1. Introduction

Increasing concerns on the air quality have urged the petroleum refining industry to produce cleaner products by removing heteroatoms containing molecules from their major products, such as diesel fuel and gasoline fuel. Regarding diesel fuel, sulfur regulation in Japan was stepped up from 200 ppm in the past regulation to 10 wtppm of Euro IV Regulation and all refineries in Japan had completed the modification of existing plant to comply with this severe regulation. Likewise, refineries in developed country, such as USA, western Europe, etc., had completed the modernization/upgrading of existing units with considerable amount of investment and produce the ultra-deep desulfurized diesel fuel, which contains less than 10 wtppm sulfur. The refineries in developing country are on the way for compliance with such severe regulation but they have difficulty on technical and financial aspects. Such difficulty in local refineries makes local government being hesitate for introducing the severer regulation since it affects the local refinery to be less competent with newly constructed refineries in Middle East. Alternate desulfurization process of diesel fuel with high capital efficiency is highly demanded by existing refiners to solve the problem.

In our previous research, activated carbon with certain physical properties has capability for removal of sulfur compounds, especially the refractory sulfur species, such as 4,6-dimethyldibenzothiophene in diesel fuel. Also, it has been confirmed that the spent activated carbon of sulfur breakthrough can be regenerated by washing with a warm aromatic solvent. Based on these characteristics of activated carbon, this paper proposes a new flow scheme with high energy and capital efficiency for clean diesel fuel production. The use of this new process in refineries enables existing diesel HDS units to produce diesel fuel with a lower sulfur content without increasing the severity in HDS reaction or reducing the throughput. Therefore, this process is applicable to existing diesel HDS units requiring modification to comply with the new, severer regulations on sulfur level. The present study technically and economically justifies applying this new process to refineries with FCC or coker facilities.

Keywords
Diesel fuel, Desulfurization, Activated carbon, Adsorption, HDS, FCC
2. Ultra-deep Desulfurization Process with Adsorptive Sulfur Removal Technology

2.1. Experimental Facts

In this paragraph, the experiment used as the basis of this paper is described.

2.1.1. Activated Carbon’s Capacity for Adsorptive Removal of Refractory Sulfur Species

One gram of activated carbon, which was dried at 110 °C under vacuum in an oven prior to adsorption, was packed into a stainless steel tube (50 mm long and 6 mm in diameter). Diesel of 50 wtppm sulfur content was fed into the tube by an HPLC pump at a rate of 0.1 mL/min. The eluted oil was sampled every 60 min and analyzed by gas chromatograph with atomic emission detector (GC-AED).

The sulfur-specific chromatograms of the eluted diesel after processing 20 mL and 40 mL through activated carbon are shown in Fig. 1.

The sulfur breakthrough profile based on this experiment is shown in Fig. 2. As a reference, the sulfur breakthrough profile with a different feed oil with a sulfur content of 300 ppm is shown as well.

Since active site for adsorption on activated carbon is limited, adsorption capability will be lost once all active sites are covered and thus feedstock with 300 wtppm of sulfur shows quick breakthrough on activated carbon. This indicates that reducing the sulfur content in feedstock is mandatory to limit the amount of adsorbent within the feasible size.

2.1.2. Regeneration

Spent activated carbon, which was saturated with sulfur and nitrogen species after multiple adsorption experimental trials, was regenerated by aromatic solvents, such as toluene, 1-methylnaphthalene, and tetralin (used ACF was dipped into 10 mL of the solvents for 2 h at 70 °C under ultrasonic radiation. Then, ACF was filtered and dried at 120 °C under vacuum.). Then, the same experiment for adsorptive removal was conducted. The amounts of sulfur and nitrogen species removed with the regenerated carbon are shown in Fig. 3.

This experimental result indicates that the adsorption mechanism for sulfur compound is “physical adsorption” and aromatic solvent has higher affinity to sulfur compound in diesel than active site on activated carbon.

2.2. Conceptual Flow Scheme

The concept of the proposed new flow scheme is illustrated in Fig. 4. The straight run (SR) diesel of 1.5 wt% sulfur is hydrotreated in the existing conventional HDS reactor to reduce the sulfur content to meet the current regulation of 50 wtppm sulfur. This stream is then further processed using adsorbers filled with activated carbon to remove the remaining sulfur compounds to meet the 10 wtppm specification.

