01 Survey 4-2-1

Gasoline Production Technology and Methods, and an Evaluation of Their Economic Viability

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Part 1—High-Quality (Low Sulfur Content) Gasoline

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1. Survey Background and Goals

Air pollution in urban regions caused by exhaust emissions from motor vehicles has become a serious issue in both advanced and developing nations. According to data on air pollution published by the Japanese Ministry of the Environment, levels of sulfur dioxide and carbon monoxide have been reduced significantly, while levels of nitroxides (nitrogen monoxide, nitrogen dioxide, etc.) and suspended particulate matter, after dropping between 1970 and 1975, have shown almost no improvement. Achievement of environmental standards has been at low levels, particularly in urban areas. One reason for this delay in alleviating air pollution is exhaust emissions from motor vehicles. The effectiveness of regulations on emissions, which have been progressing for some time, has been largely canceled out by the increase in the volume of vehicular traffic and the trend among consumers to switch from smaller to larger vehicles, such as SUVs.

In order to find a solution to this issue JCAP has been studying both automobile technology and automobile fuel quality. In particular, finding methods of reducing nitroxides has emerged as a key issue. Three-way catalysts (catalytic converters) have been used to process automobile exhaust for some time, but since the adoption of the Kyoto Protocol calls have been made for a reduction in nitroxides, making improvements in fuel economy an necessity. This has led to an increase in the number of automakers offering lean-burn engines in their vehicles. However, catalytic converters provide poor functionality in dealing with emissions from lean-burn engines, and this has resulted in the use of nitroxide eliminating catalysts in place of three-way catalysts in emissions processing systems. Some carmakers intend to use nitroxide eliminating catalysts that are very susceptible to the effects of the sulfur content in fuel, and this has caused the car industry to call for the introduction of ultra low sulfur content gasoline.

In the United States the average sulfur content of gasoline is presently 330 ppm, and regulations have been adopted mandating that the average sulfur content of gasoline shipped from refineries be lowered to 30 ppm or less between 2004 and 2008. In Europe the Auto-Oil Program I directive mandates a sulfur content of 150 ppm as of January 2000, and this must be lowered to 50 ppm or less by 2005 under Auto-Oil Program II. Quality regulations in Japan specify a maximum sulfur content of 100 ppm, but the average sulfur content is actually about 35 ppm. This is expected to be lowered still further in the years ahead, as mentioned above.

This survey focuses on high-quality gasoline, in particular low sulfur content gasoline, as one way of reducing air pollution caused by automobile exhaust emissions. It examines the production technology and methods used for ultra low sulfur content gasoline and evaluates their economy. The effective production methods for high-quality gasoline used in Japan are studied. The sources of the sulfur content of the products of the gasoline industry in Japan are limited to “sweetened” light naphtha and FCC naphtha.

With regard to other gasoline components, in the case of reformed gasoline desulfurization takes place before processing using a catalytic reformer, so the sulfur content is minimal. In the case of alkylate and isomerized gasoline as well, the processing oil itself is desulfurized beforehand, so the sulfur content of these gasoline components is not a problem. The components that increase the sulfur content of the final gasoline product are the two mentioned above. Of these, no further investigation is necessary with regard to light naphtha since a process for lowering the sulfur content through hydro-desulfurization has already become well established. However, the situation is different with FCC naphtha. Though it is possible to use standard hydro-desulfurization equipment with FCC naphtha to produce a medium for gasoline, the resulting product is useless since it fails the key requirement: comparatively high octane. This is the case because during the desulfurization process, as the desulfurization reaction is taking place, olefin (the components of the FCC naphtha have high octane number) is simultaneously undergoing a saturation reaction. As a result, the olefin content is reduced, thereby lowering the octane. In Europe and the United States catalytic crackers are used for the un-desulfurized processing oil. This is the reason why the sulfur content of the gasoline tends to be high. For this reason, there have been many attempts to develop a desulfurization technology that does not lower the octane of FCC naphtha. This survey focuses on FCC naphtha desulfurization technologies developed in Europe and the United States and examines the question of whether they can be applied to the task of producing ultra low sulfur content gasoline in Japan.

