R&D Project of Ultra Clean Petroleum Fuel Refining in Japan

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Project Background

Petroleum fuels, such as gasoline, are in widespread use for automobiles, such as passenger vehicles and trucks, and are indispensable products in modern life and economic activities in Japan. On the other hand, improvement of atmospheric environment has been claimed consecutively. So, vehicle emission regulation for harmful substances such as CO, HC and NOX has become strict more and more. In addition, from the view point of global warming issue, reducing fuel consumption has also become demanded in recent years. Adapting these situation, technology development is conducted by both automobile and oil industries. Concerning technology development of oil industries, from 2002 fiscal year, R&D projects of producing clean petroleum fuel (for example sulfur free gasoline) and improving fuel quality for clean utilization of petroleum fuels have been launched. The former is R&D project of Ultra Clean Petroleum Fuel Refining and the latter is including ICAP2 (Japan Clean Air Program 2). Both projects are being conducted by Japan Petroleum Energy Center (JPEC) with the subsidy of Ministry of Economy, Trade and Industry (METI). In this talk, the outline of R&D project of Ultra Clean Petroleum Fuel Refining in Japan is introduced.

According to COP3, Japanese automobile manufacturers are required by regulation to reduce the fuel consumption of gasoline cars by 22.8% on average from the level in fiscal 1995 by the Government. To cope with this regulation, automobile manufacturers and related companies are working on improving the fuel consumption. In several technological options, spark ignition direct injection (SIDI) engines have the potential to reduce vehicle CO2 emissions substantially (OEMs report up to 20%)1. However, the NOX storage catalyst, used in SIDI engines is further more easily contaminated by fuel sulfur than conventional three-way catalysts2. If the NOX adsorber dose not work sufficiently, the regulation of exhaust gas emission cannot be satisfied. At present, deactivated catalysts are periodically regenerated by SOx regulation. So, this project also aims to secure an inexpensive and stable supply of clean oil products by developing technology for removing sulfur (and other contaminant e.g. metals) not only from distillate converted from residual oil but also feed residual oil itself, which will help to promote the use of heavy residual oil.

Project Objectives

This project aims to help relieving global warming and atmospheric pollution by developing technology to minimize the sulfur content of fuels, especially motor gasoline. In addition, demand for heavy residual oil is rapidly declining in view of environmental pollution, in recent years. To match the oil products to the present demand structure, heavy residual oil should be converted to distillate such as gasoline and diesel fuel. And the technology for the effective and clean utilization of heavy residual oil needs to be developed. Thus, this project also aims to secure an inexpensive and stable supply of clean oil products by developing technology for removing sulfur (and other contaminant e.g. metals) not only from distillate converted from residual oil but also feed residual oil itself, which will help to promote the use of heavy residual oil.

Project structure

At present, gasoline is mainly produced by blending straight-run gasoline separated from atmospheric distillation unit, reformulated gasoline made by reforming of heavy naphtha, alkylated gasoline made by alkylation of light olefins, and cracked gasoline made by cracking of heavy oil in Fluid Catalytic Cracking unit (FCC). The cracked gasoline (FCC gasoline) includes a lot of olefins (high octane value), and it is blended to gasoline at the highest ratio. But the FCC gasoline contains much sulfur, and most of sulfur contained in the product gasoline is due to the FCC gasoline.

Unlike US and EU refineries, almost Japanese refineries had already equipped with FCC feed pretreater by SOx regulation. So, FCC gasoline sulfur is already rather low in Japan, but further reduction is needed to produce sulfur free gasoline. Adapting this advantage of Japanese refineries, efficient desulfurization technology of the FCC (or RFCC) product with minimizing the octane value loss, either treating the FCC (or RFCC) products or its feed (residual oil and VGO) should be considered. In this project, following technologies shall be developed considering optimum integration design. 1) advanced hydrodesulfurization (HDS) technology for atmospheric residual oil and VGO, as feedstocks of Residual FCC (RFCC) and FCC, respectively; 2) in-situ FCC desulfurization technology; 3) selective hydrodesulfurization technology for FCC gasoline; and 4) isomerization technology for gasoline stocks. The relationship among the respective technologies is shown in Figure 1. The details of Project elements are as follows.

### Table 1. The gasoline Sulfur Regulation trend

<table>
<thead>
<tr>
<th>Regulation</th>
<th>Regulation trend</th>
</tr>
</thead>
<tbody>
<tr>
<td>Japan</td>
<td>100ppm (Actual results (Average) of RG (Regular Gasoline): c.a.35ppm)</td>
</tr>
<tr>
<td>US</td>
<td>1000ppm (EPA)</td>
</tr>
<tr>
<td>EU</td>
<td>150ppm (EU standard)</td>
</tr>
</tbody>
</table>

Figure 1. The R&D Project Structure of Ultra Clean Petroleum Fuel Refining in Japan

<table>
<thead>
<tr>
<th>HDS Catalyst Development</th>
<th>FCC Catalyst Development</th>
<th>Selective HDS</th>
<th>Isomer. HDS</th>
</tr>
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<tbody>
<tr>
<td>Residue (or VGO) HDS</td>
<td>(Residue) FCC</td>
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</table>

Clean Fuel S below 10ppm  Minimum Octane Loss

Gasoline (At present) Sulfur Regulation S below 100ppm
Project element

1) Advanced hydrodesulfurization technology for residual oil and VGO. In the present residue desulfurization catalyst system, catalyst for removing metals with high metal trapping ability is used in proper combination with desulfurization catalyst for avoiding activity deterioration caused by the reduction of diffusion properties of the reactants. Thus, efforts have been made to develop technologies to prolong the life of catalysts by improving the resistance against metals.

