吸着工程による、新たな軽油超深度脱硫プロセスの開発

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A Doctoral Thesis

A New Integrated Process for Deep Desulfurization Process using Adsorptive Treatment

(和題：吸着工程による、新たな軽油超深度脱硫プロセスの開発)

Kyushu University
Yosuke Sano

CONTENTS

LIST OF CAPTIONS

TECHNICAL TERMS

BPSD: Barres Per Standard Day, commonly used unit of measurement for Refinery facility

CCR Platformer

Catalytic Reformer for naphtha stream with Continuous Catalyst Regeneration. Hydrotreated naphtha of paraffinic / naphthenic molecules are converted to Aromatic molecules by De-Hydrogenation.

Delayed Coker:

The process unit in refinery, treating residues from distillation units for thermal cracking to produce light distillate.

FCC: Fluid Catalytic Cracking (Unit). The residue or vacuum gas oil, whose normal boiling temperature over 360 degC treated in this unit to produce Gasoline and other light distillates.

GC-AED: Atomic Emission Detector. HP6890P and G2350A was used in this series of studies

HDS Catalyst:

The catalyst used for Hydrodesulfurization.

For Diesel Hydrodesulfurization, the Cobalt – Molybdenum (CoMo) or Nickel– Molybdenum (NiMo) supported on silica alumina / zeolite.

Hydrodesulfurization:

The typical reaction for removal of sulfur from semi-finished petroleum product. The sulfur atoms contained in molecule is removed on the active sites of HDS catalyst and converted to H_2S

LCO Light Cycle Oil, which is bi-product from FCC Unit, which is in the same distillation range as Diesel

Pump-Around:

The side drawoff from fractionator, which is to be returned to column after heat recovery.

Reformate:

Product Oil from CCR Platformer. One of the gasoline component with high octane number (usually 100 RON) due to high aromatics content (90wt%+)

Refractory Sulfur Compounds

The sulfur compounds, which are difficult to be desulfurized with HDS Catalyst. 4,6 – Dimethyl Dibenzothiophene is the typical molecule, which has steric hindrance for sulfur atom to contact with active site of HDS catalyst.

Straight Run Diesel:

Untreated diesel oil, derived from Crude Oil, whose normal boiling temperature is usually 240 degC – 360 degC, depending on the local product specification

TPD: Temperature Programmed Desorption. TPD-1-AT, Nippon Bell. Co. was used in this series of studies

CHAPTER 1
INTRODUCTION

1.1 Environmental Regulation for Automotive Fuel

The increasing concerns on the air quality have urged the petroleum refining industry to proceed with cleaner products by removing heteroatoms containing molecules from their major products, such as diesel and gasoline fuel. Presence of sulfur compounds in gasoline, diesel and marine fuel is still in the major source of air pollution since they are poisoning the catalyst for exhaust gas from Automotive. Then, untreated exhaust gas causes the environmental pollution (Acid Gas, Photochemical smog) or health issues (Azuma, etc...)

Especially in the developed country (e.g. North America, West Europe or Japan), the stricter regulation has been applied to the fossil fuel, such as gasoline, diesel and marine fuels. [1-7] Fig. 1.1a and Fig. 1.1b show the trend of sulfur regulation for gasoline and diesel in Japan.

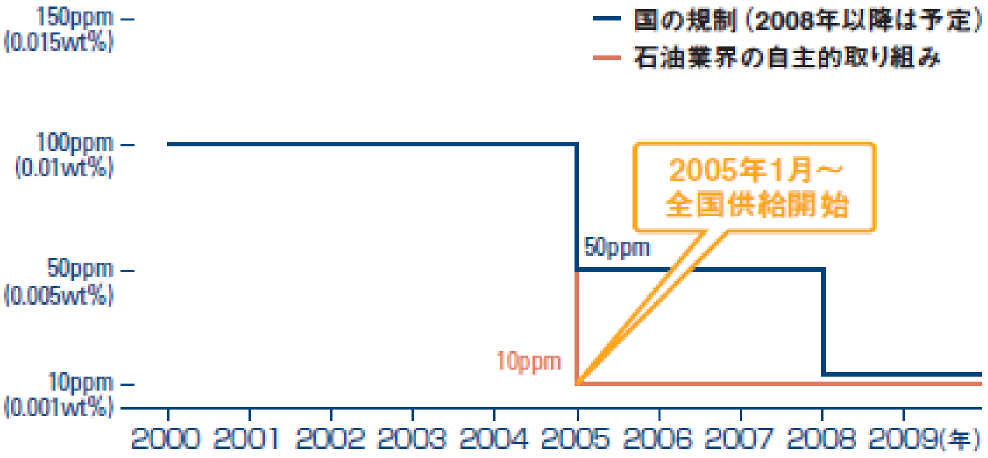

Fig. 1.1a Sulfur Regulation for Gasoline in Japan

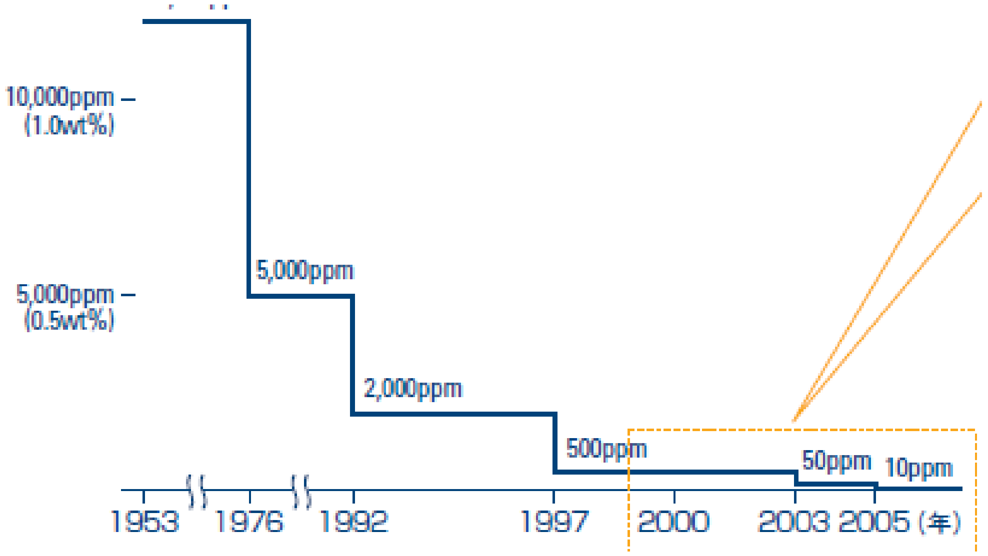

Fig. 1.1b Sulfur Regulation for Diesel in Japan

Such strict regulation has not been applied for domestic regulation in developing country, such as South East Asia, China, India and Mid / South America since many of refineries in those developing countries does not yet have the capability for clean fuel production and suffering from the severe financial problems for upgrading the existing facilities. Even though some of newly built refineries have capability for cleaner fuel production; they mainly export to developed country to gain the foreign currency.

However, worldwide effect of air pollution becomes highlighted and the severer regulations began to be applied for some of south east Asian country, e.g. 50 wt-ppm of sulfur content regulation on Gasoline in 2017 / Diesel in 2010 was in effect by Singapore Government. Since the significant growth of motive fuel consumption is expected in those developing countries, application of this regulation is strongly requested to minimize the global environmental issues.

1.2 World's Trend on Refinery Business

Although some of developed countries are facing the "peak out" of oil demand, the world-wide consumption of oils is expected to be increased, mainly lead by

China, India, Middle East and ASEAN Countries. Fig. 1.2a & Fig. 1.2b shows the forecast of regional crude oil consumption. [8 - 10]

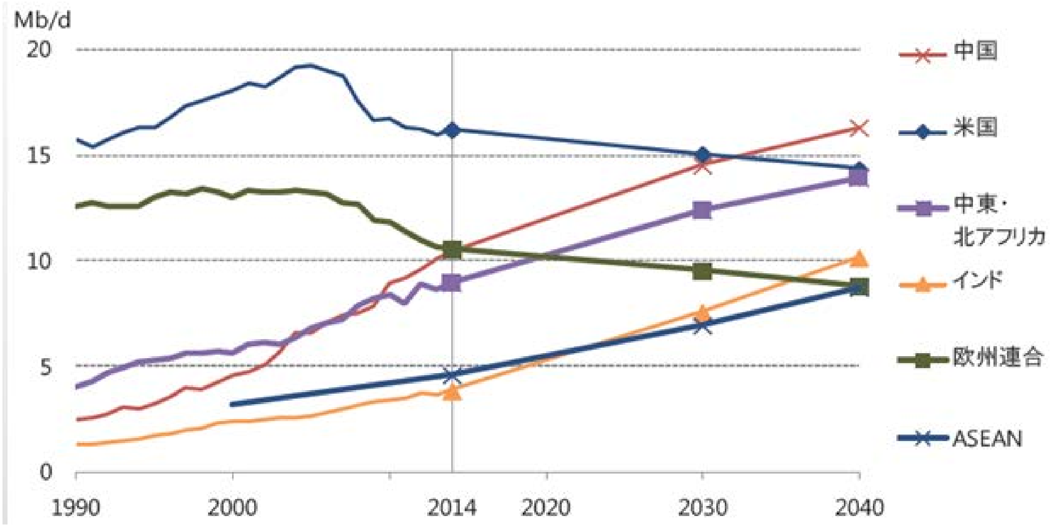

Fig. 1.2a Forecast of regional crude oil consumption

As can be seen in the Fig 1.2b and Fig 1.2c, most of growing countries have not yet applying the regulation applied in developed country but needed to be applied as soon as possible. In general, however, the stricter environmental regulation is one of the most concerned dilemma for Refiners. For compliance of new severer regulations, Refinery has three choices, the simplest approach is the reduction of throughput for increasing the Hydrogen / Oil ratio and Catalyst / Oil Ratio, 2nd one is the revamp of exiting unit and last one is to build new unit. However, none of those options assures the competitiveness of existing refinery due to loss of revenue or significant capital cost. Therefore, all existing Refiners are suffering from new regulations and new process for compliance of stricter regulation with lowest capital cost / without reduction of throughput is highly desired.

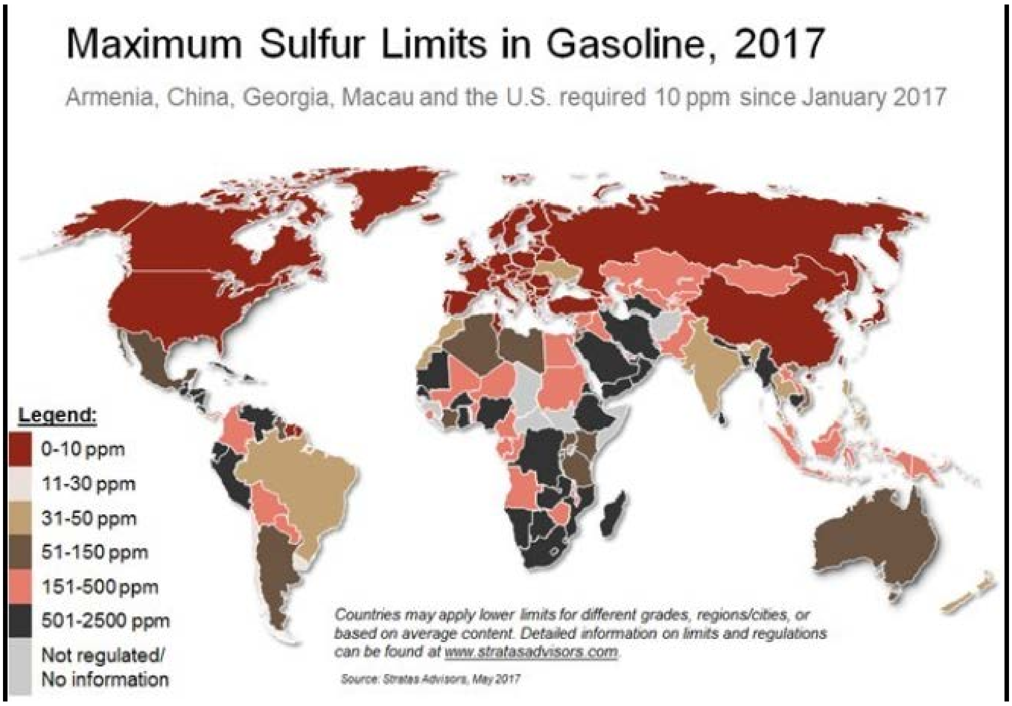

Fig. 1.2b Maximum Sulfur Limit in Gasoline, 2017

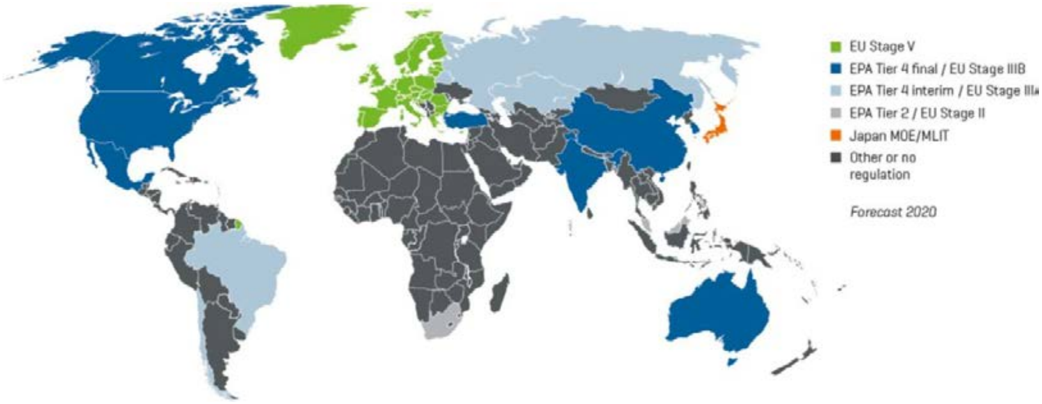

Fig. 1.2c Diesel Regulation Application, expected in 2020

1.3 Sulfur Removal Process for Diesel Fuel

The Hydrodesulfurization is the common methodology for removal of sulfur from diesel in the current refinery industry. [11] The typical process flow scheme for diesel Hydrodesulfurization facility is illustrated in Fig. 1.3.

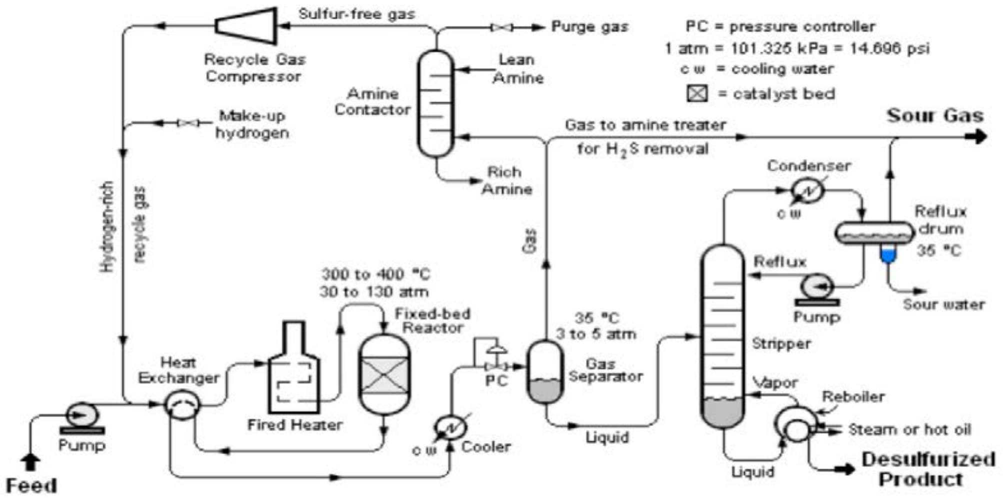

Fig. 1.3 Typical Process Flow for Diesel Hydrotreating

The feedstock of Diesel Hydrodesulfurization Unit is pumped up and mixed with Hydrogen Rich Gas. Before entering Reactor, this mixed stream is heated by heat exchanger and fired heater. In the reactor, sulfur compounds in feedstock is converted to H_2S by HDS Catalyst. The reactor effluent is then cooled down and routed to separator, where the vapor and liquid separation is taken place. The vapor will be treated by Amine for removal of H_2S, generated in the reactor and recycle back to mixer after boosting up by compressor. The liquid is to be sent to Stripper for removal of light end before sending to Storage Tank.

