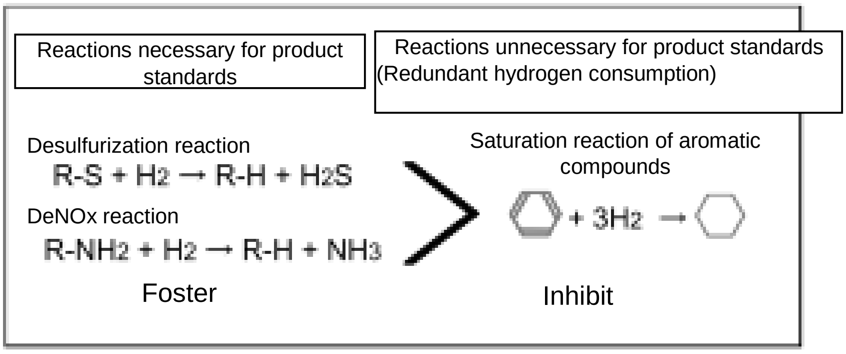

Fig. 9 Reduction point for hydrogen consumption (Conceptual image)

Also, it is generally known that decreasing hydrogen partial pressure in the desulfurization reaction inhibits the hydrogenation reaction from polycyclic aromatic compounds to monocyclic aromatic compounds, contributing to a reduction in the hydrogen consumption volume.

In addition, as the hydrogen partial pressure is decreased, the amount of hydrogen that dissolves into gas oil in the reaction tower decreases and the dissolution loss can be reduced, contributing to an effective reduction in hydrogen consumption.

Regarding the effects seen when the hydrogen partial pressure is lowered, we gathered from internal expert divisions findings on the reaction mechanism of compounds difficult to desulfurize and pilot tests. We managed to increase the accuracy of the above reaction prediction formula, conducted case studies with combinations of various temperature conditions, and finally determined the conditions with which ultra-low sulfur gas oil can be produced (See Fig. 10).

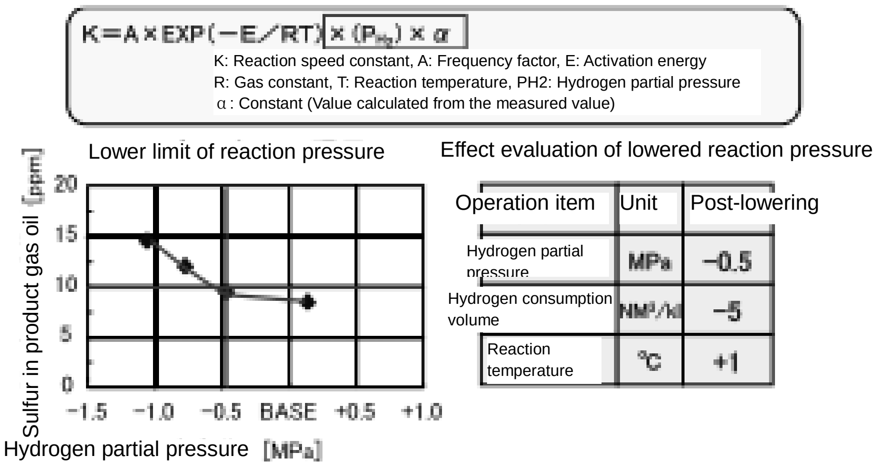

Fig. 10 Determination of lower limit of hydrogen partial pressure

When the reaction pressure is lowered by more than 0.5 MPa from the BASE condition (current status), the desulfurization reaction of compounds that are difficult to desulfurize slows down. Thus, we determined that the lower limit of hydrogen partial pressure is [BASE minus 0.5 MPa]. By lowering the hydrogen partial pressure, the hydrogenation reaction of polycyclic aromatic compounds in the uncleansed gas oil is inhibited, and the hydrogen consumption volume per kL of raw material gas oil can be reduced by 5 Nm^3.
However, it also turned out that the reaction temperature needs to be raised by one degree to supplement the desulfurization lessened by the lowered hydrogen partial pressure.
Therefore, the following problems emerged.

(a) Out-of-standard color phase: Growth of dyeing substances (aromatic compounds) is fostered and the color phase, which is a product standard, worsens.

(b) Low energy-saving effect: While energy is saved on the hydrogen producing equipment due to the lowered hydrogen consumption, energy consumption on the raw material heating furnace of 2DH equipment increases.