In this project, the desulfurization performances rather than the metal resistance of the catalyst are focused, and so new ideas shall be tested. Though existing catalysts are very active at the early stage of the desulfurization reaction, the performance quickly deteriorates sharply to less than 50% of initial activity. This early deterioration is caused by the coke formed in the reactions. Accordingly, if the formation of coke on the desulfurization catalyst can be reduced and early deterioration prevented, then a highly active catalyst can be obtained. This study aims to develop coke-resistant catalysts. The ordinary technique of controlling coke formation uses an active metal with high hydrogenation activity (Ni, W), but existing Ni catalysts have not been improved sufficiently. Consequently, this study will try to develop highly active catalysts by considering the coke formation mechanism at the acid point as an active site, and by introducing a new acidity control substance and its preparation technology. Existing catalysts have a service life of one year for residual oil containing 0.3% sulfur. This study aims to develop a highly active residue desulfurization catalyst capable of stably producing heavy oil containing 0.2% sulfur for one year, for the same quantity of feed processed by the present residue desulfurization and processing capacity.

2) In-situ desulfurization technology in fluid catalytic cracking unit (FCC). In-situ desulfurization technology of FCC catalysts is still at the test stage and has not been established industrially. These catalysts are given desulfurization properties by adding metals such as V, Zn and some kind of zeolites as inter-molecular hydrogen transfer and sulfer compounds cracking component.

This study targets not only FCC, but also residue FCC (RFCC), whose feed is residual oil, which requires more effective cracking and desulfurization functions of the heavier components than those of VGO. For the pore size distribution control and promotion of the hydrogen transfer reaction of zeolite and matrix for the rapid diffusion of the heavy components, optimization of support composition by the addition of metals as well as solid acidity control shall be performed. Catalysts having a shape-selective cracking desulfurization function are being developed, with a target of 20% less sulfur content in the product than that in the present FCC gasoline.

3) Selective hydrodesulfurization technology for FCC gasoline.

The hydrodesulfurization of FCC gasoline causes the problems of hydrogenation of olefins and reduction of octane value. This study aims to develop a catalyst and a process for hydro-desulfurizing sulfur compounds without significantly hydrogenating the olefins. The coexistence of H2S on the conventional CoMo desulfurization catalyst hinders the desulfurization and hydrogenation of n-olefins, but promotes the hydrogenation of iso-olefins. When the amount of Co is increased, the desulfurization reaction is promoted, but the hydrogenation reaction of olefins is hindered. Thus, the desulfurization active sites of the Co-Mo/Al2O3 catalysts are different from the hydrogenation active site of olefins. It is expected that if the hydrogenation active sites of olefins are selectively reduced, catalysts with high desulfurization selectivity can be prepared. For example, covering the surface of the catalyst with some kind of coke can control the hydrogenation reaction of iso-olefins. It is known that the hydrogenation reaction of iso-olefins can be controlled by introducing the vapor of basic compounds such as pyridine. This study will examine other practical catalyst modification methods, determine conditions that improve the desulfurizing properties and the process conditions. The target is to develop the catalyst and process to reduce the loss of octane value to 2.5 or less and the sulfur content to 10ppm or less when the sulfur content in the feed FCC gasoline (research octane number (RON) 90) is 50ppm.

4) Development of technology optimally combining isomerization technology for light ends. The other way to minimize the octane value loss in hydrodesulfurizing FCC gasoline, is converting produced paraffins into branched paraffins (i.e. isomerization). In the isomerization reaction of treated heavy FCC gasoline, for the C7 and C8 fractions, considerable paraffin cracking reactions are expected as side reactions unlike for the fractions C5 and C6. The isomerization reaction is more favorable in equilibrium at a lower temperature, while the cracking reaction proceeds further as the reaction temperature increases, and thus it is necessary to develop a catalyst and a process that show high activity at low temperature in order to secure the product yield. However, as the number of carbon atoms in the feed increases, the coking reaction on the catalysts may proceed rapidly.

Conventional isomerization catalysts, for example platinum supported zeolite or chlorininated alumina catalysts, is easily deactivated by small amount of sulfur compounds of the feed. Whereas, activity of the solid ultra-strong acid catalyst used in this study is hardly influenced up to a sulfur content of about 150ppm in the isomerization reaction of light napththa. And active reaction temperature zone is much lower than the conventional one, especially reducing the water content of the feed to about 1ppm. Accordingly, reducing the water content to about 1ppm by adopting the dehydration pretreatment, applying this catalyst to the heavy FCC gasoline (mainly the fractions C7 and C8), the reaction temperature can be lowered and so cracking reaction can be mitigated. The targets are to achieve a sulfur content in the treated heavy FCC gasoline of 25ppm or less, and isomerized gasoline yield of 60% or more for feed C7 to C8.

Project Milestones

The scheduled duration of the project is five years from fiscal 2002 to fiscal 2006. At the end of fiscal 2004, the mid-term fiscal year, an assessment committee will be formed, consisting of outside experts in the field mainly from academic societies and industry. This committee will assess the degree of achievement of the research and development targets, the system of implementing the project, and plan the remainder of the project. A similar assessment committee will be set up in fiscal 2007 after the completion of the project to make a final assessment of the results of the technological development and of its position in the Japanese energy policy from technological and social aspects at that time. In addition, suggestions concerning the course of research and development toward practical application after the completion of the project will be made.

Acknowledgement

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References

2. ACEA data of the sulfur effect on advanced emission control technologies,July,2000.