The spent activated carbon, which is saturated with adsorbed sulfur and nitrogen species, is processed in the regeneration step for reuse. An aromatic light distil-
late, such as heavy naphtha, from an FCC or RFCC unit, coker naphtha from a Coker Unit, or reformate from a naphtha reforming unit, is used to remove the sulfur compounds adsorbed on the activated carbon and then sent to an upstream column for fractionation. The regenerated adsorber is used again to produce 10 wtppm sulfur diesel fuel.

2.3. Energy Consumption in Sulfur Removal Process

In this paragraph, the energy efficiencies of the proposed new flow scheme and the conventional process for sulfur removal are compared.

In the proposed new flow scheme illustrated in Fig. 4, the existing HDS unit is considered a pretreatment section, removing the majority of sulfur compounds and producing 50 wtppm sulfur diesel fuel. The energy consumption in this section in the proposed new flow scheme is the same as that in the original operation, since there are no changes in the operating parameters of the existing diesel HDS unit. The additional facility for reducing the sulfur content from 50 to 10 wtppm is a post-treatment section, detailed in Fig. 5, where the remaining sulfur in hydrotreated diesel is adsorbed by activated carbon. This adsorption process does not consume any additional energy, since it is operating at ambient conditions. Therefore, no additional energy is consumed in this post-treatment section.

Accordingly, no additional energy consumption is required to achieve 10 wtppm sulfur diesel production with the proposed new flow scheme, compared with the current 50 wtppm sulfur diesel production.

However, increased severity in the existing HDS unit is required with the conventional process. The required operating conditions in the HDS reactor for production of 50 wtppm sulfur diesel and 10 wtppm sulfur diesel are compared in Table 1.

The present data are provided by the catalyst vendor (JGC C&C) on the following basis:
- Capacity: 25,000 BPSD
- Sulfur in feedstock: 1.5 wt%

In Table 1, an additional 53% of catalyst is required to reduce the sulfur content from 50 to 10 wtppm at the same hydrogen partial pressure and reactor bed temperature. This is owing to the significantly lower reaction rate in the ultra-deep desulfurization region resulting from the fact that the kinetics of the HDS reaction are exponentially proportional to the bulk sulfur content

Another major effect on energy consumption in
Table 1 is an additional 10% in hydrogen consumption. This is the result of hydrogenation of single ring aromatics, which partially occurs when the HDS reactor is targeting 10 wtppm sulfur diesel fuel production. This increases the operating costs owing to the additional hydrogen production required.

2.4. Regeneration Process

One of the most important issues for the application of the proposed new flow scheme is to develop an economic regeneration process. The detailed flow scheme is shown in Fig. 6.

In the previous research, the following was shown:

- Sulfur compounds adsorbed on activated carbon are removed by a warm, highly aromatic stream as a desorbent.
- The activated carbon so regenerated has the original capacity for sulfur removal restored.

In this paragraph, application of this regeneration process and its feasibility in a conventional refinery scheme, shown in Figs. 7 and 8, is explained.

In the refinery configuration of Fig. 7, the most suitable stream for regeneration of activated carbon is FCC heavy naphtha, considering its aromaticity and reprocessing path. The coker naphtha from the Coker Unit in the refinery configuration in Fig. 8 has the equivalent characteristics.

The first step in the regeneration process is drying using a warm nitrogen purge to recover the diesel product captured in the adsorption bed. Then, the FCC heavy naphtha, as a desorbent, is continuously supplied from the FCC main fractionator — heavy naphtha pump-around section to the adsorption bed for regeneration. The heavy naphtha is purged and sent to the LCO over-flash section. Since the adsorbed sulfur compounds are mostly dimethyldibenzothiophene (DMDBT) or trimethyldibenzothiophene (TMDBT) of T.B.P ˚366-380 °C, the majority (more than 70%) of these components are sent to bottom section for fuel oil blend stocks by distillation. The effect on the FCC main column with this additional stream is analyzed by ProII simulator using operating data from an existing refinery (refer to Table 2).