2. Survey Content and Findings

The automobile gasoline demand structure in the United States comprises more segments than those of Japan or Europe. Gasoline is produced from many components processed using a variety of types of secondary equipment, such as catalytic crackers (FCC), hydro-crackers, and cokers. Unlike in Japan, where both VGO-HDS and Residue-HDS are in place to supply low-sulfur fuel oil for generating electric power, in the United States gasoline components are procured without having passed through. The sulfur content of the gasoline component from FCC equipment is particularly high at 1,000 to 5,000 ppm. Thus, at present the gasoline produced tends to have a high sulfur content. Even though reducing the amount of sulfur in the processing oil would be a logical first step toward meeting the sulfur content regulations due to take effect in 2004, there are only limited sources of supply for such low-sulfur processing oil. Since procuring a sufficient supply will be difficult, two proposals have been made as possible solutions: desulfurizing the raw oil fed into catalytic crackers and desulfurizing the FCC gasoline product. The former has the disadvantage of involving high construction costs, since the equipment composition of the entire refinery would have to be rebuilt in order to accommodate the expanded production volume. The latter would minimize construction and operating costs by lowering the sulfur content of the FCC gasoline directly. As a result, many desulfurization technologies for FCC gasoline have been developed, especially in the United States. On the other hand, there is less demand in Europe for FCC gasoline desulfurization technology than in the United States. This is true because processed North Sea crude oil has an even lower sulfur content than is typical in Japan and also because of the high level of demand for diesel fuel. We therefore predict that in the years ahead the trend toward low-sulfur gasoline and diesel fuel will proceed simultaneously with the rebuilding of the equipment compositions of entire refineries.

In contrast to the above, since both VGO-HDS and Residue HDS is already widespread in Japan due to the need to supply low-sulfur fuel oil for electric power generation, automobile gasoline remains at a sulfur content level of 30 ppm on average. This is already far below the sulfur content limit of 100 ppm since the processing oil has been desulfurized before FCC processing. Thus, there has been almost no technical development work in the area of gasoline desulfurization.

Figure 1 illustrates differences between gasoline the production processes used in Japan and the U.S.A. as well as the sulfur content levels of the final product.

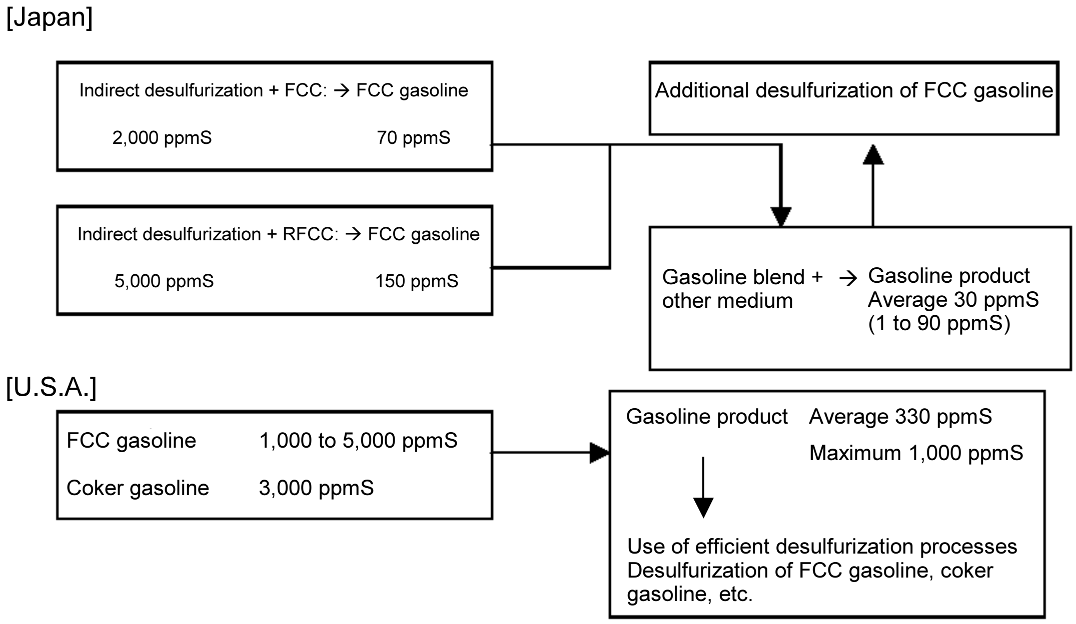

Figure 1 **Differences Between Gasoline Production Processes and Sulfur Content Levels in Japan and U.S.A.**