The reaction kinetics in reactor is depending on the structure of molecules and heavy-aromatic sulfur compounds (so called Refractory Sulfur Compounds) has significantly lower reactivity than other compound with sulfur. [12 - 17] Accordingly, the removal of this Refractory Sulfur Compounds is the controlling factor for sulfur content in final diesel product.

On the other hand, the desulfurization of Refractory Sulfur Compounds is strongly inhibited by the co-present inhibitors H_2S, NH_3 and organonitrogen compounds. [18 - 21] Hence, most of the attempts to achieve the “less than 10 wt-ppm of sulfur content” from Straight Run Diesel have been focused to increase the reactivity of the catalyst for the refractory sulfur compounds and resistivity against inhibitors. New catalysts have been developed to provide the more active sites with morphology of molybdenum sulfide on the support, and/or more acidity, which is known to facilitate the Hydrogenation and isomerization of 4,6-Dimethyl Dibenzothiophene to relieve the steric hindrance of such refractory sulfur compounds. The resistivity against inhibition by H_2S is also to be strengthened. Gas phase inhibitors, such as H_2S and NH_3, could be removed in a two-stage reaction configuration, proposed by Choi, et. al, in which pure Hydrogengas refreshed the reaction atmosphere between the first and second stage reactor. Some of nitrogen compounds, in particular, alkylated carbazoles, are rather refractory to survive until the last stage of deep Hydrodesulfurization, inhibiting the conversion of sulfur compounds to H_2S.

Also, there is the reaction inhibiting materials. NH_3 and basic nitrogen compound is one of the known compounds. They occupy the acidic site on HDS Catalyst, slowing down the reaction.

1.4 New approach for Ultra Low Sulfur Diesel via Adsorption

The series of researches in this Doctoral dissertation are purposed for the discovery of energy & economically efficient sulfur removal process to produce the diesel with sulfur content of less than 10 wt-ppm. The adsorption by using the adsorptive capability of Activated Carbon.

The experimental in Chapter 2 shows that the Activated Carbon has remarkable capability for removal of Nitrogen & Sulfur Compounds in Straight Run Diesel, which is connected to the drastic improvement on reactivity of subsequent Hydrodesulfurization using conventional CoMo Catalyst. The several experimental are also examined to comprehend the relationship between amount of adsorbed nitrogen / sulfur compounds and surface property of Activated Carbon, operating temperature and type of feedstocks.

Then, the quantitative analysis for relationship between remaining Nitrogen / Sulfur compounds and Hydrodesulfurization reactivity were made in the Chapter 3. The result of this quantitative analysis indicated that there is a “sweet spot” for treatment, where the extent of reactivity improvement is remarkable.

The experimental in Chapter 4 shows that the spent Activated Carbon (no more adsorption capability) can be regenerated by using the aromatic solvent, e.g. Toluene. Together with experimental facts attained in the Chapter 2 & 3, the new integrated process is proposed in the Chapter 4.

Chapter 5 shows how to implement this new technology into actual industry and evident its feasibility based on the several years experience in Engineering, Procurement and Construction for Refinery Process. The reality found in the refinery industry provided an idea for actual implementation of new process proposed in Chapter 4.

The actual implementation of new technology proposed in this research will accelerate the application of severer regulation for sulfur in diesel. This will directly contribute to the environmental protection.

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CHAPTER 2

ADSORPTIVE REMOVAL OF SULFUR AND NITROGEN COMPOUNDS FROM A STRAIGHT RUN DIESEL OVER ACTIVATED CARBONS FOR ITS DEEP HYDRODESULFURIZATION

2.1 Introduction

The nitrogen compounds of both basic and neutral natures in Straight Run Diesel are known as the inhibitors for deep Hydrodesulfurization of refractory sulfur compounds especially at their low level in the range of 10–200 wt-ppm [1]. Basic nitrogen compounds tend to show strong inhibition to Hydrodesulfurization of Straight Run Diesel but many of them are to be denitrogenated at rather initial stage of Hydrodesulfurization. The neutral nitrogen compounds, such as carbazoles or its alkylate, has lower reactivity than most of sulfur compounds in Straight Run Diesel and tend to stay through the whole stage of deep Hydrodesulfurization. In the last stage of Hydrodesulfurization reaction, refractory sulfur compounds are Hydrodesulfurized to achieve sulfur level less than 10 wt-ppm [2], which is the common specification for diesel product in developed country, and its reactivity is affected by remaining inhibitors at this stage. Hence, their removal prior to the Hydrodesulfurization is very effective to reduce the remaining sulfur content as previously reported [3-6], even if they were denitrogenated at the last minute of Hydrodesulfurization.

There are some proposals of the pre-treatment for Diesel to remove nitrogen compounds by silica or silica–alumina prior to Hydrodesulfurization [3-6]. However, there are still some windows to improve the cost and performance in terms of the adsorbent. Removal level of nitrogen compounds, efficiency and effects of sulfur removal, regeneration of adsorbent and oil recovery must be delicately balanced. Song and Ma [7] proposed selective adsorption for removing sulfur at ambient temperature (SARS) process to achieve ultra clean diesel and gasoline. They used 5 wt-% metal loaded on silica gel as an adsorbent. Feed oil was not real diesel, but model compounds which did not contain the nitrogen compounds. Although detail information on the adsorbent was not disclosed, their adsorbent showed rather fast breakthrough over 10 wt-ppm after eluting about 5 ml of model diesel. IRVAD and S-Zorb process also utilize adsorption to remove the heteroatoms in gasoline and diesel. But, operating temperature of them are reported to be over 240 degC (IRVAD) and 340 – 410 degC (S-Zorb) [8-10]. Yang and coworkers [11,12] reported that Cu and Ag-exchanged Y-type zeolites were very effective to selectively adsorb the thiophene and the used adsorbents could be regenerated by heating them at 350 degC under flowing air.

Several new approaches have been proposed and some of them were practically examined to achieve the ultra deep Hydrodesulfurization [13]. However, more efficient and more economical process is still desired despite various efforts by researchers in the world. Critical barriers for achieving ultra deep Hydrodesulfurization are very low reactivity of refractory sulfur compounds under conventional conditions and strong inhibition by H_2S, NH_3, nitrogen, and even aromatic compounds against ultra deep Hydrodesulfurization. Such inhibitors retard the Hydrodesulfurization, very markedly in the region of 0–100 wt-ppm of sulfur content [1,14-17].

Activated Carbon and Activated Carbon fiber have been recognized to be versatile absorbents for gaseous and liquid substrates [18,19]. Their surface structure and properties can be controllable to propose better adsorbent [20 – 22]. In this study, sulfur and nitrogen compounds were removed from Straight Run Diesel through the dynamic adsorption over some Activated Carbon materials at room temperature. A particular Activated Carbon of very large surface area was examined in detail.

2.1.1 The effect of further activation of Activated Carbon on Adsorption Capability

Activated Carbon. MGC-B and OG-20A were treated by H_2O_2, $H2SO_4$ and HNO_3, followed by dried out operation at 180 degC, 400 degC and 600 degC, respectively for further activation. Then, proceed with the same adsorption experimental as described in Section 2.2.1. Prior to the experimental for adsorption, the Activated Carbon of further activation were analyzed by TPD apparatus.

This experimental is purposed to see if any relationship between surface properties of Activated Carbon and its adsorption capability for nitrogen compound in Straight Run Diesel.

2.2 Experimental

2.2.1 Adsorption for Nitrogen and Sulfur Compounds in Straight Run Diesel

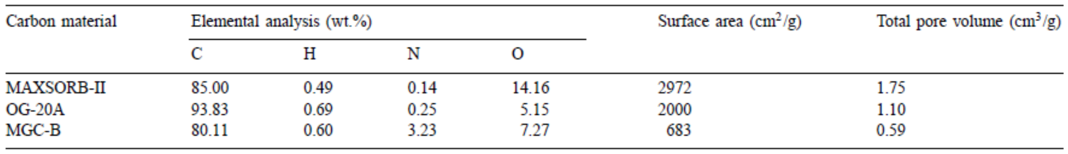
Straight Run Diesel (11,780 wt-ppm of sulfur content and 260 wt-ppm Nitrogen), which was provided by a Japanese commercial refinery, was used in this study as a feedstock for adsorptive treatment by Activated Carbon. Normal Boiling Point of component in Straight Run Diesel are in the range of 240 – 360 degC with carbon number of C_{12} – C_{20}. Most of sulfur compounds in Straight Run Diesel were benzothiophenes (BT), dibenzothiophenes (DBTs). Carbazoles (Cz) were found in nitrogen-specific chromatogram of Straight Run Diesel.

With regard to the adsorbent, three types of Activated Carbon - MAXSORB-II, OG-20A and MGC-B were used in this experimental. The key properties of those Activated Carbons are listed in Table 2.2.1.

Prior to the experimental for adsorption, the Activated Carbon materials were dried at 110 degC under vacuum oven for removal of water on the surface. As a batch type adsorption experimental at the first place, 1 g of this dried Activated were put in the 120 ml of Straight Run Diesel and mixed under ambient pressure & temperature (30 degC). Then, the filtered liquid was analyzed by GC-AED for changes in the distribution of sulfur and nitrogen components.

Secondary, the adsorption experimental of continuous operation was carried out. The dried Activated Carbon materials were packed into the stainless-steel tube of 50 mm length and 6 mm diameter. Then, Straight Run Diesel was fed into the tube by an HPLC pump (Shimadzu, LC-10AD) at the rate of 0.1 ml/min under the pressure of 20 psi. The eluted oil was sampled for 30 s (0.05 ml) at every 60 min and analyzed by GC-AED. The sulfur and nitrogen content in total recovered oil for 6 hrs. operation (36 ml) was also analyzed by GC-AED. In this experimental, the tube filled with Activated Carbon was maintained at constant temperature of 30 degC by water bath. In order to check the impact from adsorption temperature on Activated Carbon’s capability for adsorption of sulfur / nitrogen compound in Straight Run Diesel, this experimental was carried out with MAXSORB-II at 10 degC and 50 degC.

Table 2.2.1 The characteristics of the carbon materials examined in the present study



Carbon material	Elemental analysis (wt.%)				Surface area (cm^2/g)	Total pore volume (cm^3/g)
	C	H	N	O		
MAXSORB-II	85.00	0.49	0.14	14.16	2972	1.75
OG-20A	93.83	0.69	0.25	5.15	2000	1.10
MGC-B	80.11	0.60	3.23	7.27	683	0.59

2.2.2 Adsorption for Sulfur Compounds in Other Petroleum Products

By using same experimental apparatus and procedure explained in Section 2.2.1, following petroleum products / byproducts were treated:

- FCC Gasoline, whose sulfur content is 64 wt-ppm
- Hydrotreated Kerosene, whose sulfur content is 10 wt-ppm
- LCO, whose sulfur content is 8,900 wt-ppm

This experimental was conducted with batch operation, using 0.3 g of Activated Carbon for treating 20 ml of oil at 30 degC. The collected liquid was analyzed by GC-AED.

2.3 Result

2.3.1 Removal of nitrogen and sulfur over MAXSORB-II, a particular Activated Carbon of the largest surface area

The carbon-, sulfur-, nitrogen-chromatograms of treated Straight Run Diesel (120 ml oil / 1 g MAXSORB-II) are illustrated in Fig. 2.3.1a.

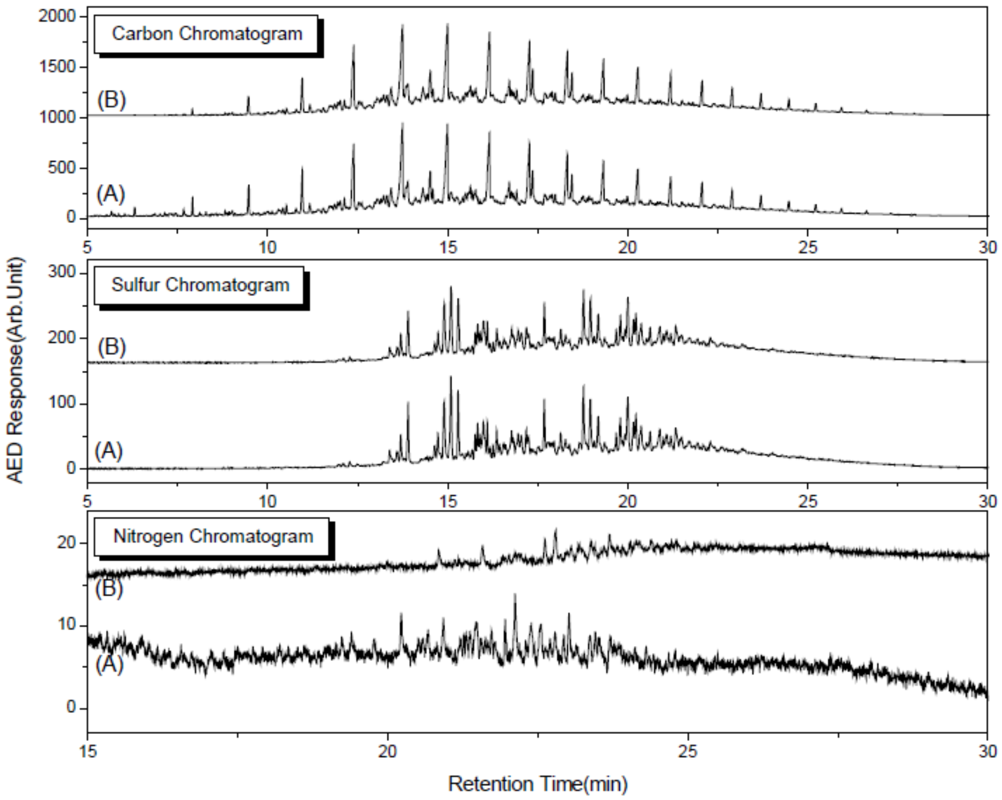


Fig. 2.3.1a Carbon, sulfur, and nitrogen chromatograms of (A) Straight Run Diesel and (B) treated Straight Run Diesel.

There was no difference between the carbon - chromatograms of Straight Run Diesel and that of treated Straight Run Diesel. On the other hand, smaller peaks are found in the sulfur – chromatograms of treated Straight Run Diesel. As for the nitrogen – chromatograms, remarkably smaller peaks are found in the treated Straight Run Diesel than Non-Treated Straight Diesel.

The sulfur chromatogram for eluted oil in initial stage of adsorption experimental is also illustrated in the Fig. 2.3.1a.

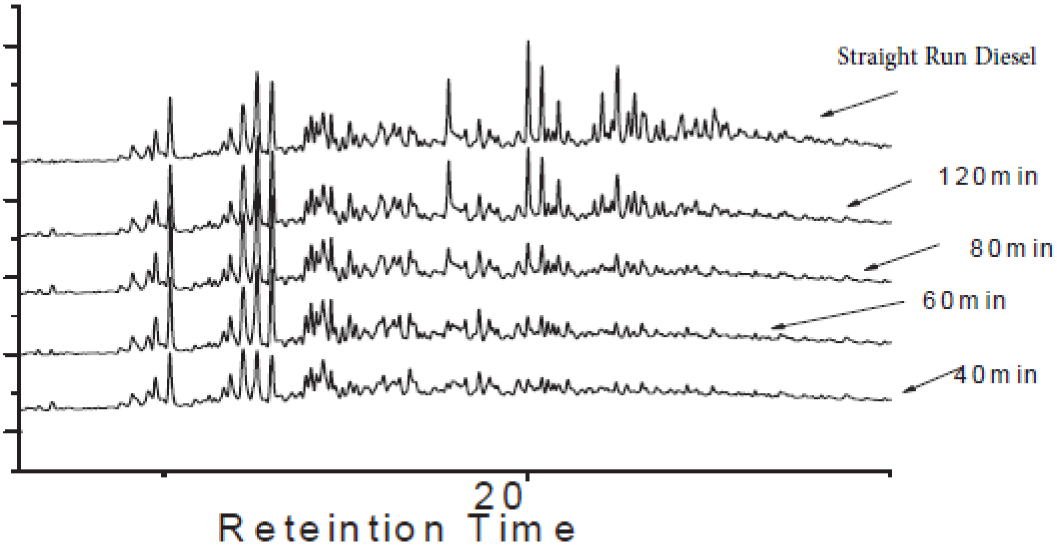


Fig. 2.3.1b Sulfur chromatograms of Straight Run Diesel and treated Diesel.