(c) Shortened life span of catalyst: Deposition of carbon of hydrocarbon compounds on a catalyst causes the catalyst to degrade, leading to the shortened life span of the catalyst.

(a) Color phase prediction of product gas oil when hydrogen partial pressure is lowered

The past experience tells us that the color phase deteriorates as the reaction temperature rises. However, for 10 ppm production, the correlation is not quantitatively grasped, making it impossible to determine the limit value. So, we started to gather findings on the color phase from catalyst makers and internal expert divisions. On the assumption that condensation-polymerized polycyclic aromatic compound which is a dyeing substance is produced by condensation polymerization of di-benzo thiophene and polycyclic aromatic compound, we predicted this reaction path (See Fig. 11).

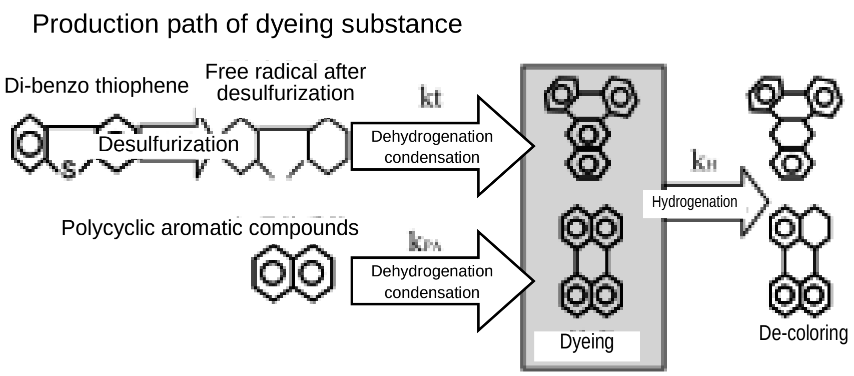

Fig. 11 Reaction path of dyeing substance

By combining the reaction speed formula based on this reaction path with the results of pilot tests, we managed to establish the quantitative prediction method of the color phase from the composition of uncleansed gas oil of 2DH equipment in this refinery and the operation variables. As a result, it is now possible to predict the color phase by the outlet temperature of the reaction tower. Even when the reaction temperature is raised by one degree, the outlet temperature of the reaction tower can be controlled in a lower level than the dyeing limit temperature.

(b) Review of temperature profile

The issues of product standards and of the life span of the catalyst have been resolved. However, from the viewpoint of energy saving, the degradation of desulfurization activityneeds to be supplemented by the reaction temperature, and it may lead to an increase in energy consumption by the raw material heating furnace of 2DH equipment. This case aims to reduce hydrogen consumption by lowering the hydrogen partial pressure and at the same time decrease energy consumption by slashing the load on hydrogen producing equipment; however, the effect will be cut by the increase in energy at the raw material heating furnace of 2DH equipment. Here, what we noticed is that the outlet temperature of reaction tower is still lower than the dyeing limit temperature. Specifcally, there is a way to utilize the reaction heat by adjusting the cooling hydrogen that controls the reaction heat in the reaction tower and raise the mean value of the reaction temperature. In other words, we thought the load on the raw material heating furnace could be lessened by widening the difference between the inlet temperature and outlet temperature of reaction tower (hereafter ΔT) even if the average reaction temperature remains the same (See Fig. 12).