2.1 Overview of FCC Gasoline Desulfurization Technologies

FCC gasoline desulfurization technologies are designed to substantially reduce the sulfur content of automobile gasoline while minimizing the extent to which the octane is reduced. They also aim to keep construction and operating costs as low as possible by achieving a high liquid yield with minimal hydrogen consumption. In order to reduce the overall sulfur content of gasoline it is also necessary to thoroughly desulfurize the straight-run light naphtha used for varieties other than FCC gasoline. It is though, however, that this can be achieved by eliminating light mercaptans using existing hydro-desulfurization or sweetening processes. Therefore, this survey is confined to new technologies for desulfurizing FCC gasoline.

New technologies for desulfurizing FCC gasoline fall into two broad categories: hydrogenation and adsorption. The former has three types. The first suppresses octane loss during hydro-desulfurization by isomerizing saturated hydrocarbons (OCTGAIN and ISAL processes). The second maintains the octane hydro-desulfurization without hydrogenating it (SCAN fining and PrimeG+ processes). The third eliminates reaction products of sulfur compounds and olefin from the system through distillation, selectively desulfurizing while suppressing olefin hydrogenation (CDHydro, CDHDS, and OATS processes).

The latter category (adsorption processes) is published as the S Zorb process, in which uses a fluidized bed for hydrogenation adsorption; the TREND process (under development, not yet publicly unveiled), which uses a moving bed; and the IRVAD process (development apparently abandoned), in which slurry is used to move the adsorbent.

In the next section we list the major desulfurization technologies for FCC naphtha.

2.2 Non-Selective Hydrogenation Desulfurization Processes

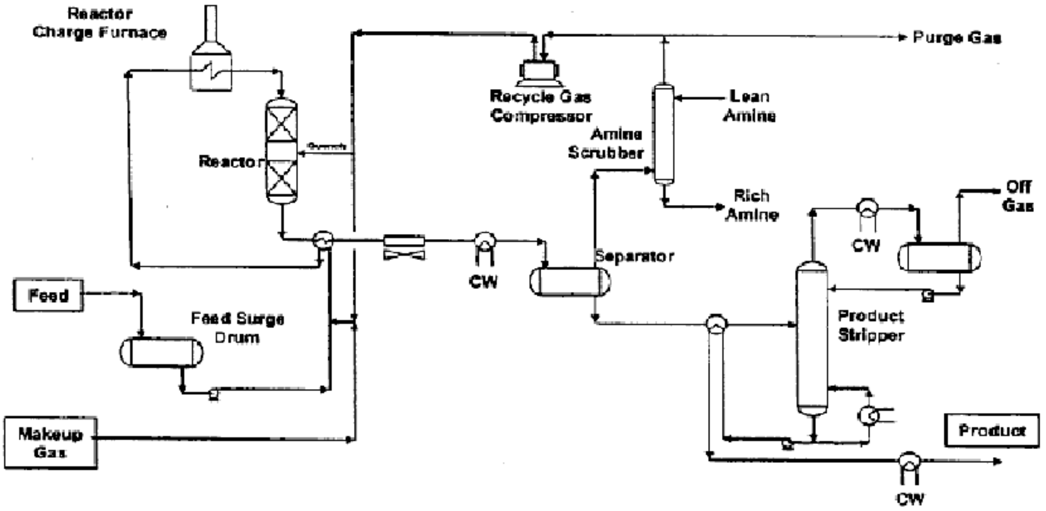

Figure 2 OCTGAIN Process

Exxon-Mobil's OCTGAIN process is an example of a non-selective hydrogenation desulfurization method. A distinctive feature of this process is that thorough hydrogenation is performed in order to boost the desulfurization level, and a paraffin isomerization reaction is then used to compensate for the octane reduction caused by olefin saturation. In this way, octane loss is kept to a minimum.