In the initial stage of this experimental, the peaks of sulfur compounds of higher boiling point (peaks in right side of chromatogram) are reduced but the height of those peaks are gradually increased. Also, the peaks of sulfur compounds of lower boiling point (peaks in left side of chromatogram) in eluted oil at 120 min. shows higher peak than feedstock. This means that the adsorbed sulfur compounds in the initial stage on Activated Carbon is desorbed in the later stage, possibly by sulfur compounds of higher boiling point

2.3.2 Adsorption performance among Activated Carbon materials for sulfur and nitrogen compound in Straight Run Diesel

Fig. 2.3.2 illustrates the removal ratio of the sulfur and nitrogen compound in Straight Run Diesel over three Activated Carbon materials through 6 hrs. experimental. Among three kinds of Activated Carbons, MAXSORB-II of highest surface area and highest oxygen content shows remarkable adsorption capability for nitrogen compound in Straight Run Diesel. Also, Fig. 2.3.2 indicates that MGC-B of lower surface area than OG-20A showed 30% more nitrogen compound removal ratio than OG-20A. This indicates that the Oxygen functional group on surface of Activated Carbon plays roles in the adsorption of Nitrogen Compound in Straight Run Diesel.

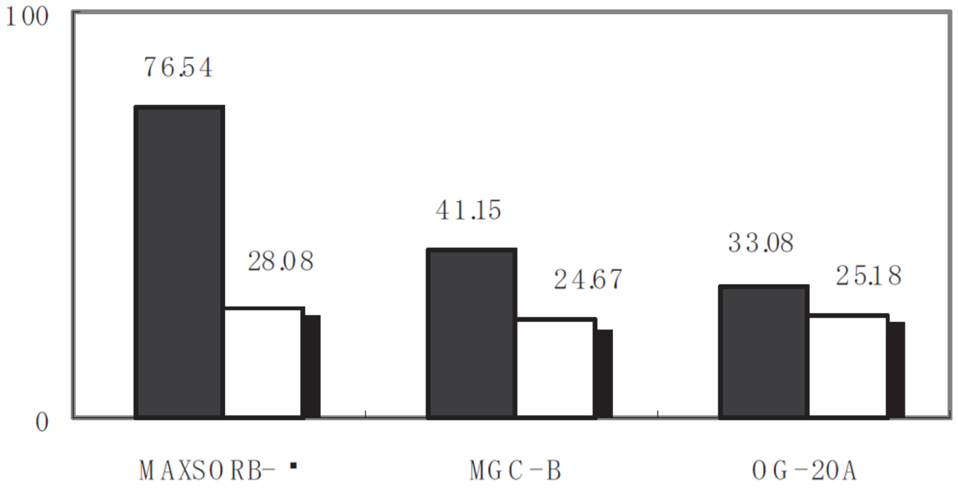


Fig. 2.3.2 Sulfur and Nitrogen removal ratio among three Activated Carbons.

With regards to the adsorptive removal of sulfur compound in Straight Run Diesel, MAXSORB-II of highest surface area shows the highest adsorption capability as well. However, the removal ratio was proportional to neither surface area, pore volume, nor other hetero molecules in Activated Carbon.

2.3.3 Adsorption performance with MAXSORB-II for sulfur and nitrogen compound in Straight Run Diesel

Fig. 2.3.3 shows the breakthrough profiles during adsorptive removal of the sulfur and nitrogen compounds over the Activated Carbon at various temperatures (10 degC, 30 degC, and 50 degC). The removal extents of nitrogen compounds were basically independent on the adsorption temperature as shown in Fig. 2.3.1a. In contrast, adsorption at the higher temperature reduced the adsorption of total sulfur compounds, which is typical phenomena in physical adsorption process.

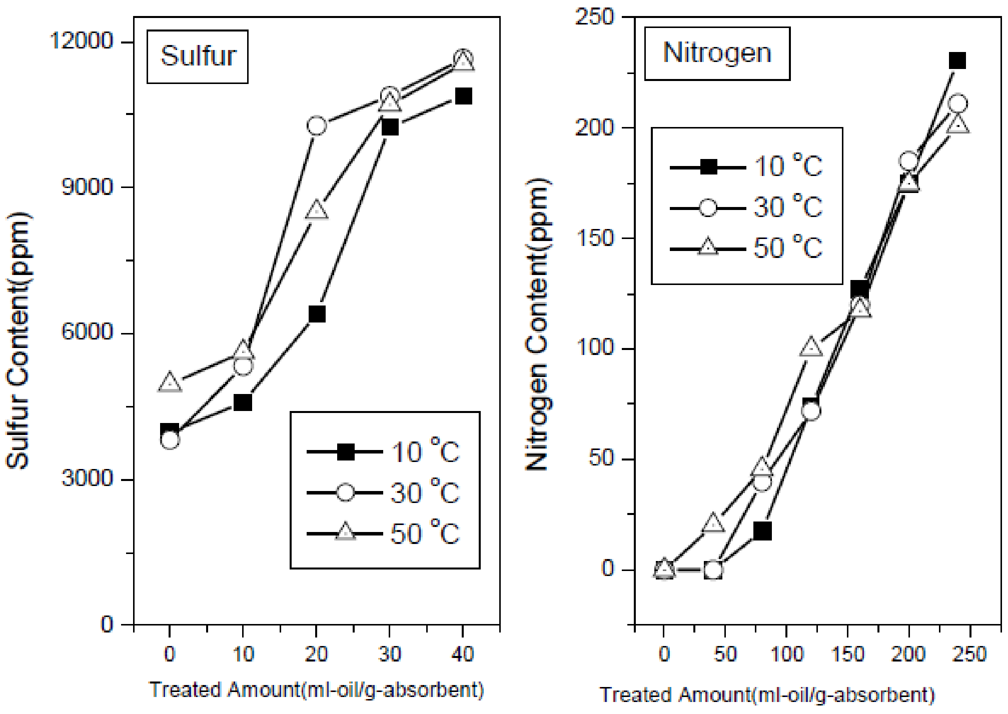


Fig. 2.3.3a Sulfur and Nitrogen breakthrough profiles of Straight Run Diesel on MAXSORB-II at various adsorption temperatures.

Fig. 2.3.3b illustrates sulfur and nitrogen contents in treated Straight Run Diesels sampled at various elution times. The 37% of total sulfur compounds were left in the first 0.05 ml of the treated Straight Run Diesel. The content increased rapidly to 90% by 20 ml elution and then slowly to 100% by 45 ml elution. The slow increase of sulfur compounds from 20 to 40 ml elution corresponded to the removal of refractory sulfur compounds such as 4,6-DMDBT and 4,6,X-TMDBT as described below. Only 10% of refractory sulfur compounds were left in the first 0.05 ml of the eluted Straight Run Diesel. The content increased slowly to reach 100% by 55 ml elution, showing longer breakthrough profile than the total sulfur content. Preferential adsorption of refractory sulfur compounds was definite over MAXSORB-II.

Adsorption of nitrogen compounds was much more effective than that of sulfur compounds. The nitrogen content remained at much lower level than the sulfur content in Straight Run Diesel. First 0.05 ml of eluted Straight Run Diesel contained no nitrogen compounds at all. The nitrogen content increased gradually to reach 100% by 150 ml elution. The removed amounts of total sulfur, refractory sulfur, and nitrogen compounds until their 100% breakthrough were calculated; 0.098 g total sulfur, 0.042 g refractory sulfur, and 0.039 g total nitrogen over 1 g MAXSORB-II, respectively, at 30 deg C.

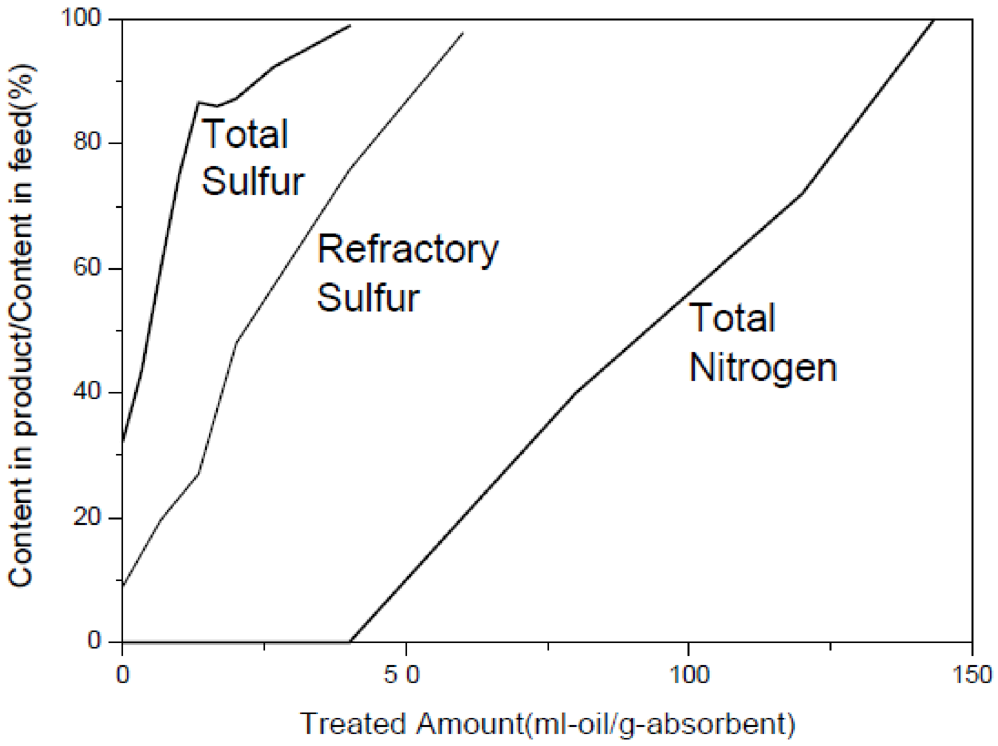


Fig. 2.3.3b Sulfur and nitrogen breakthrough profiles of Straight Run Diesel on MAXSORB-II at 30 degC.

2.3.4 Further activation of Activated Carbon and its impact to adsorption capability on Nitrogen Compound in Straight Run Diesel

Fig. 2.3.4c and Fig. 2.3.4d showed the nitrogen breakthrough profiles by treated MGC-B and OG-20A series. H_2O_2-, H_2SO_4, HNO_3-treated Activated Carbons, which dried at 180 degC, 400 degC and 600 degC respectively, showed better adsorption than those of “as-received” ones.

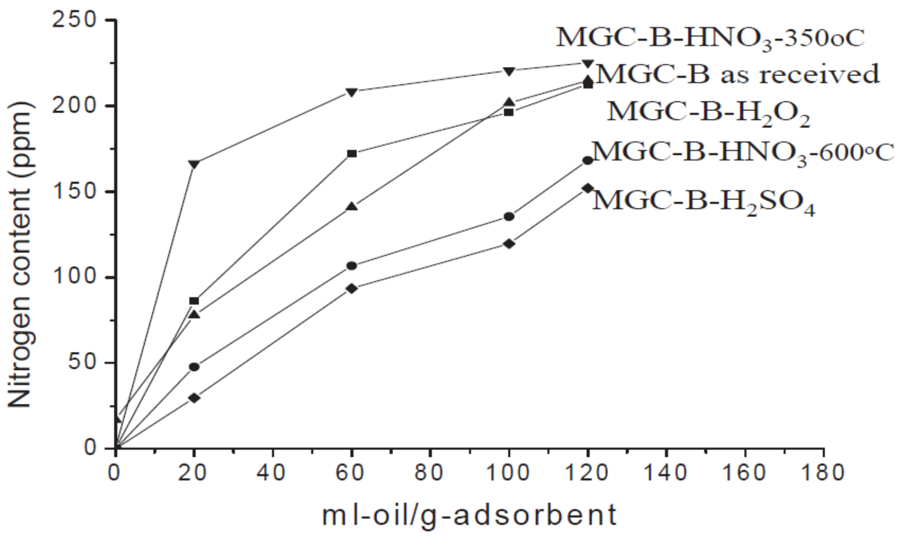


Fig. 2.3.4a Breakthrough profiles of MGC-B series

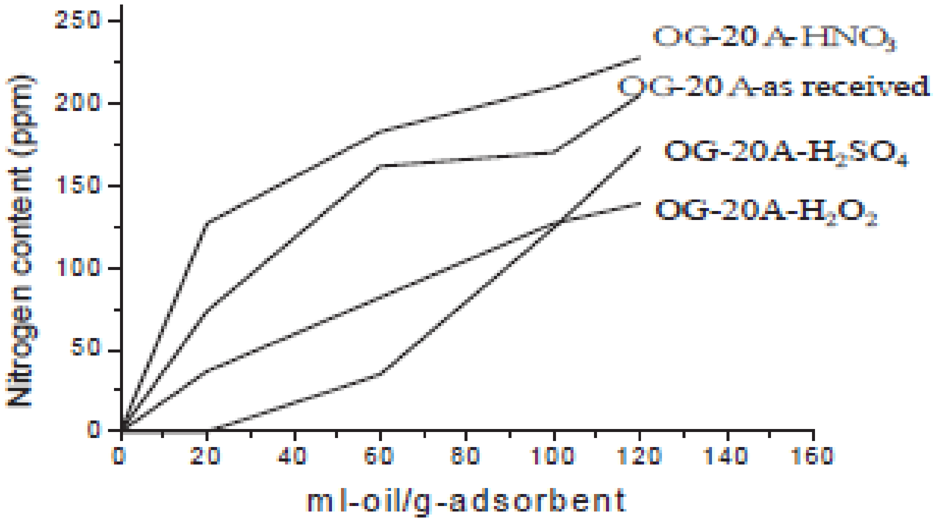
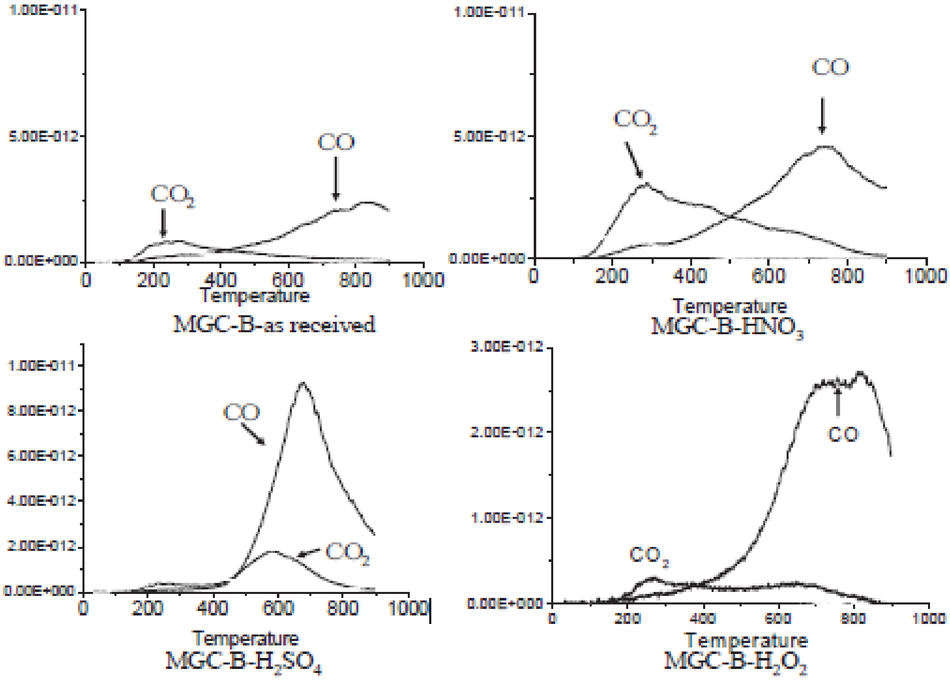


Fig. 2.3.4b Breakthrough profiles of OG-20A series

Fig. 2.3.4c and Fig. 2.3.4d showed the TPD spectrums of these Activated Carbons, where Activated Carbon of larger adsorption capacity for nitrogen compound shows the CO peak at 600 - 800 degC and those of low adsorption capacity for nitrogen compounds showed CO_2-peak at 200 - 400 degC.