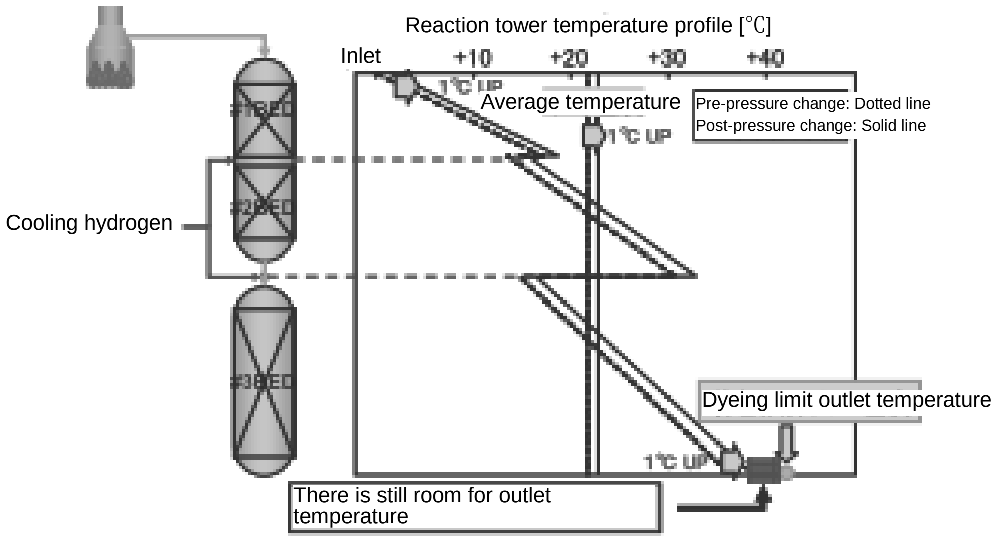

Fig. 12 Point of reviewing temperature profile

This method allows us to lower the driving power of compressor by decreasing the cooling hydrogen. Due to the heat exchange between the raw material oil and the outlet oil of reaction tower that occurs when the outlet temperature of reaction tower is raised to the dyeing limit temperature (+4℃ in Fig.13), the inlet temperature of raw material oil heat furnace can be increased. Conversely, the outlet temperature of the raw material oil heat furnace can be decreased by lowering the reaction tower inlet temperature (minus one degree in Fig. 13). Thus, it is possible to lessen the load on the heating furnace.

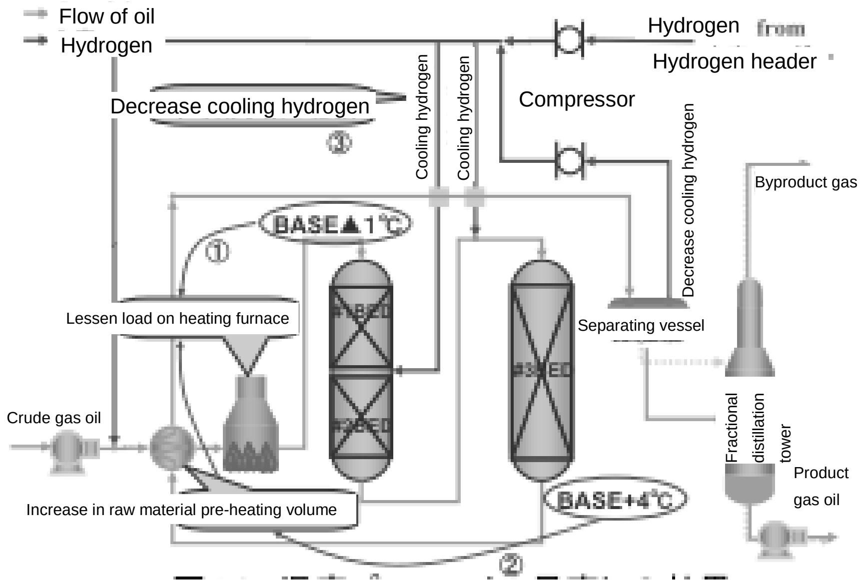

Fig. 13 Effect of reviewing temperature profile

(c) Study of impact on catalyst life span when hydrogen partial pressure is lowered

There is a possibility that the life span of the catalyst is shortened when the hydrogen partial pressure is lowered to increase the reaction temperature by one degree. Therefore, we predicted the life span of a catalyst and confirmed there is no problem (See Fig. 14). This refinery sets the life span of a catalyst as two years in line with the regular repair period. It turned out that two or more years of life span of a catalyst can be met even when the reaction temperature is increased by one degree.