Table 1 OCTGAIN Process Desulfurization Examples

		Feed	Desulfurized Oil (Condition 1)	Desulfurized Oil (Condition 2)
Sulfur (wt, ppm)		2,800	300	57
Octane				
Research method	(RON)	91.8	88.4	85.2
Motor method	(MON)	80.0	79.1	77.0
Road octane rating	(R + M)/2	85.9	84.5	81.1
C5 + yield	(vol.%)	98.1	97.6	96.6
Composition	(wt.%)			
n-Paraffin		4.1	5.7	9.1
iso- paraffin		16.1	18.0	23.7
Olefin		24.8	21.9	13.2
Naphthene		12.5	11.9	11.3
Aromatics		41.5	42.5	42.7

Table 1 lists examples of desulfurization using the OCTGAIN process. As the degree of desulfurization rises, the content of olefin decreases and the isoparaffin content increases. Though it is impossible to say for sure since the properties of the desulfurized oil from heavy FCC gasoline are not publicly available, we believe that it would be preferable to separate the light distillates beforehand and eliminate the mercaptans, rather than to process full-range FCC gasoline.

2.3 Selective Hydro-desulfurization Processes

Examples of selective hydr-desulfurization processes include Exxon-Mobil's SCANfining, IFP's Prime G+, CDTech's CDHydro and CDHDS, and BP Amoco's OATS process. The first two use a fixed-bed catalyst for selective hydro-desulfurization such that the high-octane olefin is not hydrogenated. In contrast, CDTech uses catalyst distillation and BP Amoco uses an approach based on olefin alkylation.

A description of CDTech's CDHydro and CDHDS is provided below.

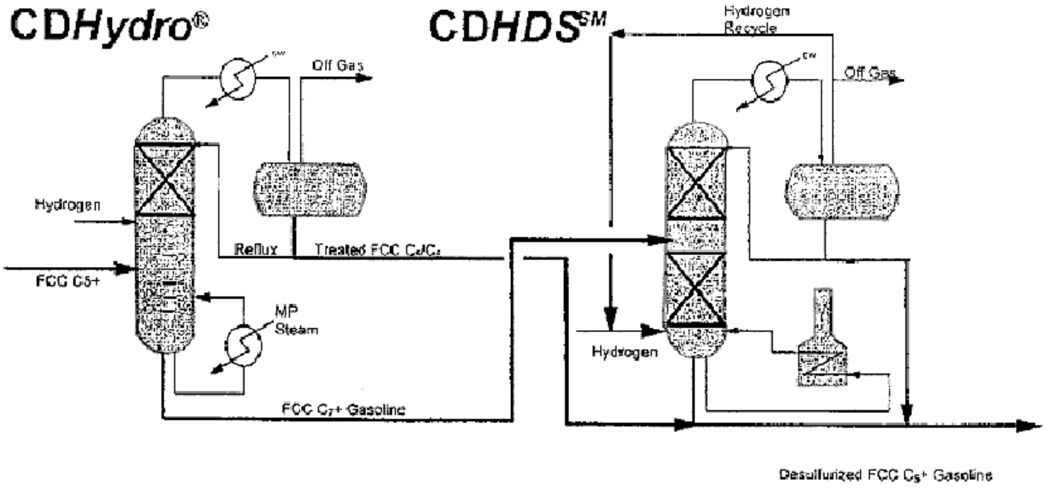

Figure 3 CDHydro and CDHDS Process Flow Diagram

Figure 3 is a flow diagram of the CDHydro and CDHDS processes. The initial stage is dehexanizing within the CDHydro column. The C7+ distillate is fractionated and sent to the CDHDS process. From the light portion, a heaver unsaturated sulfide is separated through a hydrogenation reaction (thioetherification reaction) with dienes and mercaptans that is triggered by the catalyst at the bottom of the CDHydro column. This is sent, together with the heavy distillate, to the CDHDS process for desulfurization. In the center of the column, the C5 diolefin is hydrogenated, turning into olefin. At the very top, the olefin undergoes an accelerated isomerization reaction. This succession of reactions desulfurizes the mercaptans and reduces diolefin contained in the light distillate, resulting in 1 ppm or less sulfur component. No data is available on the degree to which the olefin contained in the light distillate becomes saturated, but octane loss is minimized by isomerizing the olefin.