This experimental shows the consistent tendency of experimental result in Section 2.3.2, where the nitrogen removal ratio is highly related to oxygen molecules in Activated Carbon.



MGC-B-as received

MGC-B-HNO_3

MGC-B-H_2SO_4

MGC-B-H_2O_2

Fig. 2.3.4c TPD results of MGC-B series

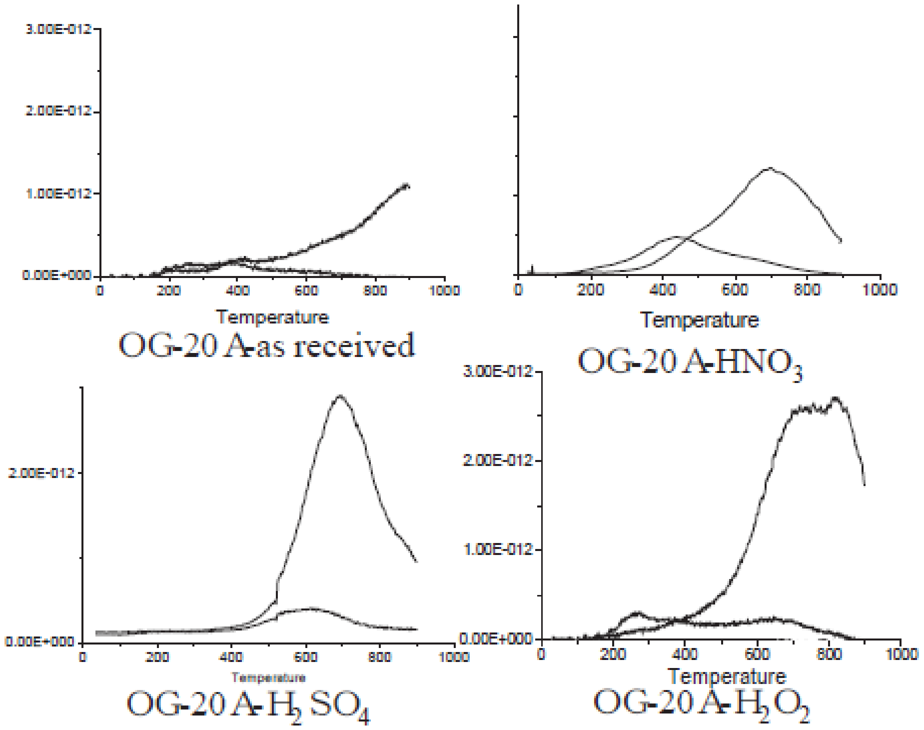


Fig. 2.3.4c TPD results of OG-20A series

2.3.5 Adsorptive removal of sulfur compounds from various petroleum products

Fig. 2.3.5a shows the sulfur chromatogram for FCC Gasoline of (A) “As received Gasoline” and (B) “Treated Gasoline”.

Adsorptive sulfur removal from FCC Gasoline is highly attractive for refiner since conventional hydrotreating scheme enhance the octane loss due to saturation of olefin component. However, Activated Carbon did not remove the sulfur compounds in FCC Gasoline, even though the sulfur content in feedstock is only 64 wt-ppm. This experimental result indicates that the adsorption of sulfur compound found in the adsorptive treatment for Straight Run Gas oil is not direct interaction between Sulfur Molecule and Activated Carbon but the affinity of bulk liquid against surface of Activated Carbon.

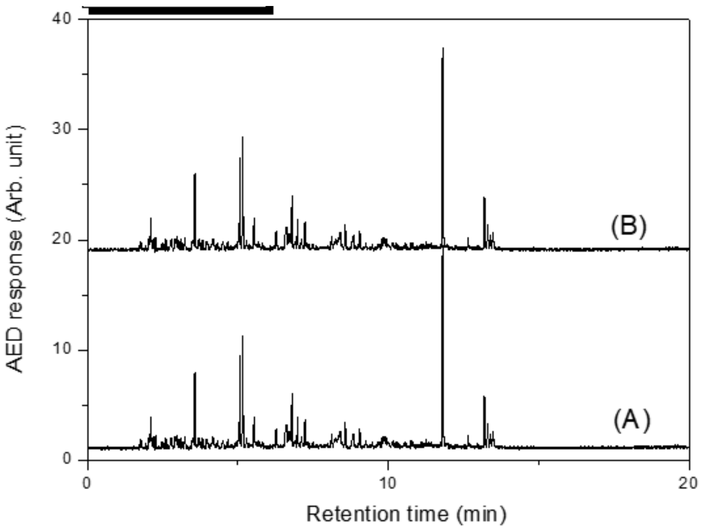


Fig. 2.3.5a Sulfur Chromatogram of (A) FCC Gasoline (B) Treated FCC Gasoline

Fig. 2.3.5b shows the sulfur chromatogram for (A) “As received Kerosene” and (B) “Treated Kerosene”. Alkylated benzothiophenes (peak number of 5 - 6) in kerosene were not adsorbed over Activated Carbon at all while Dibenzothiophene (4) and alkylated Dibenzothiophenes (1 – 3) in kerosene were adsorbed. These characteristics are consistent with the experimental result in Straight Run Diesel. However, refinery industry may not be very interested in this fact since there is no technical difficulty for hydrotreating Kerosene.

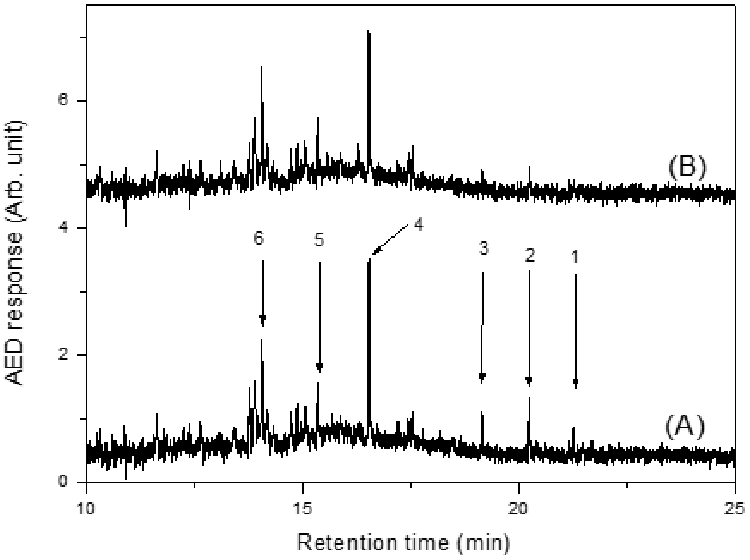


Fig. 2.3.5b Sulfur Chromatogram of (A) Kerosene. (B) Treated Kerosene.

Fig. 2.3.5c shows the sulfur chromatogram for (A) “As received LCO” and (B) “Treated LCO”. Although sulfur component is removed, the adsorption bed was plugged when proceed with adsorption experimental described in Section 2.2.1. This may be caused due to the gummed materials, which are polymerized olefin material.

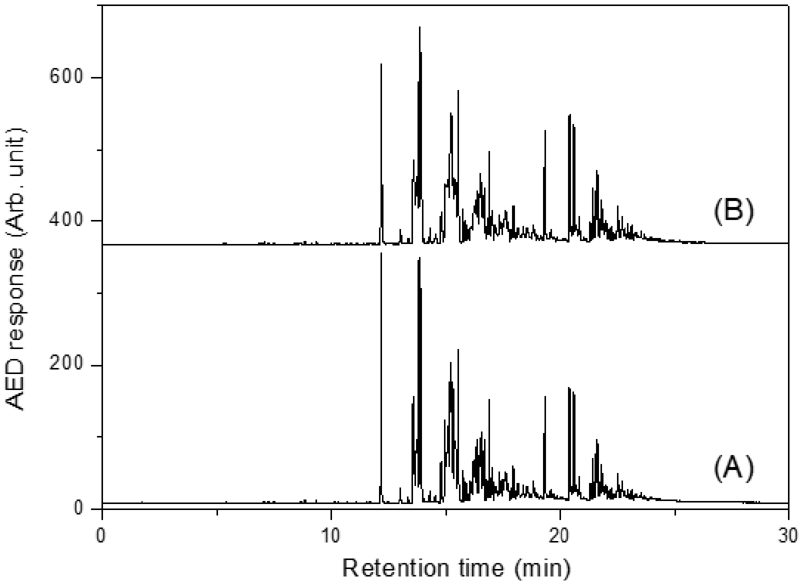


Fig. 2.3.5c Sulfur Chromatogram of (A) LCO (B) Treated LCO

2.4 Discussion

MAXSORB-II was found particularly active to remove both nitrogen and sulfur compounds in Straight Run Diesel although all three carbon materials examined in the present study showed much higher removal capacity than silica gel and alumina, which had been reported as effective adsorbents for nitrogen compounds in the Diesel. Its adsorption capacity (0.098 g total sulfur and 0.039 g total nitrogen) was much larger than Cu-exchanged Y-zeolite (1.40 wt.%) [11]. Although some decrease in adsorption capability were found in higher temperature, its remarkable ability for sulfur and nitrogen compound at ambient temperature will provides the advantage on operation cost as well.

As indicated in the Section 2.3.1 in this Chapter, the remaining nitrogen content in treated oil is very low. Therefore, the Activated Carbon as adsorber has high potential for commercial use as a pre-treatment section of diesel hydrotreating facility to increase the reactivity in Hydrodesulfurization reaction by eliminating the nitrogen compound of its inhibitor. Those very large surface area and high oxygen content may be explained as a reason for its high performance. MAXSORB-II has been disclosed to be prepared through KOH activation of green coke [20, 23], which results in very high cost at present. Therefore, further development of Activated Carbon for lower cost with higher adsorption capability is desired. The experimental results described in Section 2.3.4 of this Chapter showed the improved capability of nitrogen removal by acid treatment. This fact suggests that there is possibility for improving the adsorption capability with more economical process.

As for the sulfur removal, the experimental results shown in Section 2.3.1 in this Chapter indicated that the number of sulfur compounds in Straight Run Diesel is too large in comparison with Activated Carbon’s adsorption capability. Therefore, desulfurization of Straight Run Diesel solely with adsorption by Activated Carbon can not be the practical solution. However, Activated Carbon’s unique characteristic of “higher selectivity for removing the sulfur compounds of high boiling point “shows the potential for practical use as post treatment of Hydrodesulfurization.

Finally, Activated Carbon was tried to be used for adsorptive removal of sulfur compounds in FCC Gasoline, Hydrotreated Kerosene and LCO in Section 2.3.5 in this Chapter. However, none of the experimental result supports the needs of further studies.

2.5 Conclusion

The present section emphasizes following two points:

1. A particular Activated Carbon, MAXSORB-II, showed the excellent performance in the removal of nitrogen compounds in Straight Run Diesel by adsorption.
2. The number of sulfur compounds in Straight Run Diesel is too large in comparison with Activated Carbon’s adsorption capability.

3. The adsorption capability of Activated Carbon for nitrogen compound in Straight Run Diesel can be increased by further treatment with acid. The oxygen functional groups on surface of Activated Carbon plays roles on it.

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CHAPTER 3

EFFECTS OF NITROGEN AND REFRACTORY SULFUR COMPOUNDS REMOVAL ON THE DEEP HDS OF DIESEL

3.1 Introduction

In the series of study in Chapter 2, it was found that the Activated Carbons of high surface area has capability for removing not only the much more nitrogen compounds than silica but also heavier sulfur compounds from Straight Run Diesel [1-5]. The roles of nitrogen and refractory sulfur compounds on the Hydrodesulfurization have been extensively studied to clarify their inhibiting effect in the HDS mechanisms by using model mixture [6]. However, the results so far reported by many research groups could not draw a universal rule about the effects of removal extent of such compounds on the achievable sulfur content in the successive Hydrodesulfurized product due to the wide variation of reaction conditions and feed compositions. Quantitative description about effects of nitrogen and sulfur compounds in the feed oil on its deep Hydrodesulfurization can provide a practical guideline to specify the feedstock composition for achieving ultra low sulfur diesel.

In this Chapter, the pre-removal of nitrogen compounds has been reported to be very effective on the achievable sulfur content of Diesel [7,8], where nitrogen contents were varied at several levels and total sulfur content was fixed. However, both refractory sulfur content and nitrogen content in Straight Run Diesel must be counted to obtain the exact relationship between compositions of feed Diesel and achievable sulfur content in Hydrodesulfurized Diesel since Activated Carbon removed also refractory sulfur compounds to some extent. Such a relation is very useful to design the removal facility and operating conditions since the pre-treated feed must be evaluated about its achievable sulfur content with under HDS conditions.

The present study in this Chapter attempted to describe more quantitatively the removal effects of both nitrogen and refractory sulfur compounds on the Hydrodesulfurization of Straight Run Diesel. Combination of alumina and Activated Carbon of large surface area allowed the selective removal of refractory sulfur compounds as well as nitrogen compounds to provide a series of feed Diesels having various nitrogen and refractory sulfur contents. Such oils were Hydrodesulfurized over a conventional catalyst under the same condition to obtain a series of sulfur contents in the product oils which could be compared to the contents of nitrogen and refractory sulfur compounds in feed oils

3.2 Experimental

Straight Run Diesel (11,780 wt-ppm of sulfur content and 260 wt-ppm Nitrogen), which was provided by a Japanese commercial refinery, was used in this study as a feedstock for adsorptive treatment with Activated Carbon, followed by Hydrotreating with Catalyst. By changing the ratio of Straight Run Diesel and MAXSORB-II of Activated Carbon, treated Straight Run Diesel of 20 wt-ppm, 40 wt-ppm and 60 wt-ppm of nitrogen content was produced. In this operation, the refractory sulfur compounds (Dimethyl Dibenzothiophene and heavier) are also removed from Straight Run Diesel.

The Straight Run Diesel and pretreated Straight Run Diesel were Hydrodesulfurized over a commercially available HDS Catalyst ($CoMo/SiO_2–Al_2O_3$, surface area 208 m^2/g cat, pore volume 0.3 cm^3/g cat, acidity 0.7 $mmolNH_3/g$ cat) in an autoclave-type reactor (100 ml internal volume). Prior to the Hydrodesulfurization reaction, HDS Catalyst must be proceed with sulfiding operation, where heated at 360 degC in Hydrogen with 5% Hydrogen sulfide to replace the oxygen atom on Molybdenum to sulfur atom.

10 g of oil and 1 g of sulfide HDS Catalyst were charged into the autoclave-type reactor at room temperature. This reactor was heated to 340 degC by 50 min under initial Hydrogen pressure of 5.0 MPaG where Hydrodesulfurization reaction was taken place for 2 hr. The Hydrodesulfurized product of 0.5 ml was collected through a sampling tube fitted to the reactor and analyzed with GC-AED.

Similarly, feedstock for Hydrodesulfurization reaction with various combination of sulfur and nitrogen content by using OG-20A, MGC-B and Alumina. These feedstocks have proceeded with Hydrodesulfurization reaction for analysis of its kinetics.

3.3 Result

3.3.1 Hydrodesulfurization of treated Straight Run Diesels

Fig. 3.3.1a compares sulfur-chromatograms of Hydrodesulfurized products from the non-treated and treated Straight Run Diesels. The non-treated Straight Run Diesel and the treated Straight Run Diesels had the nitrogen contents of 260, 60, 40, 20 wt-ppm and the refractory sulfur content of 1680, 980, 920 and 860 wt-ppm, respectively.

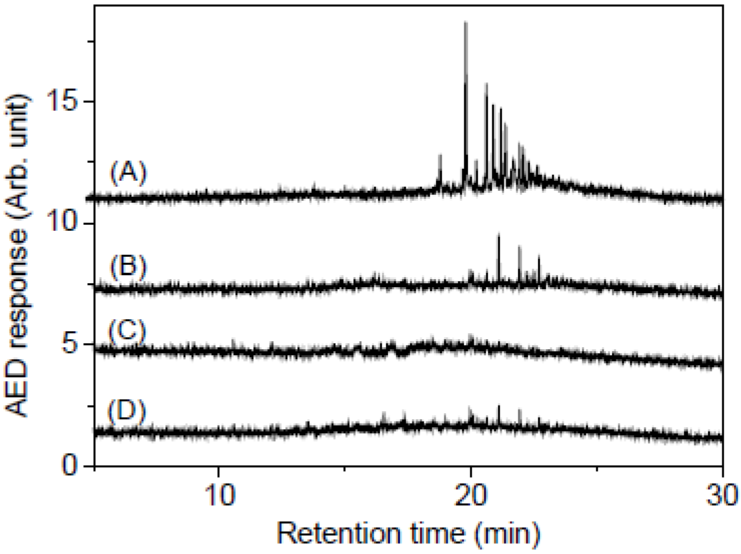

Fig. 3.3.1a Sulfur-chromatograms of Hydrodesulfurized products from (A) Straight Run Diesel and (B–D) treated Straight Run Diesels. Nitrogen contents were (A) 260, (B) 60, (C) 40 and (D) 20 wt-ppm. The content of refractory sulfur compounds were (A) 1680, (B) 980, (C) 920 and (D) 860 wt-ppm.