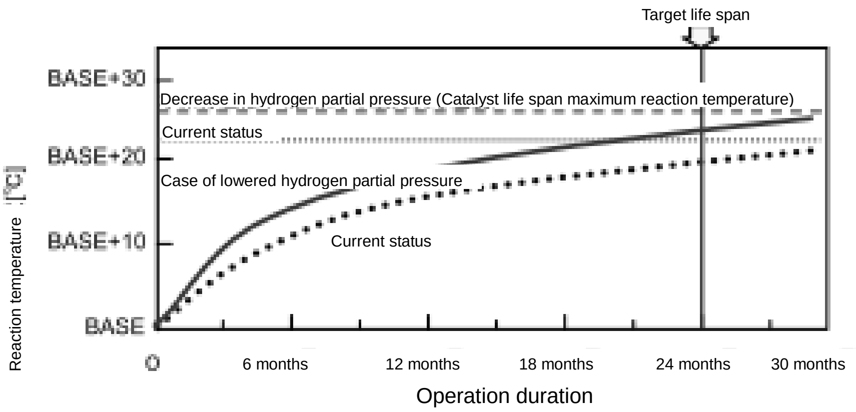

Fig. 14 Study of catalyst life span

3. Evaluation of this case

(1) Energy saving

Thanks to the measures taken in this case, we accomplished the energy saving of 1,760 kl/year for crude oil equivalent, which exceeds the plan (1,400 kl/year), leading to the CO_2 reduction of 5,300 t per year. This is equivalent to approximately 50% of the volume of CO_2 that increased as a result of the measure for 10 ppm sulfur level in gas oil.

(a) Lowered hydrogen partial pressure

From the prediction based on the catalyst chemistry theory, by lowering the hydrogen partial pressure in the reaction tower, we managed to reduce the hydrogen volume consumed by 2DH equipment for other purposes than desulfurization. As a result, the load on the hydrogen producing equipment decreased and the fuel volume consumed by the reformation furnace of the hydrogen producing equipment reduced.

(b) Utilization of reaction heat

By applying the catalyst chemistry theory at the operation site in the chemical engineering way, we made it possible to change by +5℃ the control value of ΔT of the reaction tower catalyst layer. As a result, the temperature profile of the catalyst layer was optimized, the control value of the reaction tower inlet temperature was decreased, the control value of the outlet temperature was increased, the load on the raw material heating furnace was lessened due to the decreased reaction tower inlet temperature, and the preheat temperature of the raw material gas oil rose due to the increase in the reaction tower outlet temperature. All these effects contributed to the major energy saving.

Table-1 Energy-saving Effect

Issue	Energy-saving target (plan)	Energy-saving effect (result)	
	Reduction in fuel	Reduction in fuel	Reduction in CO_2
	(Crude oil equivalent kL/y)	(Crude oil equivalent kL/y)	(Ton/y)
1. Lowered hydrogen partial pressure	600	660	2,000
2. Utilization of reaction heat	800	1,100	3,300
Total	1,400	1,760	5,300

(2) Advancement / Creativity

(a) It is generally known that the desulfurization reaction can be selectively fostered for hydrogenation of polycyclic aromatic compounds in the hydrogenation desulfurization equipment by lowering hydrogen partial pressure. This time, we succeeded in quantitatively determining the lower limit of hydrogen partial pressure of this refinery's 2DH equipment, which processes gas oil fraction derived from relatively heavy crude oil. We analyzed the actual operation data, conducted pilot tests, and studied them with other internal related departments to establish the highly accurate reaction model formula. From this model formula, we determined the minimum hydrogen partial pressure that satisfies the standard of product sulfur level.

(b) When the hydrogen partial pressure is lowered, the decreased desulfurization activity needs to be supplemented by the increase in reaction temperature. Deterioration of the color phase, which accompanies the rise in reaction tower outlet temperature, was an obstacle to implementation. We established a hypothesis about reaction mechanism of dyeing substance growth in molecular level and succeeded in establishing a reaction speed formula related to dyeing substance growth from a catalyst maker's findings and our own pilot test results. The increase in reaction temperature that accompanies the decrease in the above hydrogen partial pressure is predicted to be at the level where the product color phase can be made within the standards. This increase can be applied to a real machine.

(c) In applying the above newly gained knowledge on the chemical reaction to a real machine, we not only increased the reaction temperature but also fully utilized the reaction heat for raw material preheat or the like. In other words, by increasing ΔT higher than now with the same reaction temperature, lowering the reaction tower inlet temperature, and raising the reaction tower outlet temperature, we succeeded in lessening the load on the raw material heating furnace, which increases the heat exchange volume between the outlet fluid and the raw material. In addition, by transferring the catalyst layer load from an earlier stage to a later stage, we created the effective measure from a viewpoint of using up catalyst.