Figure 4 shows the results of CDTech's calculations of the estimated sulfur content reduction and octane loss, if its desulfurization process were used on FCC gasoline in Japan. The graph on the left shows the anticipated results if the both light and heavy distillate is desulfurized, and that on the right is the anticipated results if the only heavy distillate is desulfurized. In both cases there is a drop of about 1 in the road octane rating when the sulfur content is reduced to 10 ppm.

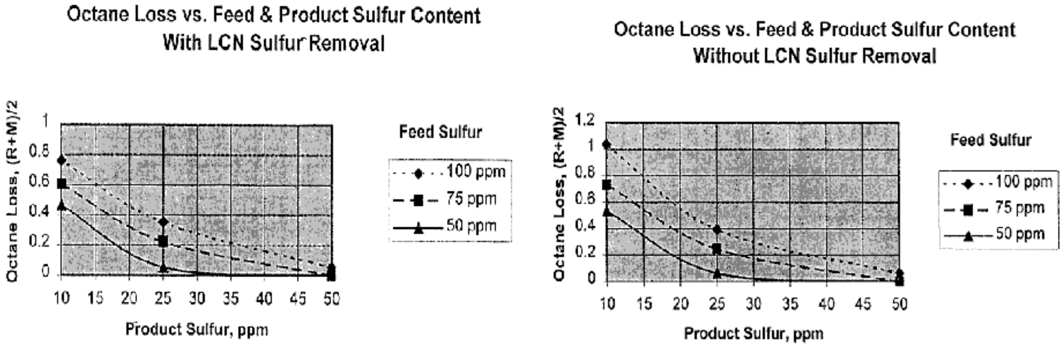

Figure 4 Calculations by CDTech of Effects of Desulfurizing FCC Gasoline in Japan

Notable features of the CDHydro process include the elimination of mercaptans by thioetherification, olefination through the selective hydrogenation of C6 dienes, octane increase by conversion of α-olfin into β-olfin, and reduced vapor pressure. Four such systems are presently in operation in order to supply olefin as feed for alkylation and MTBE equipment.

2.4 Adsorption Desulfurization Processes

It is well known that hydrogen sulfide adsorbs zinc oxide. Based on this, processes have been developed that remove sulfur by adsorbing and eliminating mercaptans and diolefin contained in FCC gasoline. Desulfurization takes place under the presence of hydrogen in order to accelerate the reaction between the sulfur compounds and the adsorbing agent, but less hydrogen is consumed than is the case with hydro-desulfurization processes. R&D work has focused on different methods—fluidized bed, moving bed, and slurry—for conveying the adsorbing agent through the reaction column and regeneration column. Phillips's S Zorb process uses a fluidized bed for hydrogenation adsorption. The IRVAD process, developed by Black & Veatch Pritchard and Alcoa Industrial Chemicals, uses slurry and consumes almost no hydrogen. The use of a moving bed is represented by the TREND process, which is being promoted by the U.S. Department of Energy, with R&D work undertaken by Kellogg Brown & Root.

Figure 5 is a simplified process flow diagram for the S Zorb process. An adsorption hydrogenation desulfurization reaction takes place in a fluid state in the presence of hydrogen. The sulfur content of the sorbent (adsorbing agent) is then subjected to air oxidation in the regeneration column. This process allows the sorbent to be reused. A catalytic reaction takes place in a fluid state between the raw FCC gasoline and hydrogen from the bottom of the fluid bed reaction column and the sorbent introduced at the top. The sorbent that has adsorbed the sulfur compounds is conveyed to the regeneration column, where it undergoes air oxidation and is regenerated. The sulfur compounds of the sorbent is oxidized by the air and processed by a sulfur collector. The oxidized sorbent is purged using nitrogen, returned to its original state using hydrogen, and then conveyed back to the reaction column. The regeneration process and the adsorption reaction take place intermittently and continuously in a fluid state. In other words, the steps that make up the restoration process—spraying the sorbent into the top of the reaction column, purging the sorbent from the bottom of the reaction column, regeneration by air oxidation, nitrogen purging, supply of new sorbent, hydrogen purging—are repeated over and over and their timing is skillfully controlled.