The adsorptive treatment for removing nitrogen compound and refractory sulfur compound in Straight Run Diesel was found very effective to enhance the Hydrodesulfurization Reaction, results in the reduced sulfur content in reaction effluent. While Hydrodesulfurized products of non-treated Straight Run Diesel shows 193 wt-ppm of remaining sulfur content, the Hydrodesulfurized products of treated Straight Run Diesel shows 11 wt-ppm, 8 wt-ppm and 7 wt-ppm of remaining sulfur content, respectively. This evident that the reduction of nitrogen level to be less than 60 wt-ppm obtained by adsorptive treatment accelerated Hydrodesulfurized to achieve the sulfur level less than 15 wt-ppm under the conventional Hydrodesulfurized conditions regardless of the contents of refractory sulfur compounds.

On the other hand, the nitrogen-free Straight Run Diesel can be obtained by using alumina as an adsorbent but the sulfur content of its Hydrodesulfurized product was reduced to only 41 wt-ppm under same condition. This fact supports the partial removal of refractory sulfur compounds, which is happened in Activated Carbon only, plays an important role of reducing the remaining sulfur content in Hydrodesulfurized product. Fig. 3.3.1b & Fig. 3.3.1c compare the sulfur and nitrogen chromatogram of Straight Run Diesel, treated by (1) Alumina and (2) MAXSORB-II of Activated Carbon.

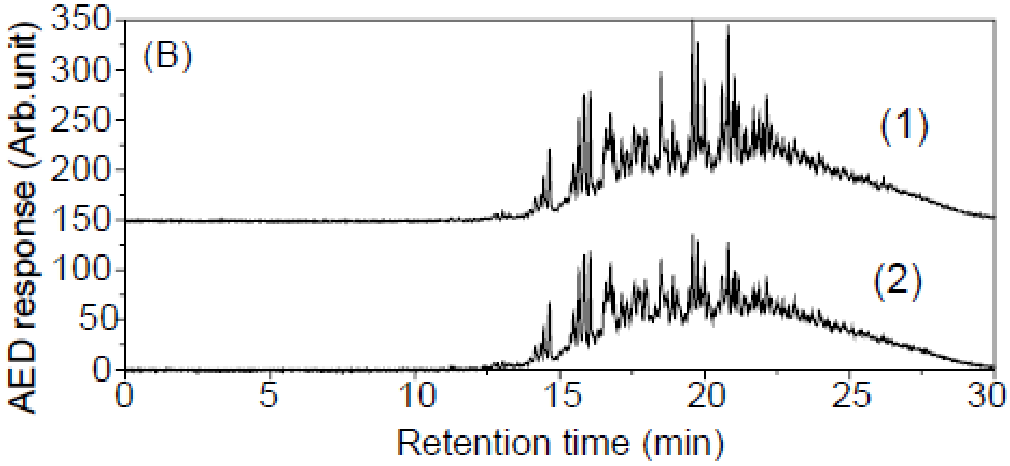

Fig. 3.3.1b Sulfur-chromatograms of treated Straight Run Diesel
(1) Alumina and (2) MAXSORB-II of Activated Carbon.

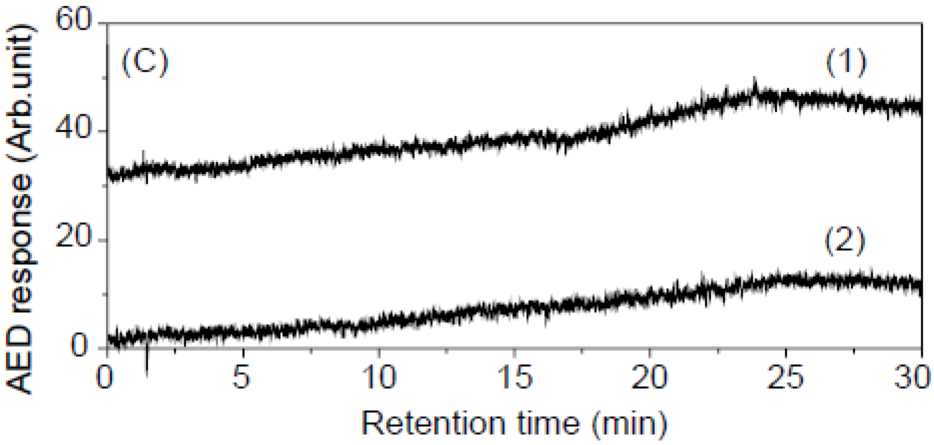

Fig. 3.3.1c Nitrogen-chromatograms of treated Straight Run Diesel (1) Alumina and (2) MAXSORB-II of Activated Carbon.

3.3.2 Hydrodesulfurization of treated Straight Run Diesels

Fig. 3.3.2a plots the remaining sulfur content in Hydrodesulfurized Diesel against Nitrogen Content in feedstock of Hydrodesulfurization Reaction, which is Straight Run Diesel treated with Activated Carbons.

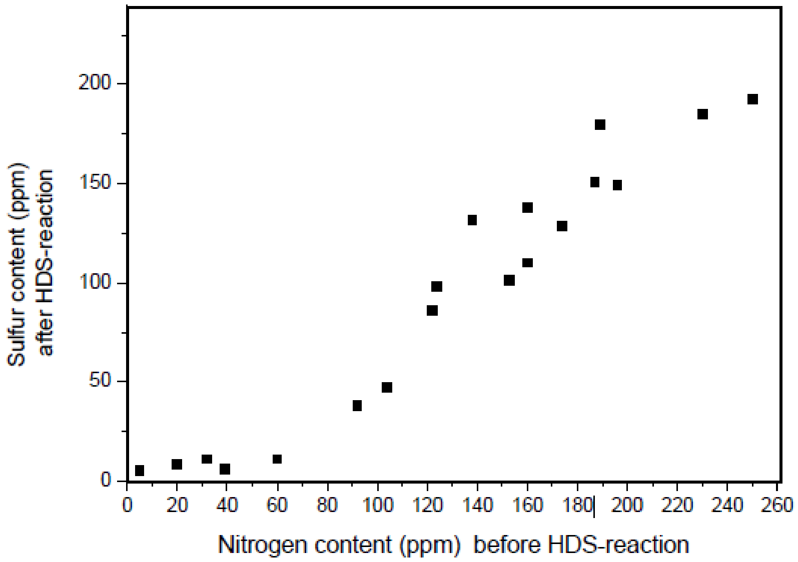

Fig. 3.3.2a Plot of sulfur content in Hydrodesulfurized oil with nitrogen content in feed oil.

In the range of nitrogen content in feedstock of less than 100 wt-ppm and remaining sulfur content in Hydrodesulfurized Product of less than 50 wt-ppm, the remaining sulfur content is reduced linearly as nitrogen in feedstock reduced. However, it was found that the reduction of nitrogen content in feedstock is not contributing the reduction of remaining sulfur content in Hydrodesulfurized Product if it is less than 60 wt-ppm.

Fig. 3.3.2b plots the remaining sulfur content in Hydrodesulfurized Diesel against Content of refractory sulfur compounds in feedstock of Hydrodesulfurization Reaction at the fixed nitrogen content of 35 wt-ppm.

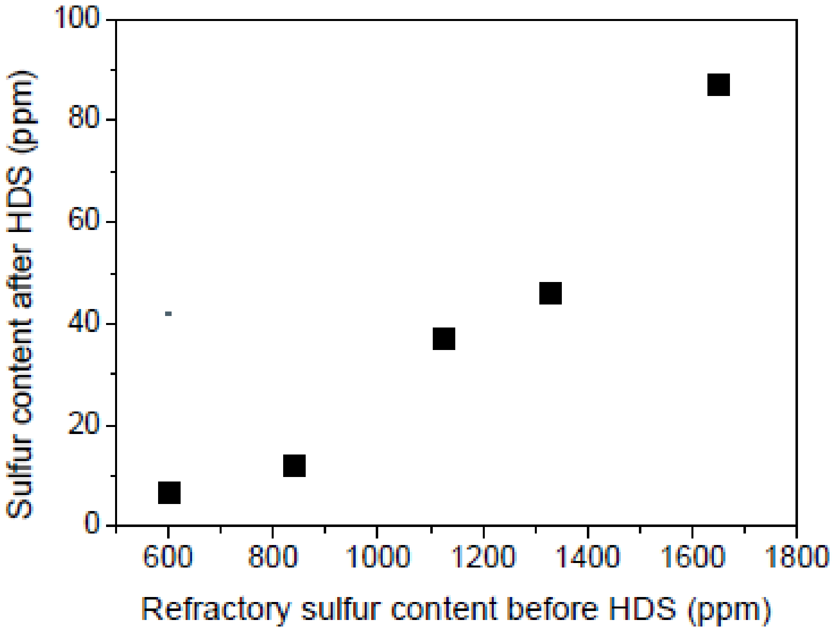

Fig. 3.3.2b Plot of sulfur content in Hydrodesulfurized oil with refractory sulfur compounds in feed oil, whose nitrogen content is 35 wt-ppm.

Similarly, the remaining sulfur content in Hydrodesulfurized Product is proportionally reduced when the remaining sulfur content if it is less than 20 wt-ppm of remaining sulfur compounds in Hydrodesulfurized Product but not linearly reduced in further range. The consistent tendency was found in the Fig. 3.3.2c, where the content of refractory sulfur compounds in feedstock is 900 wt-ppm and 1,200 wt-ppm / nitrogen contents in feedstock is varied from 0 wt-ppm to 60wt-ppm with 20 wt-ppm intervals

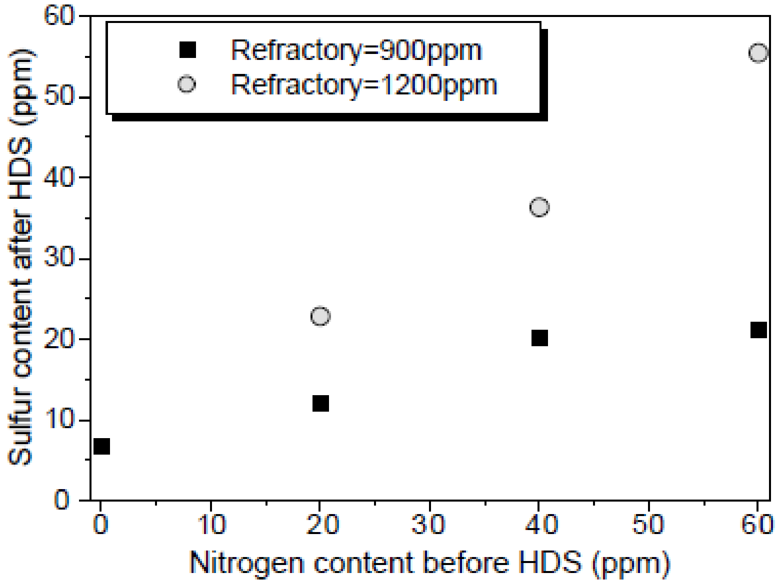

Fig. 3.3.2c Hydrodesulfurized of treated oils with various content of nitrogen compounds at fixed content of refractory sulfur compounds.

3.3.3 Hydrodesulfurized Reaction kinetics when the content of both nitrogen and refractory sulfur compounds in feed oil were varied

Even without adsorptive treatment on feedstock, the reactive sulfur compounds will be disappeared from Hydrodesulfurized product. This indicates that the reduction kinetics of reactive sulfur compounds is very rapid and the remaining sulfur content in Hydrodesulfurized product is governed principally by the remaining content of refractory sulfur compounds. Therefore, we may approach that the reaction kinetics of diesel desulfurization is equivalent to reaction kinetics of refractory sulfur compounds.

Per studies by Topsoe [9,10] and other Catalyst Manufacturers, Kinetics for Hydrodesulfurization of refractory sulfur compounds is described by the following equation:

$$r_{\text{refractory}} = \frac{\mathrm{d}C_{\text{refractory}}}{\mathrm{d}t} = k_{\text{refractory}} \times C_{\text{refractory}}$$

where $k_{refractory}$ (h^{-1}) and $C_{refractory}$ (wt-ppm) are the apparent rate constant and content of refractory sulfur compounds, respectively. The rate constant can be described by Langmuir–Hinshelwood type equation to include the inhibition terms of nitrogen compounds on the same active site for refractory sulfur compounds as following:

$$k_{\text{refractory}} = \frac{k^*_{\text{refractory}}}{1 + a \times C_{\text{refractory}} + b \times C^d_{\text{nitrogen}}}$$

The inhibition terms of H_2S and NH_3 were not included in this equation as those are constant value in this experience. By using all data obtained in the present study, the values of $k^*_{refractory}$, a, b and d are determined statically as 3.3 h^{-1}, 0.00039 wt-ppm^{-1}, 0.00275 wt-ppm^{-1} and 0.75, respectively. This equation with these values allows to calculate the Hydrodesulfurized rates of refractory sulfur compounds. Calculated values of $k_{refractory}$ are compared with those of observed $k_{refractory}$ as shown in Fig. 3.3.3. The observed values of $k_{refractory}$ agreed well with the calculated ones, indicating proper description of Equation above for the inhibition of nitrogen compounds on the Hydrodesulfurized of refractory sulfur compounds.

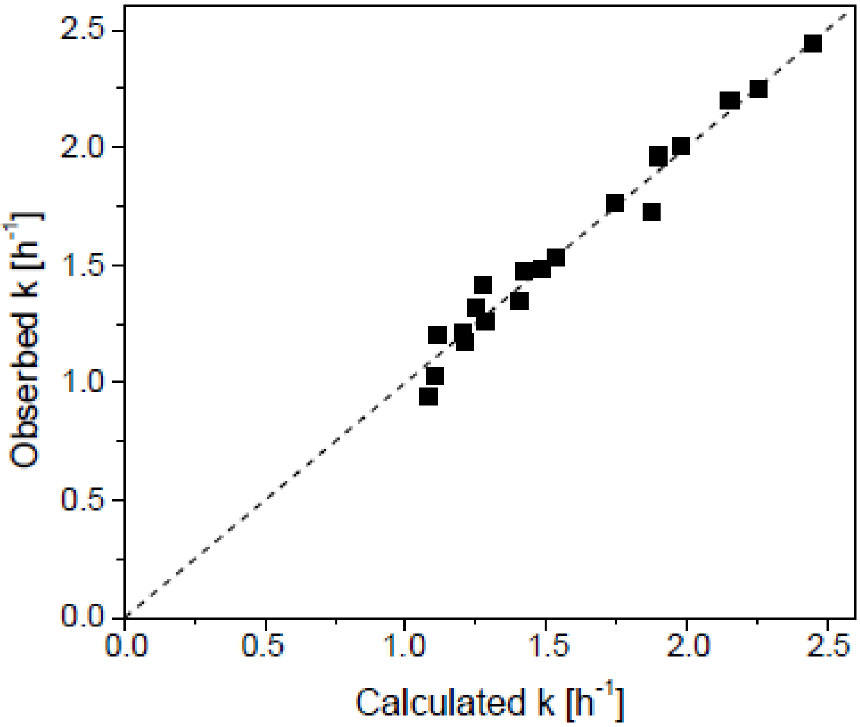

Fig. 3.3.3 Plot of calculated reaction constant with observed reaction constant.

3.4 Discussion

3.4.1 Contribution of nitrogen and refractory sulfur compounds removal to deep Hydrodesulfurization

Ultra deep desulfurization of Diesel to reduce sulfur level to be less than 10 wt-ppm can be achieved by Hydrodesulfurization. As the reactive sulfur compounds are converted to H_2S at the early stage of Hydrodesulfurization Reaction, the Hydrodesulfurization of refractory sulfur compounds governs the remaining sulfur content in Hydrodesulfurized Diesel.