The present data given from the process simulator is on the following basis:
- FCC unit capacity: 65,000 BPSD
- Regenerant supply return: 300 BPSD

The results shown in Table 2 indicate that this proposed new scheme does not significantly affect the FCC unit operation and refinery energy balance.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Comparison of FCC Main Fractionator Operating Conditions</th>
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<tbody>
<tr>
<td></td>
<td>Original operation</td>
</tr>
<tr>
<td>Heavy naphtha/LCO gap&lt;sup&gt;a)&lt;/sup&gt;</td>
<td>10.6 °C</td>
</tr>
<tr>
<td>LCO/SLO gap&lt;sup&gt;a)&lt;/sup&gt;</td>
<td>25.3 °C</td>
</tr>
<tr>
<td>LCO P/A duty</td>
<td>20.1 MW</td>
</tr>
<tr>
<td>HCO P/A duty</td>
<td>45.3 MW</td>
</tr>
</tbody>
</table>

<sup>a</sup> ASTM D86 gap between 95% distillate of light stream and 5% distillate of heavy stream.
The final step is the drying of the adsorption bed using nitrogen under vacuum conditions to remove the hydrocarbons captured in the adsorption bed.

3. Feasibility Study against the Conventional Approach

3.1. Additional Equipment and Their Size

Based on the experiment, the average amount of activated carbon required to reduce the sulfur content from 50 to 10 wtppm was 1 g of activated carbon per 120 mL of treated oil, as shown in Fig. 2(B).

Thus, for 25,000 BPSD of diesel fuel production, 22 m³ of activated carbon is required as an adsorbent, with an adsorber change out period of 12 h. As shown in Fig. 5, four adsorbers are installed-two in operation (lead-lag arrangement), 1 in regeneration and 1 in stand-by. Switching the adsorbers is done automatically, with an interlock, by monitoring the sulfur content in each adsorber outlet.

Based on this configuration, the major equipment required is summarized in Table 3. As an order of magnitude estimate, the provision of these new facilities requires less than 20 million USD for engineering, procurement and construction.

3.2. Required Modification in Existing Facilities for Conventional Process

As indicated in Table 1, an additional 53 % of catalyst is required for the HDS reactor reduce the sulfur content of diesel fuel produced from 50 wtppm sulfur to 10 wtppm, if there are no changes in the other parameters.

In a revamp project, the operating conditions (e.g., hydrogen partial pressure, reactor inlet temperature, etc.) are optimized to minimize modification of the existing facilities. However, process studies sometimes produce unfavorable conclusions. Compliance with a 10 wtppm sulfur specification for diesel fuel requires the following major modifications:

- Replacement or modification of the reactor.
- Modification of the H₂ supply facilities to increase the H₂ purity in the recycle gas.
- Replacement of heat exchangers or fired heaters to reduce the pressure drop in the recycle loop.

As an order of magnitude estimate, such modifications require more than 100 million USD for engineering, procurement and construction, as well a prolonged shutdown period, which reduces the refiner’s revenue. In order to mitigate these effects, some of refiners decided to reduce the throughput of the existing HDS unit for 10 wtppm sulfur and build a new diesel HDS unit to compensate for the reduced throughput. This approach costs only a few million USD, depending on the size of the new unit.

4. Discussion and Conclusion

The proposed new scheme using the adsorptive process, is technically and economically justified for ultralow sulfur diesel fuel production. However, the following further studies are required before installing commercial scale facilities:

- Development of activated carbon with a higher adsorption capacity by adjustment of the surface properties (e.g., surface area, pore volume).
- Development of adsorber internals that prevent channeling in the adsorption and regeneration processes.
- Study to determine the optimal cycle length and life of activated carbon.

As noted in section 3. of this paper, the conventional process —achieving the lower sulfur content in diesel fuel by increasing the severity of HDS reactor— requires major modifications of the existing facilities when the major equipment in the existing facilities do not have a sufficient margin. In addition, operating at the severer conditions increases the already high safety risks due to corrosion, since the cost of replacing equipment and piping with that of a higher material grade is economically prohibitive.

However, the proposed adsorptive sulfur removal
process produces the 10 wtppm sulfur diesel with minimal effect on the existing refinery operation, as shown in section 2. Also, the capital investment required for the facilities in the proposed new scheme is 5 to 10 times less than that for the conventional process, which will lower the barrier for refiners and local governments to apply the severer regulation.

Considering the urgent need to reduce the environmental pollution of fossil fuels, the earliest development of commercial-scale facilities using this proposed new flow scheme is needed to meet market demand.

References