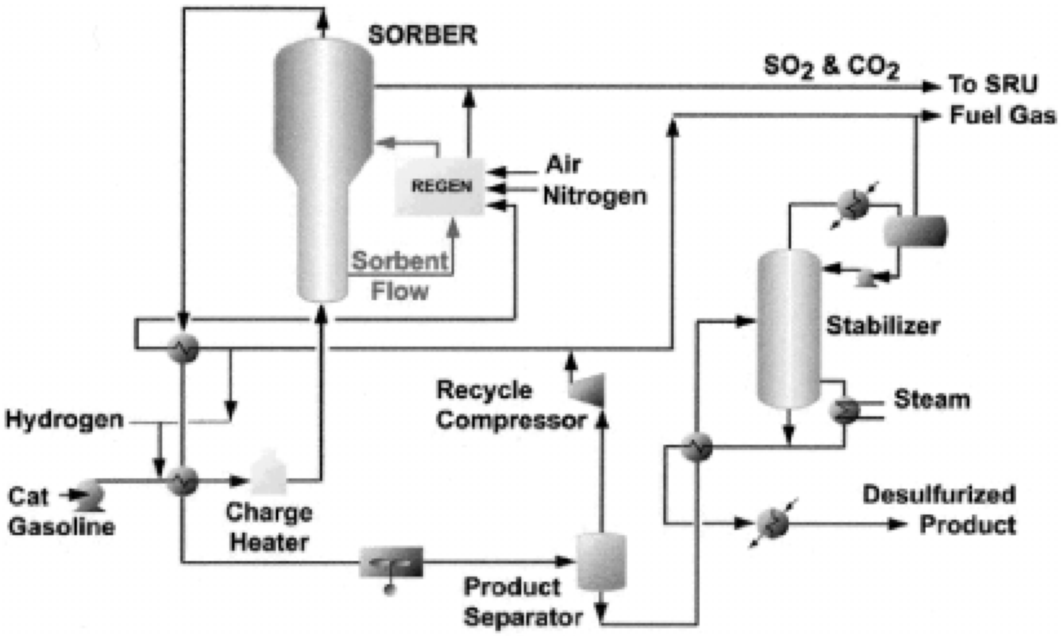

Figure 5 S Zorb Process Flow Diagram

Phillips has not provided a detailed logical description of the reaction mechanism used by the S Zorb process, but they have made public the reaction formula shown in Figure 6 below for S Zorb's hydrogenation adsorption process. The hydrogen attacks the sulfur compounds, weakening the atomic bonds of the sulfur atoms so that they can react with the sorbent. In this way ethyl benzene is produced from benzothiophene.

In terms of hydrogenation adsorption reactivity, the S Zorb process reaction formula can be understood by noting that, though triggering hydrogenation adsorption of thiophene is difficult, thiophene or benzothiophene with a side chain are highly reactive. In addition, they are ten times as reactive as thiophene with mercaptans and sulfides.

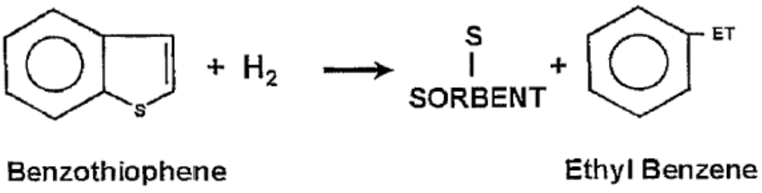

Figure 6 S Zorb Hydrogenation Adsorption Reaction Formula

According to the documentation provided by Phillips, processing raw FCC gasoline with a sulfur content of 1,100 ppm and an olefin content of 27.8 vol. % using a hydrogenation adsorption reaction produces desulfurized fuel with a sulfur content of 25 ppm and an olefin content of 26.6 vol. %. Figure 7 below shows the change in the composition of the raw fuel (feed) and the desulfurized product brought about by the S Zorb process. Figure 8 illustrates the octane loss due to S Zorb process, the change in the composition of the feed and the product, and the road octane loss. It is thought that the S Zorb process has almost no olefin hydrogenation effect.