In this regard, as indicated in the experimental facts in this chapter, the removal of the nitrogen content and content of refractory sulfur compound shows remarkable improvement on the reactivity of Hydrodesulfurization. In other word, the nitrogen compound and refractory sulfur compound shows are considered as serious inhibitors for Hydrodesulfurization reaction.

Hence, the reduction of nitrogen compounds and/or refractory sulfur compounds at the pre-treatment step is very effective to reduce the sulfur content in Hydrodesulfurized product. In such a case, removal of nitrogen compounds through the adsorptive treatment over silica, alumina, silica–alumina and Activated Carbon showed the considerable improvement of its Hydrodesulfurization reactivity as reported in previous literatures [1-5,11,12] and Fig. 3.3.2b. Among such adsorbents, Activated Carbon showed the exceptional performance, removing refractory sulfur compounds as well as nitrogen compounds. Removal of both compounds results in the deeper Hydrodesulfurization than the removal of just nitrogen alone as reported in a previous paper [1-5] and shown in Fig. 3.3.2c of the present study.

3.4.2 Kinetics of Hydrodesulfurized

Langmuir–Hinshelwood kinetics has been widely applied in the Hydrodesulfurization of DBT and alkylated DBTs. However, the nitrogen effects were not extensively studied on kinetic bases, in particular, by using the practical feed yet.

We set up a simple equation as indicated in Section 3.3.2 by adding the inhibiting terms of refractory sulfur compounds and nitrogen compounds. Laredo et al. reported the following kinetic model for Hydrodesulfurization of DBT which was inhibited by indole, indoline and o-ethylaniline, respectively [6]:

$$k^*_{\mathrm{DBT}} = \frac{k_{\mathrm{DBT}}}{1 + K_{\mathrm{N}} \times C^n_{\mathrm{N}}}$$

where K_N is the apparent adsorption equilibrium constant of nitrogen compounds (l/mol), $C_{nitrogen}$ and n the initial nitrogen compound concentration (mol/l) and the fitting exponent, respectively. There were good relations between calculated values and observed values in the report. Laredo et al. proposed n value of carbazole as 0.5 in Hydrodesulfurization of DBT [6] while our results indicate n value of 0.75, which was estimated in deep range Hydrodesulfurization. Such a difference may suggest that the inhibition by carbazoles is more sensitive to their contents in the real Diesel at deep Hydrodesulfurization region than that observe in the model mixtures.

Topsoe et al. showed Equation below, which could be used to describe the kinetics for very deep desulfurization of Diesel over NiMoS and CoMoS catalysts [10]:

$$r = \frac{k \times C^n_{\mathrm{sulfur}} \times P_{\mathrm{H_2}}}{1 + K_{\mathrm{H_2}}S \times P_{\mathrm{H_2}}S} + \frac{k \times C^m_{\mathrm{sulfur}} \times P_{\mathrm{H_2}}}{1 + K_{\mathrm{F}} \times C_{\mathrm{F}}}$$

In this equation, the first term represents the direct extraction route, which is enhanced by an increase of the Hydrogen partial pressure and inhibited by the presence of H_2S.

The second term represents the Hydrogenation route, which is also enhanced by an increase of the Hydrogen partial pressure and inhibited by the presence of aromatic compounds, and in particular heterocyclic compounds such as carbazoles (denoted by F in the equation). In the present report, the first term and P_{H_2} were regarded to be constant and second term was investigated in detail.

Nitrogen compounds and refractory sulfur compounds must competitively adsorb on the active site for Hydrogenation of their aromatic rings, which is believed as the first step of their elimination reactions. As described above, non-basic nitrogen compounds such as carbazoles adsorb also preferentially on the active site, inhibiting the Hydrodesulfurization of refractory sulfur compounds.

Refractory sulfur compounds such as 4,6-DMDBT are Hydrodesulfurized on the same active sites as nitrogen compounds. The bottleneck step in Hydrodesulfurization of refractory sulfur compounds may be their adsorption on these sites. Hence, Hydrodesulfurization of refractory sulfur compounds is strongly inhibited by nitrogen compounds and the inhibition effects can be described as a Langmuir–Hinshelwood equation (3). The value of d in Eq. (3) was 0.75, indicating the inhibition severity per one molecule of nitrogen compounds becomes bigger as the content of nitrogen compounds is lower. Eq. (3) explains well the trends found in Fig. 3.3.2b; the removal of nitrogen compounds governed the achieved sulfur content after Hydrodesulfurization when nitrogen content is higher than 100 wt-ppm. However, the achieved sulfur content after Hydrodesulfurization is governed by the content of refractory sulfur compounds not by that of the nitrogen compounds when the nitrogen content is lower than 100 wt-ppm.

The data bank of our present study is not large enough to analyze the results of Hydrodesulfurization in the whole range by the equations. As the first approximation, the initial content of nitrogen and refractory sulfur compounds in the feed oil are assumed to be influential on the sulfur contents after Hydrodesulfurization reaction over the same catalyst under the same conditions. The good agreement of observed and calculated values of Hydrodesulfurization in Fig. 3.3.3 indicates the validity of the first approximation, confirming the effectiveness of both nitrogen and sulfur compounds removal by the adsorptive pretreatment for deep Hydrodesulfurization of Diesel.

3.5 Conclusion

There is liner relationship between nitrogen contents of Hydrodesulfurized feed oil and sulfur content of Hydrodesulfurized product at the range of nitrogen content more than 100 wt-ppm. Also, it is essential to remove the refractory sulfur compounds to improve the Hydrodesulfurized reactivity as well.

However, in accordance with Langmuir–Hinshelwood type equation described in this chapter, the Hydrodesulfurization reaction kinetics in the ultra deep desulfurization region (> 10 wt-ppm as target) will be very low due to its low sulfur content. Therefore, the pre-treatment for removing the sulfur and nitrogen compound may not be the best option to achieve the ultra deep desulfurization of diesel oil.

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CHAPTER 4

TWO-STEP ADSORPTION PROCESS FOR DEEP DESULFURIZATION OF DIESEL OIL

4.1 Introduction

This study proposes an integrated process for deep desulfurization including the adsorption steps as shown in Fig. 4.1, which is consist of Pre-Treatment Step, Conventional Hydrodesulfurization Step and Post Treatment Step.

As presented in Chapter 2 and Chapter 3, the reaction kinetics in conventional Hydrodesulfurization is remarkably improved when Straight Run Diesel is processed by adsorptive Pre-Treatment Step, using Activated Carbon. Also, Post-Treatment Step using Activated Carbon will remove the sulfur compounds in Hydrodesulfurized Diesel by adsorption and can reduce the sulfur content from 50 wt-ppm to less than 10 wt-ppm. This will relax the severity in Conventional Hydrodesulfurization Step since reaction kinetics of Hydrodesulfurization is very low in this region.

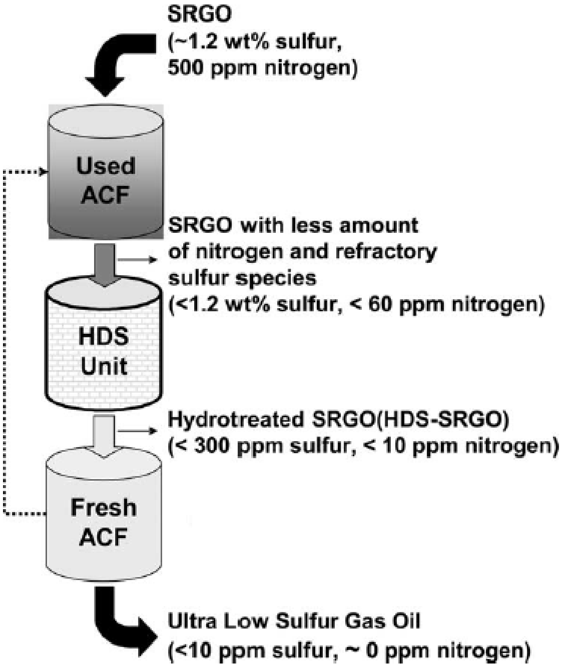

Fig. 4.1 The concept of consecutive adsorption process.

The key issues in this section is to prove the following two points:

- Activated Carbon has capability to produce the ultra deep desulfurized diesel oil with less than 10 wt-ppm of sulfur content.
- Activated Carbon, which is breakthrough on sulfur adsorption, can still be utilized for nitrogen adsorption
- Activated Carbon has ability to be regenerated and reused.

4.2 Experimental

4.2.1 Adsorptive treatment of Hydrotreated Diesel

0.3 g of Activated Carbon of OG-20A was dried at 110 degC under vacuum for 2 hrs. and packed into the stainless-steel tube of 50 mm length and 6 mm diameter. Hydrodesulfurized Diesel was fed into the tube by an HPLC pump at the rate of 0.1 ml/min and at the pressure of about 20 psi. The adsorption temperature was maintained at 30 degC by a water bath. The eluted oil from adsorption bed was sampled as much as 0.05 ml at every 60 min and their sulfur contents were analyzed by GC-AED. This experimental has been carried out for two sets of Hydrodesulfurized diesel were used as feedstocks, one contains 50 wt-ppm of sulfur compounds and the other contains 300 wt-ppm of sulfur compounds.

4.2.2 Re-use of Activated Carbon after adsorptive treatment of Hydrodesulfurized Diesel Product

With same operating conditions described in section 4.2.1, Hydrodesulfurized Diesel was fed into the tube with Activated Carbon until the sulfur content in eluted oil reached at 10 wt-ppm. Once sulfur content in eluted oil reached at 10 wt-ppm, feedstock was changed to Straight Run Diesel and continue the operation. The eluted oil was collected until accumulated liquid reached to 27 ml. The collected oil was Hydrodesulfurized by using an autoclave-type reactor of 100 ml internal volume. Catalyst used in the Hydrodesulfurized was a commercially available CoMo/SiO_2–Al_2O_3, which was pre-sulfided by 5% H_2S/H_2 at 360 degC for 2 h. 10 ml oil, 1 g catalyst, and 50 kg/cm^2 Hydrogen gases were mixed in the reactor. Reaction temperature was set at 340 degC and kept for 2 hrs. After the reaction, the liquid is collected and analyzed by GC-AED for sulfur content.

4.2.3 Changes in adsorption capability with various additives

10 wt% of toluene, decane, decaline, tetralin and 10 – 50 wt% of 1-metylnaphthalene were mixed with 30 ml of Hydrodesulfurized Diesel, whose sulfur content is 300 wt-ppm. 0.3 g of Activated Carbon (OG-20A) was dipped in each liquid and stirred. Then, the collected liquid was analyzed with GC-AED and adsorbed amount of sulfur components were calculated.

This experimental was purposed to investigate how the aromatic, paraffinic and naphthenic material impacts on Activated Carbon's capability for removing the sulfur compounds from Hydrodesulfurized Diesel.

4.2.4 Regeneration of the used Activated Carbon fiber

After adsorptive treatment described in Section 4.2.2, the remaining diesel in adsorption bed were purged out by nitrogen gas. After complete purge out, toluene, 1-methyl naphthalene and tetralin was fed into the adsorption bed. The eluted liquid from adsorption bed was collected every 10 ml and its sulfur and nitrogen content was analyzed with GC-AED.

Used Activated Carbon, breakthrough with sulfur and nitrogen compounds after adsorption experiment, was washed by toluene, 1-methyl-naphthalene and tetralin for regeneration. Used Activated Carbon was dipped into the 50 ml of solvents for 2 hrs. at 70 degC under ultrasonic radiation. The solvent used for regeneration was also analyzed by GC-AED for desorbed nitrogen and sulfur compounds.

Activated Carbon was filtered and dried at 120 degC under vacuum and proceed with adsorptive treatment for Straight Run Diesel. With analysis for treated oil, the amount of adsorbed sulfur and nitrogen compounds over regenerated Activated Carbon was calculated.

4.3 Result

4.3.1 Feed characterization

The sulfur/nitrogen chromatogram of Straight Run Diesel / Hydrodesulfurized Diesel are illustrated in Fig. 4.3.1 and those quantitative values are summarized in Table 4.3.1.

The sulfur chromatogram shows the peaks in retention time less than 20 min, representing Benzothiophenes (BTs) and dibenzothiophenes (DBTs) as a major sulfur compounds in Straight Run Diesel. Although those peaks are disappeared in Hydrodesulfurized Diesel, (1) 4-methyl dibenzothiophene (4-MDBT), (2) 4,6-dimethyldibenzothiophene (4,6-DMDBT) and (3) 2,4,6-trimethyl dibenzothiophene (2,4,6-TMDBT) are still shown. These components are so called “refractory sulfur compounds”, which have lowest reactivity among the sulfur compounds contained in Straight Run Diesel. The most abundant sulfur molecule in Hydrodesulfurized-Straight Run Diesel was 4,6-dimethyldibenzothiophene.

Most of nitrogen compounds found in Straight Run Diesel were carbazoles (Cz) as indicated in Fig. 4.3.1. Refractory nitrogen compounds, such as (4) 1-methylcarbazole (1-MCz), (5) 1,8-dimethylcarbazole (1,8-DMCz) and (6) 1,4,8-trimethylcarbazole (1,4,8-TMCz) were found in Hydrodesulfurized Diesel. However, adsorptive treatment of Hydrodesulfurized Diesel by Activated Carbon, removed almost all of nitrogen compounds.

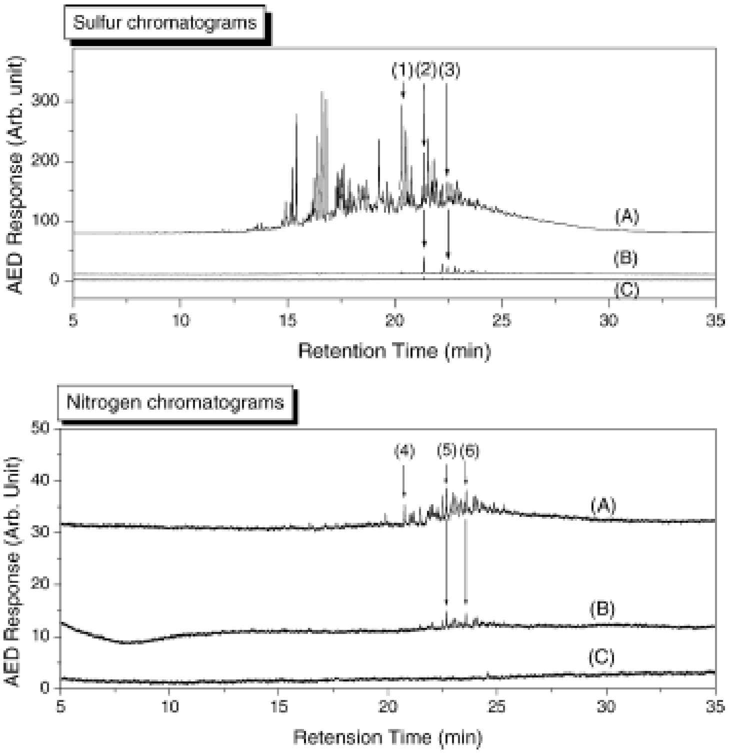

Fig. 4.3.1 Sulfur and Nitrogen chromatograms of (A) Straight Run Diesel, (B) Hydrodesulfurized Diesel (C) Hydrodesulfurized Diesel with adsorptive treatment.

Table 4.3.1a Sulfur and nitrogen content in Diesel Oils

	Sulfur (ppm)	Nitrogen (ppm)
SRGO	11780	260
HDS-SRGO	300	30
AD-HDS-SRGO	50	0[a]

[a] Below 1 ppm.

4.3.2 Adsorptive removal of sulfur compounds in Hydrodesulfurized-Straight Run Diesels

Fig. 4.3.2a shows the sulfur chromatograms of Hydrodesulfurized Diesel (50 wt-ppm of sulfur content) and its treated oils with Activated Carbon. The treated oils after 20 ml feeding over 1 g of Activated Carbon showed only two peaks of mono-methyl DBTs and one peak of dimethyl-mono-ethyl DBT. 97% of sulfur compounds in Hydrodesulfurized Diesel was removed when 1 g of Activated

Carbon treated 20 ml of oil and 88% of sulfur compounds in Hydrodesulfurized Diesel was removed when 1 g of Activated Carbon treated 40 ml of oil.