(3) Versatility / Applicability

Since this case focused on the review of operation variables (reaction temperature), by selecting proper reaction pressure conditions and reducing cooling hydrogen, the method allows us to curb the facility investment and minimize the energy for use. Thus, this method can be widely and commonly applied to hydro-desulfurization equipment. In this case, the simple recovery year for the alteration cost is around 0.1 year. Since we were able to establish the tool to quantitatively grasp the quality standard like the color phase, which is difficult to control, to the limit by analyzing chemical reactions in the molecular level, the base for long-term stable operation has been established.

(4) Continuity / Sustainability

We are studying the impacts on machines when hydrogen partial pressure is lowered. As the gas volume increases by lowering the pressure, we used a versatile process simulator to build a model about the change in process state and presented numerically the process data. For the heating furnace, heat exchanger, compressor, and measuring instruments like thermometer, we confirmed from the fluid analysis result of the flow pattern whether there is any problem in terms of differential pressure, vibration, erosion, etc. As a result, we made a little modification to the following two points to sustain the eternal integrity of the facilities.
(a) Replacement of a thermometer protective tube to prevent vibration due to the Karman vortex
(b)To protect machines in an emergency, a method to cool a compressor cylinder was changed from thermo siphon cooling to forcible cooling.

Gas volume increases as the pressure is lowered.

↓

Numerically compile process data using a versatile process simulator.

↓

Fully confirm impacts on machines.

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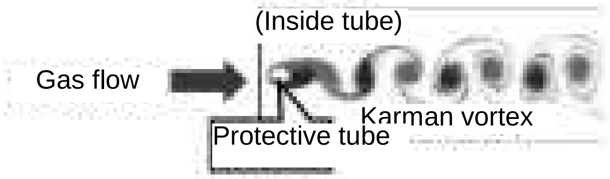
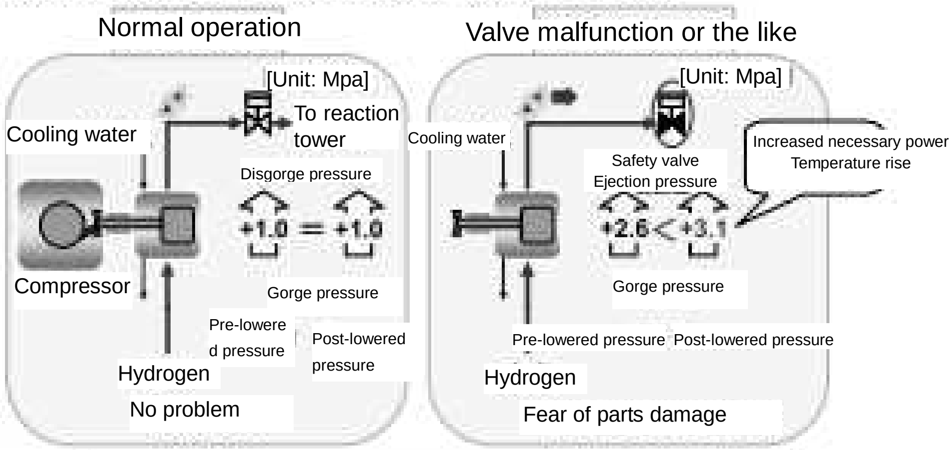
Facility measures were taken for two points that pose the machine damage possibility.

① Replacement of thermometer in protective tube vibration area

Some parts pose the possibility of Karman vortex due to change in gas flow speed.



②Cooling method change for a cylinder of hydrogen gas supply compressor



Cooling method changed from thermo siphon to forcible cooling

(c) Study of impact on catalyst life span

As mentioned earlier, we pondered the catalyst life span and studied the method and confirmed that there was no problem. We have never seen any problems since we adopted the method.

4. Accompanying effects

In this case, we pursued an in-depth analysis of the catalyst reactions. By examining mainly improvements by operational conditions, we accomplished the energy-saving target that has excellent cost effectiveness without extensive modification of machinery.

(Cost: 8 million yen, recovery year: 0.1 year)

In this case, thanks to the association between staff department and on-site engineers, the consolidation of the reaction theory, which optimizes the reaction tower temperature profile, and the practical findings at the job site was realized, leading to energy-saving effects. Also, young engineers learned not only the reaction theory but gained expertise in applying the theory to real equipment. Thus, they attained the concrete approach techniques to resolving issues and enjoyed the achievement, while they grew a lot. From now on, we are determined to repeatedly tackle energy-saving improvements in equipment and continue activities to contribute to a reduction in energy consumption and the prevention of global warming.