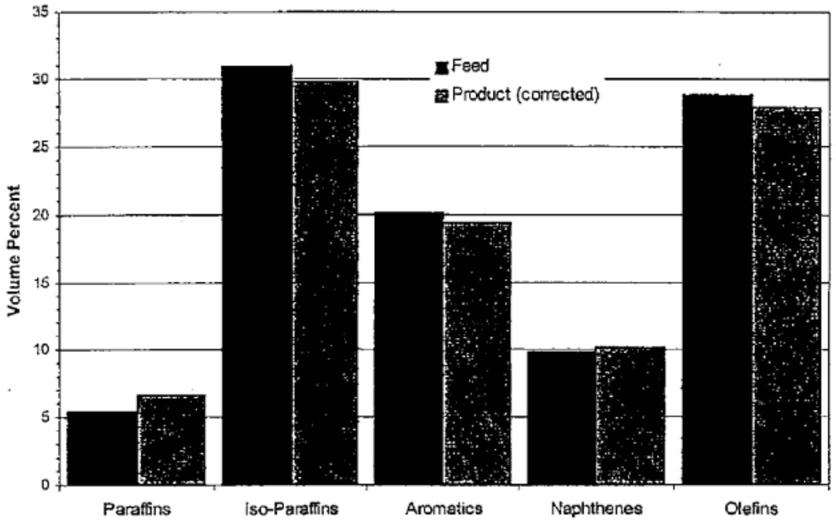

Figure 7 **Change in Composition of Feed and Product due to S Zorb Process**

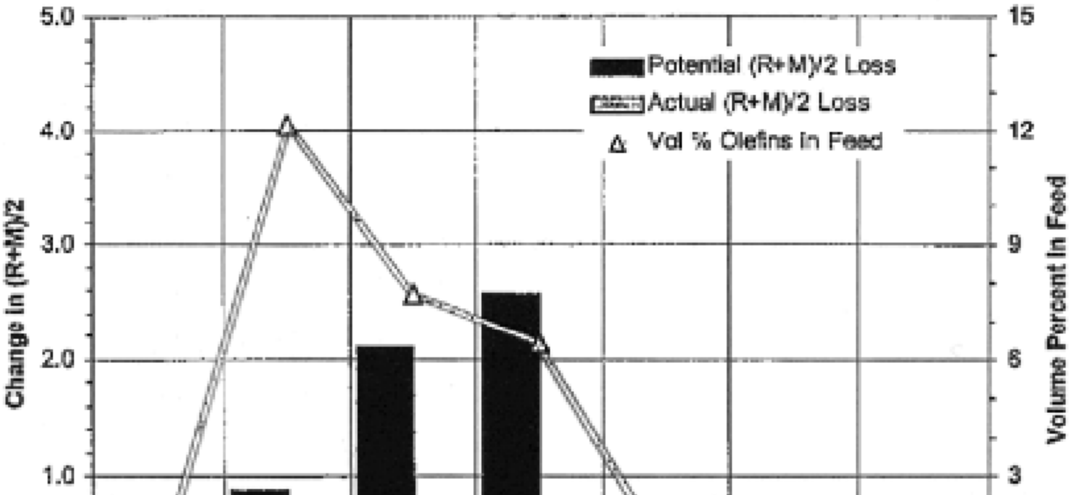

Figure 8 **Octane Loss due to S Zorb Process**

2.5 Evaluation of Economic Viability of FCC Gasoline Desulfurization Technologies

In order to evaluate processes (refinery equipment) for potential future introduction, it is necessary to consider what each candidate process uses as feed and what it produces, as well as what its processing capacity is. It is also important to consider the level of investment that will be required as well as the operating costs and the utilities needed. Finally, demand in Japan and the refining equipment already installed in Japan’s refineries must be taken into account when attempting to predict the future viability of each process.

To satisfy the requirements mentioned above, this survey applied linear programming to calculate production balance, which is widely used by petroleum refining companies when drafting their operating plans.

The processes evaluated are Octgain 125, Octgain 220, and Scanfining from Exxon-Mobil; Prime G from IFP; CDHydro and CD-HDS from CDTech; and S Zorb from Phillips. In order to obtain consistent results from the evaluations, data extracted from materials published by the U.S. Environmental Agency is used as the basis for the construction costs, utility costs, etc., used to prepare the tables below for each process listed.