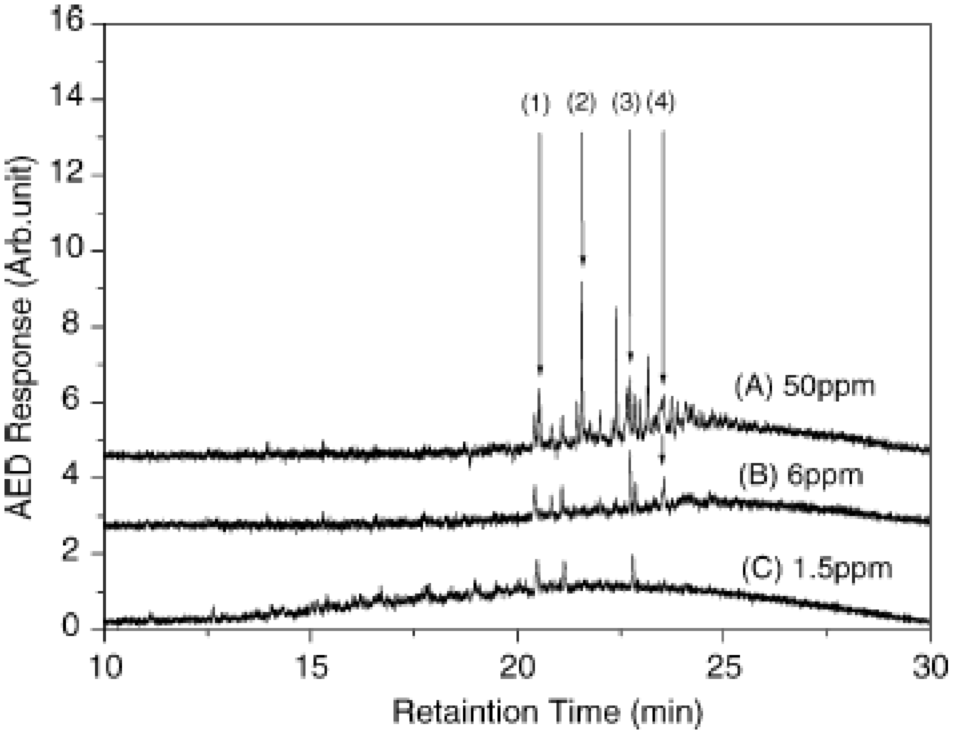

Fig. 4.3.2a Sulfur chromatograms of (A) Hydrodesulfurized Diesel, treated after (B) 40 ml and (C) 20 ml of oil.
(1) 4-Methyldibenzothiophene,
(2) 4,6- dimethyl dibenzothiophene,
(3) 4-ethyl, 6-methyldibenzothiophene,
(4) 4,6- diethyl dibenzothiophene.

Fig. 4.3.2b shows the sulfur breakthrough profiles of Hydrodesulfurized Diesels with 50 wt-ppm and 300 wt-ppm of sulfur compounds. By using 1 g of Activated Carbon, sulfur content in treated oil exceed 10 wt-ppm (breakthrough) when sulfur content in feedstock is 50 wt-ppm and 70 ml of oil is processed by. In case of feedstock with 300 wt-ppm of sulfur content, only 12 ml oil can be treated before breakthrough.

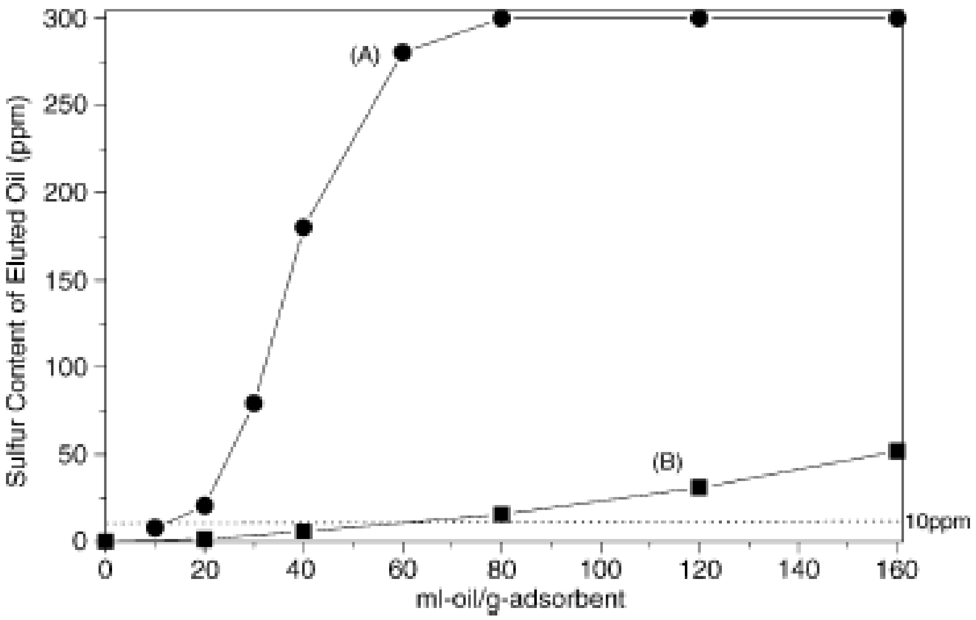

Fig. 4.3.2b Sulfur breakthrough profiles of Hydrodesulfurized Diesel with (A) 300 wt-ppm (B) 50 wt-ppm of sulfur content.

4.3.3 Effects of aromatic additives

Fig. 4.3.3 shows the sulfur chromatograms of (A) Hydrodesulfurized Diesel, treated with Activated Carbon and (B) Hydrodesulfurized Diesel plus 50 wt% 1-methylnaphthalene, treated with Activated Carbon. All peaks for sulfur components in (B) are higher than (A). This indicates that the addition of 1-methylnaphthalene reduced the adsorption capability of Activated Carbon for sulfur compounds.

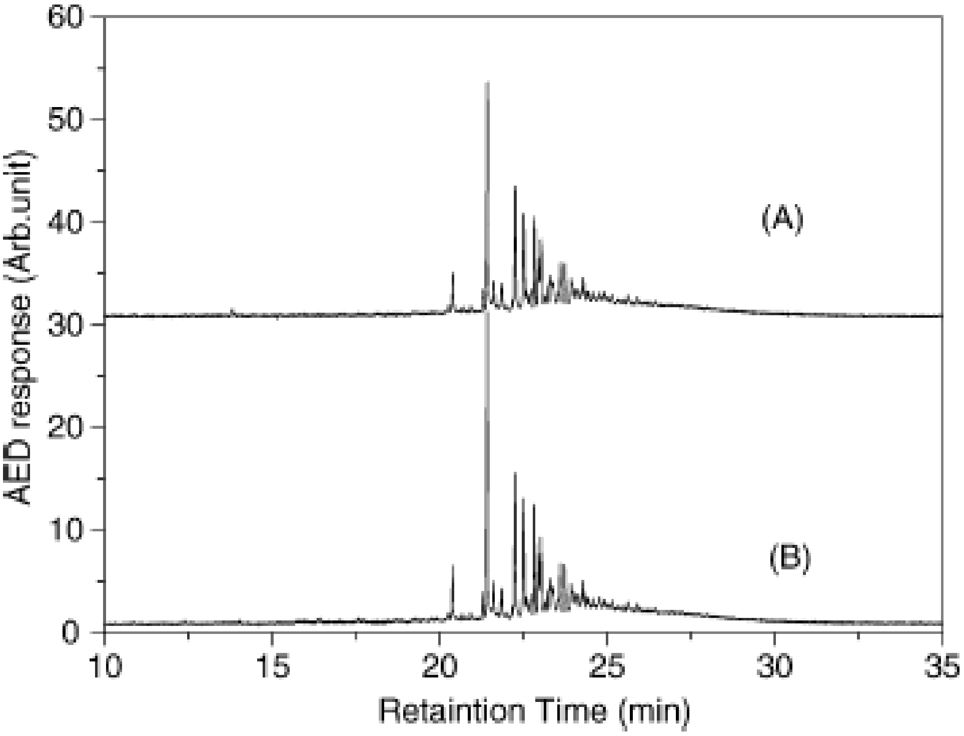

Fig. 4.3.3 Sulfur chromatogram of treated diesel of:
(A) Hydrodesulfurized Diesel (No additives)
(B) 50 wt% of 1M-Naphthalene added Hydrodesulfurized Diesel

Table 4.3.3 shows the removed amount of sulfur compound by Activated Carbon, among the several additives to Hydrotreated Diesel. Adding the Decane (paraffine) and Decaline (naphthene) results in the slight reduction of the adsorption capability. On the other hand, addition of aromatic compounds, such as toluene, naphthalene, tetralin shows remarkable reduction on the adsorption capability. Among the aromatic compounds, 2-ring aromatics has bigger negative impacts on adsorption capability than 1-ring aromatics.

Table 4.3.3 The effects of coexists on adsorption capacity of sulfur compounds

Feed	Removed amount of sulfur species (mg-sulfur)
HDS-SRGO	3.13
HDS-SRGO + 10%-decane	2.67
HDS-SRGO + 10%-decalin	2.92
HDS-SRGO + 10%-1-metyl naphthalene	1.82
HDS-SRGO + 30%-1-metyl naphthalene	0.42
HDS-SRGO + 50%-1-metyl naphthalene	0.23
HDS-SRGO + 30%-toluene	1.88
HDS-SRGO + 30%-tetralin	1.46

4.3.4 Adsorptive removal of nitrogen compounds in Straight Run Diesel over Activated Carbon

Fig. 4.3.4a shows the nitrogen breakthrough profiles of Straight Run Diesel over (A) Virgin OG-20A. (B) Spent OG-20A, treated 100 ml of Diesel with 300 wt-ppm of sulfur content (C) Spent OG-20A, treated 100 ml of Diesel with 50 wt-ppm of sulfur content (D) Spent OG-20A, treated 20 ml of Diesel with 300 wt-ppm of sulfur content.

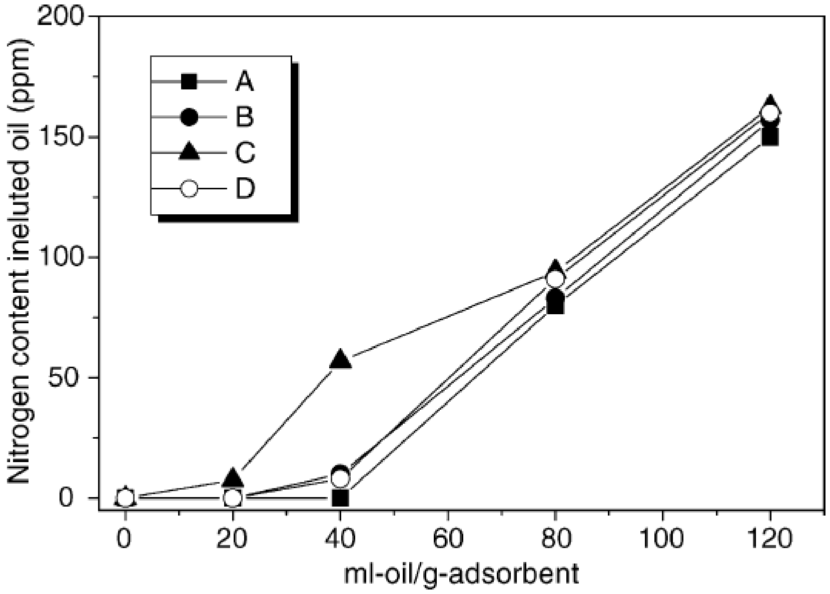

Fig. 4.3.3a Nitrogen breakthrough profiles from Straight Run Diesel over virgin and spent OG-20A

Almost all of spent Activated Carbons showed the same profiles for removal of nitrogen compound as virgin Activated Carbon. This experimental result indicates that the Activated Carbon of breakthrough for sulfur removal is still be valid for removal of nitrogen compound and their active site for adsorption is different.

Fig. 4.3.4b shows the sulfur chromatograms of collected treated oil in this experimental. The used Activated Carbon for Diesel of 50 wt-ppm sulfur content remains the capacity of removing sulfur compound in Straight Run Diesel while Activated Carbon for Diesel of 300 wt-ppm does not show the capacity of removing sulfur compound in Straight Run Diesel.

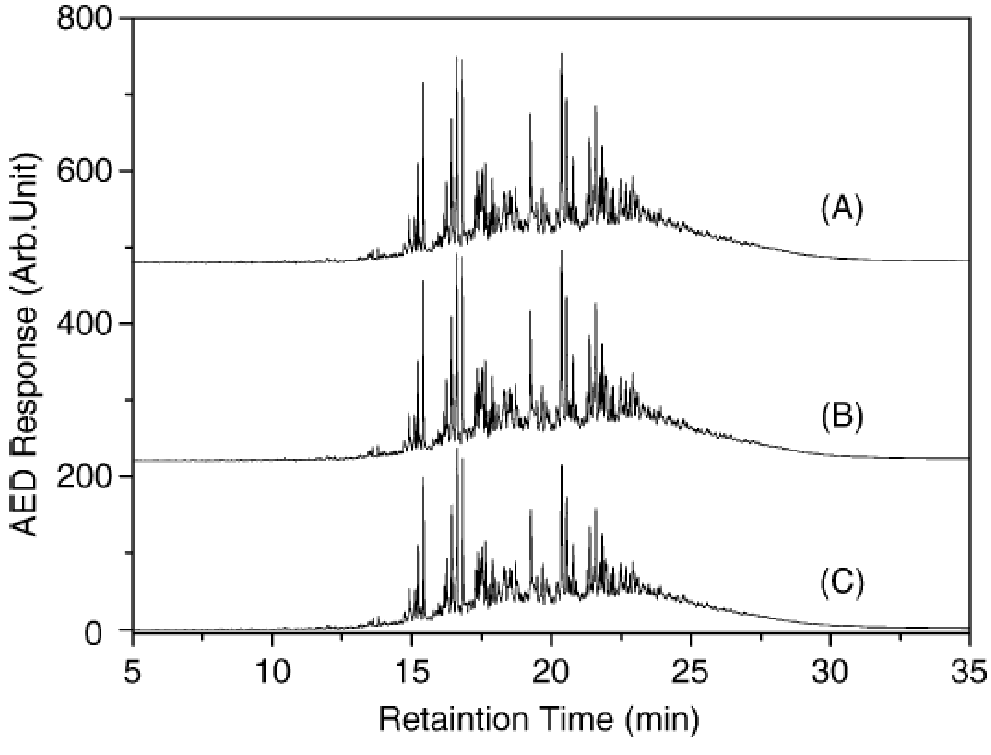

Fig. 4.3.4b Sulfur chromatograms of:
(A) Straight Run Diesel, Straight Run Diesel treated by Spent OG-20A

(B) treated 100 ml of Diesel with 300 wt-ppm of sulfur content (C) treated 100 ml of Diesel of 50 wt-ppm of sulfur content.

Fig. 4.3.4c shows the sulfur chromatograms of Hydrodesulfurized product of (A) Straight Run Diesel (11780 wt-ppm of sulfur content, 260 wt-ppm of nitrogen content) and (B) treated Straight Run Diesel (11400 wt-ppm of sulfur content, 40 wt-ppm of nitrogen content). over used Activated Carbon.