Table 2 List of FCC Naphtha Desulfurization Processes

	Octgain 125	Octgain 220	Exxon Scanfining	IFP Prime G	CDTech	Phillips S Zorb
Processing capacity (bbl/day)	15,000	31,000	25,000	24,000	30,000	25,000
Investment (million $)	14.9	23.8	16.8	21.7	18.5	13.8
Hydrogen consumption (M^3/kL)	66	23	14	22	18	12
Power consumption (KwH/kL)	12.6	9.4	3.8	8.2	2.8	4.4
Steam use (kG/kL)	—	214	128	180	70	13
Home-use fuel (L/kL)	13.6	5.8	2.4	1.5	5.3	6.3
Catalyst cost ($/BBL)	0.43	0.22	0.22	0.01	0.25	0.27
Cooling water (Ton/kL)	6.0	5.4	3.2	3.1	1.3	3.1
Yield loss (%)	5	0.7	0	0.8	0	0
Octane loss	0	0.1	1.0	1.3	1.0	0.75

The results calculated from the above data are shown in the summary of economic viability of different types of FCC gasoline desulfurization facilities shown in Table 3.

Note that the construction index values listed in the table assume the installation of one system per refinery, based on the FCC naphtha desulfurizing equipment sufficient to meet the required processing capacity calculated by linear programming and classified and aggregated according to the types of Japanese refineries and their refining equipment. The index values express the cost of each process as relative evaluations, calculated in such a way that S Zorb (the least expensive system) has a construction index value of 500. Also, the variable index values are relative values calculated by taking the S Zorb system as the base case.

Table 3 Summary of Economic Viability of FCC Naphtha Desulfurization Equipment

Process	Exxon-Mobil			IFP	CDTech	Phillips
	Octgain 125	Octgain 220	Scanfining	Prime G	CD-Hydro + CD-HDS	S Zorb
Required capacity (1,000 kL/year)	22,558	23,175	23,093	23,049	23,093	23,148
Construction index	877	696	607	815	557	500
Depreciation index[1]	175	139	121	163	111	100
Variable index	207	119	134	119	102	100
Evaluation index[2]	382	259	256	282	214	200

[1] The depreciation index is 20% of the construction index and includes depreciation cost, repair cost, interest, etc.

[2] The evaluation index is the total of the depreciation index and the variable index. It is intended as an overall evaluation.

Our evaluation of the individual processes includes a summary of the economic viability of the different types of FCC naphtha desulfurization equipment in Table 3. Here the differences between the types of FCC naphtha desulfurization equipment and processes is measured in terms of the effects on the annual production cost (variable index) of operating expenses, including hydrogen consumption, cost of utilities such as the volume of steam and fuel used, and the volume of catalyst used, as well as the desulfurized FCC naphtha yield and the degree of octane loss. For example, a decrease in the yield of desulfurized FCC naphtha must be compensated for using other gasoline components , and this will show up in an increase in the operation of the catalytic reforming equipment. In addition, if performing desulfurization results in desulfurized FCC naphtha with a lower octane rating, this must be compensated for by some other high-octane component , and as in the preceding example it will show up in an increase in the work that must be performed by the catalytic reforming equipment. Since each of the processes has either one or both of the above effects each imposes a load on the catalytic reforming equipment, though the specific amount of operation required differs. When looked at in terms of production of product, an increase in the volume of naphtha, the feed fed into the catalytic reforming equipment, results in a decrease in the product production volume of LPG or naphtha, the feed for hydrogen, as is stated in our evaluations of the individual processes. Ultimately, the differences in the capacities of the different processes can be expressed in terms of the degree to which the product production volume is reduced, or in other words the increase in the volume of product that must be imported (increase in import costs). In making an overall judgment based on our findings, we note that FCC naphtha desulfurization will be an extremely effective refining process in a future situation in which gasoline quality regulations place no limits on aromatics or olefin content and sulfur content is the only issue. Of the desulfurization processes we evaluated in terms of economic viability for this survey, we can say that S Zorb from Phillips and the CDTech processes are the ones that ought to be examined first as candidates for implementation.