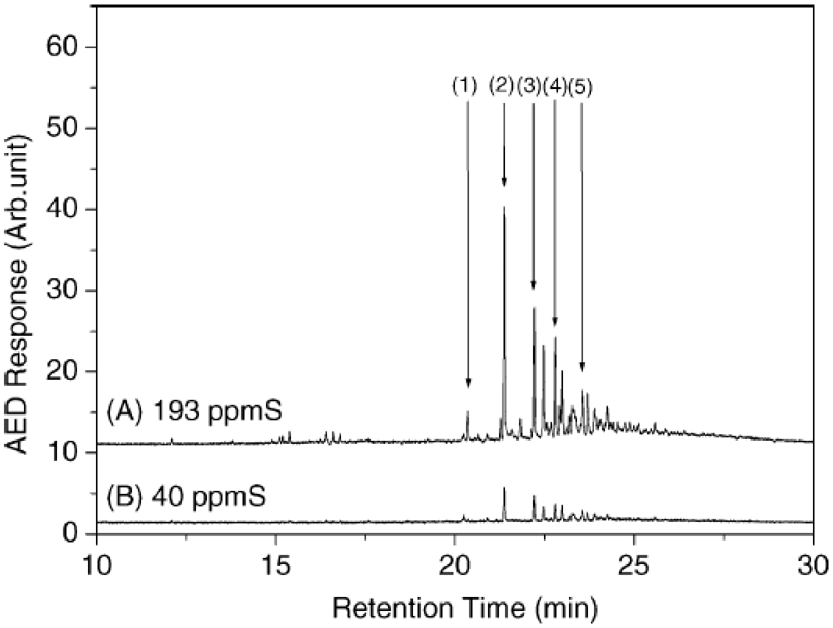

Fig. 4.3.4c Sulfur chromatograms of Hydrodesulfurized products from (A) Straight Run Diesel (B) treated Straight Run Diesel
(1) 4-Methyldibenzothiophene,
(2) 4,6- dimethyl dibenzothiophene,
(3) 4-ethyl, 6-methyldibenzothiophene,
(4)1,4,6-trimethyldibenzothiophene,
(5) 4,6-diethyldibenzothiophene.

This experimental result indicates that the kinetics of Hydrodesulfurization Reaction is improved even by adsorptive treatment with spent Activated Carbon, which is breakthrough with sulfur adsorption.

4.3.5 Regeneration of spent Activated Carbon

The sulfur and nitrogen content in eluted solvent (toluene, 1-methyl naphthalene and tetralin) from spent Activated Carbon are plotted in Fig. 4.3.5a.

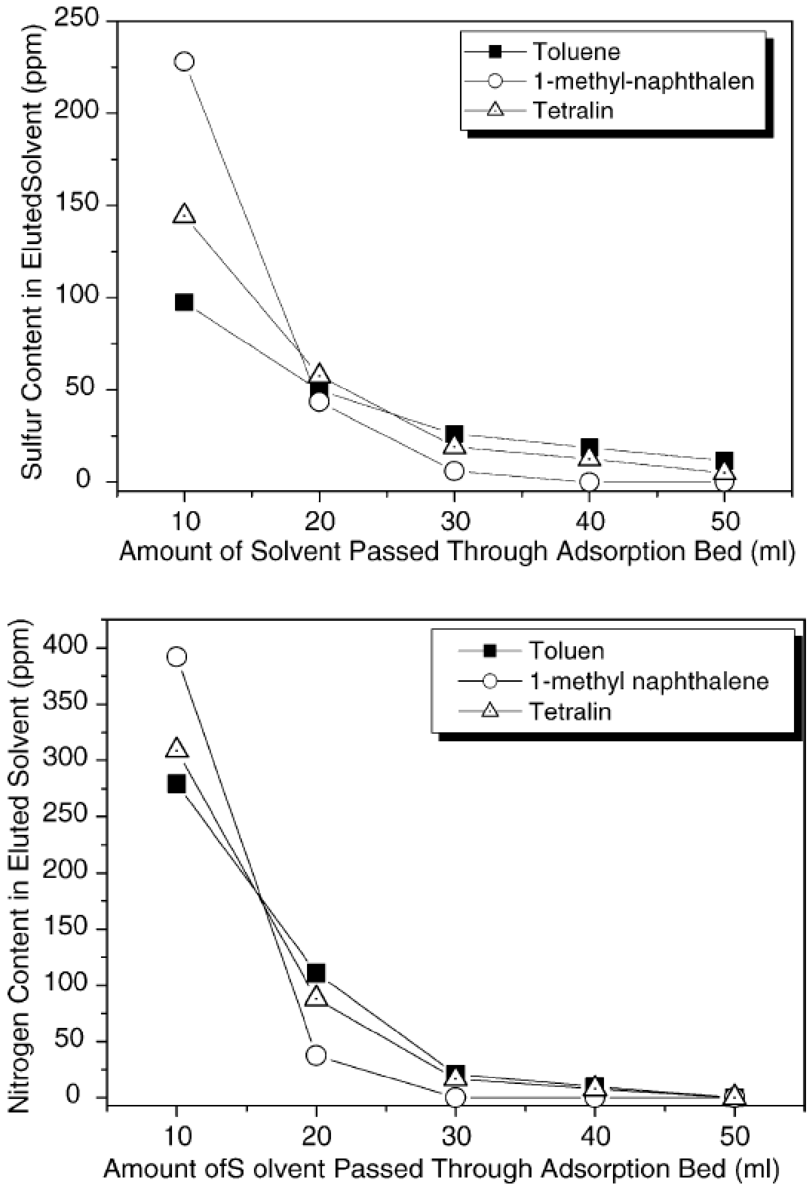

Fig. 4.3.5a Sulfur and nitrogen content of eluted solvents from spent Activated Carbon.

Among three solvents, 1-Methylnaphthalene contains the highest sulfur and nitrogen content in 1st drop to 15 ml of eluted oil. This fact is consistent with the experimental results described in Section 4.3.4 and indicates that 1-Methylnaphthalene has higher affinity to Activated Carbon / inhibit the adsorption of sulfur molecule to Activated Carbon.

Fig. 4.3.5b shows the removal amount of sulfur compounds in Hydrodesulfurized Diesel and nitrogen compounds in Straight Run Diesel over the regenerated Activated Carbon. Regenerated Activated Carbon showed the same adsorption capacity for nitrogen in Straight Run Diesel and sulfur compounds in Hydrodesulfurized-Straight Run Diesel.

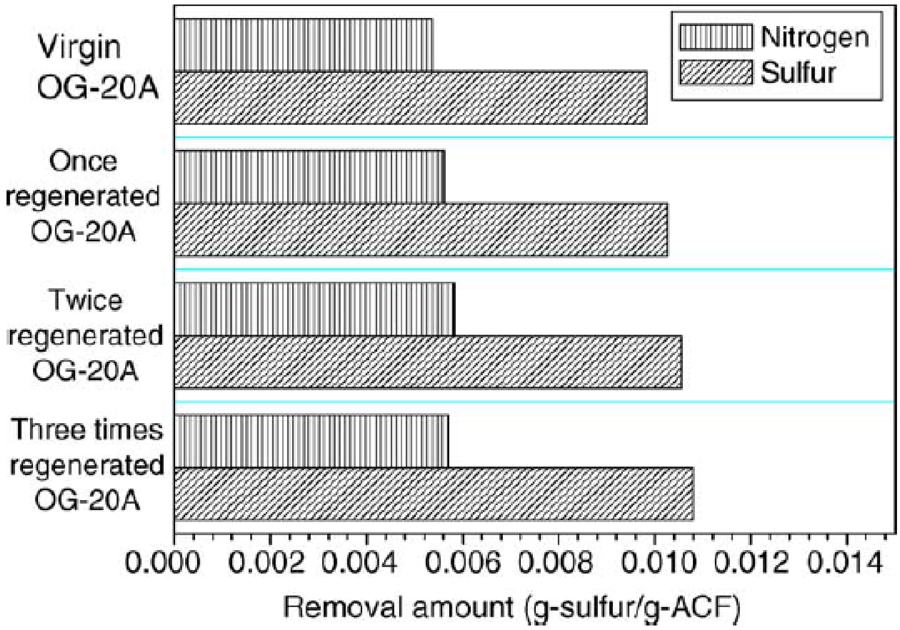

Fig. 4.3.5b Removal amount of sulfur compounds in Hydrodesulfurized Diesel and nitrogen in Straight Run Diesel over virgin and regenerated Activated Carbon.

4.4 Discussion

The achievements described in this Chapter are summarized as followed.

1. Sulfur component in Hydrodesulfurized Diesel (50 – 300 wt-ppm) can be adsorbed with Activated Carbon and reduced to less than 10 wt-ppm.
2. Spent Activated Carbon of sulfur breakthrough remains the capability for removing nitrogen compounds in Straight Run Diesel. Adsorptive treatment with this Spent Activated Carbon showed remarkable improvement of reactivity in Hydrodesulfurization.
3. Used Activated Carbon can be successfully regenerated by the aromatic solvent without losing the adsorption capability for sulfur and nitrogen compound in Diesel.

Adsorptive removal of sulfur compounds from Hydrodesulfurized Diesel with 300 wt-ppm of sulfur content to get the ultra low sulfur diesel described in the present paper may be impractical due to very short operation time to breakthrough as shown in Fig. 4.3.2b. However, slightly deeper Hydrodesulfurized Diesel with 50 wt-ppm of sulfur content, which could be easily attained with the conventional Hydrodesulfurized reaction when nitrogen compounds in Straight Run Diesel are removed prior to Hydrodesulfurized, showed much longer breakthrough time to reach 10 wt-ppm of sulfur content. Thus, the present process requires Hydrodesulfurization of Straight Run Diesel to be less than 50 wt-ppm of sulfur content in order to obtain the acceptable amount of treated oil. Furthermore, early eluted Diesel can be used for fuel cell because it contained less than 1 wt-ppm of sulfur content. Hydrodesulfurized of Straight Run Diesel to be less than 50 wt-ppm of sulfur content could be achieved more easily by the pre-treatment to remove nitrogen compounds over Activated Carbon as described in our previous papers [1-4] and Fig. 4.3.5c. Thus, Activated Carbon bed can be used consecutively for the adsorbent for the both of pre- and post-treatment steps.

In the experimental conducted in this Chapter, it was found that addition of aromatic solvent decreased the adsorption capacity of Activated Carbon. Especially, 1-methylnaphthalene of even 10% decreased the adsorption amount of sulfur to be a half. Such results suggested the limitation of the present process to treat the highly aromatic Diesel such as light cycle oil. However, this result suggested the possibility for regeneration of spent Activated Carbon, which is the essential process to apply this scheme commercially.

As described in Section 4.3.5, the studies in this Chapter proved that the Activated Carbon bed breakthrough with sulfur and nitrogen compounds can be successfully regenerated by conventional aromatic solvents. Hence, the life time of adsorbents, which is a very important factor in the practical operation, is believed to be long enough to minimize the operation cost. Repeated use of Activated Carbon does not lower the performance but reduce the cost of adsorbent. When the pre- and post-treatment steps have each adsorption bed, four adsorption beds must be installed (two for adsorption, two for regeneration) for continuous operation whereas the present integrated process needs three (two for two adsorptions, one for regeneration) as shown in Fig. 4.3.5. This leads to the reduction of initial investment.

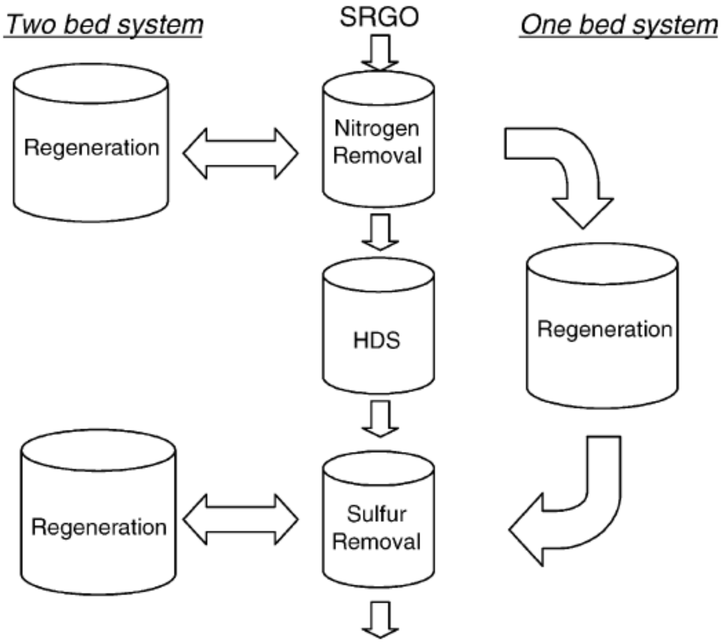

Fig. 4.4 Comparing the one bed system with two bed system

This process may be attractive to refiners even they have capability to produce the diesel product with less than 10 wt-ppm of sulfur content. It is very critical task to assure the sulfur content of diesel oil to be less than regulated value, that is 10 wt-ppm in Euro IV. In general, refineries control the reaction temperature, space velocity and Hydrogen/feed oil ratio to maintain the product specifications. However, the tolerance range in operating condition must be very narrow if the product specifications are ultimately limited. Hence, some kinds of back up facility should be installed to protect the fails of product quality, which is frequently encountered in the practical operation. Since additional reactor or blending facility for this purpose may not be the realistic solution due to economics. The present authors suggest the adsorption bed as the backup facility to desulfurize the diesel having off-specification.

4.5 Conclusion

A novel integrated process including adsorption system for pre- and post-treatment of Diesel was proved to achieve ultra deep desulfurization by using the OG-20A (Activated Carbon) as an adsorbent. Consecutive use of Activated Carbon for Hydrodesulfurized Diesel and Straight Run Diesel reduced the number of adsorption bed, loss of feed oil and severity of Hydrodesulfurization by removing the nitrogen and refractory sulfur compounds in Straight Run Diesel. Sulfur content in Hydrodesulfurized Diesel as a feedstock to is recommended to have less than 50 wt-ppm for minimizing the regeneration cycles.

4.6 References

[1] Y. Sano, K.-H. Choi, Y. Korai, I. Mochida, Applied Catalysis B 49 (2004) 219.

[2] Y. Sano, K.-H. Choi, Y. Korai, I. Mochida, Energy Fuels 18 (2004) 644.

[3] Y. Sano, K.-H. Choi, Y. Korai, I. Mochida, American Chemical Society Division of Fuel Chemistry 48 (1) (2003) 138.

[4] Y. Sano, K.-H. Choi, Y. Korai, I. Mochida, American Chemical Society Division of Fuel Chemistry 48 (2) (2003) 658.

CHAPTER 5

COST AND ENERGY EFFICIENT PROCESS FOR ULTRA LOW SULFUR DIESEL FUEL PRODUCTION

5.1 Introduction

Many of refiners in developing country is suffering from committing the new severer regulation on fuel oil, especially for diesel. Increasing concerns for environmental pollutions motivates the local government for applying the severer regulation. However, refiners in developing country have difficulty to modify their existing facilities with following reasons:

- Financial Constraint – The local refiners has serious constraint for making the profit due to the presence of Maga-sized exporting refineries in Middle East. Their operation cost is very competitive by its scale merit, higher product yield of latest technology, lower operation cost of new equipment, lower labor cost etc…
- Space Constraint – The most of refinery in the developed country experienced the several major revamp projects for increasing the throughput to meet the demand of local market. Therefore, the required plot area is not available in the same plot area of existing facility and feasibility of revamp project is drastically reduced
- Aged facilities – Most of the facilities in existing units are aged and severer operating condition for new specification enhances the risk for incident due to corrosion and erosion. The most of refiner hesitates to proceed with revamp project due to this safety reasons.
- Constraint in related facilities – Changes in the operating condition in Diesel Desulfurization Unit may cause the impact on the Hydrogen production unit, amine regeneration unit and sour gas treating unit and utility supply system. This cascading effect may provide the similar constraint described above.

In these connections, the adsorptive treatment with Activated Carbon as pre- and post-treatment of Hydrodesulfurization will be highly likely fits.

In this Chapter, feasibility study has been conducted for implementation of the "Post-Treatment" Section described in Section 4. The study basis is as per following conditions, which are often found in typical refineries in Southeast Asia and South America:

- Local government wishes to implement the severer specification for diesel in the local market (from 50 wt-ppm to 10 wt-ppm)
- An existing Hydrodesulfurized unit is in operation at full capacity to produce with 50 wt-ppm diesel, there have been several revamps in the past, and available plot area for further revamps is limited.
- FCC, RFCC or Coker Unit is in operation in the existing refinery complex.

The background for limiting the feasibility study in post treatment is because the extent of benefit in applying the pre-treatment section is highly depending on the existing facilities and difficult to be quantified.

5.2 Basis of Study

5.2.1 Conceptual Flow Scheme

The concept of the proposed new flow scheme is illustrated in Fig. 5.2.1. The Straight Run diesel of 1.5 wt% sulfur is Hydrodesulfurized in the existing conventional Hydrodesulfurization reactor to reduce the sulfur content to meet the current regulation of 50 wt-ppm of sulfur content. This stream is then further processed using adsorbers filled with Activated Carbon to remove the remaining sulfur compounds to meet the 10 wt-ppm of sulfur content.

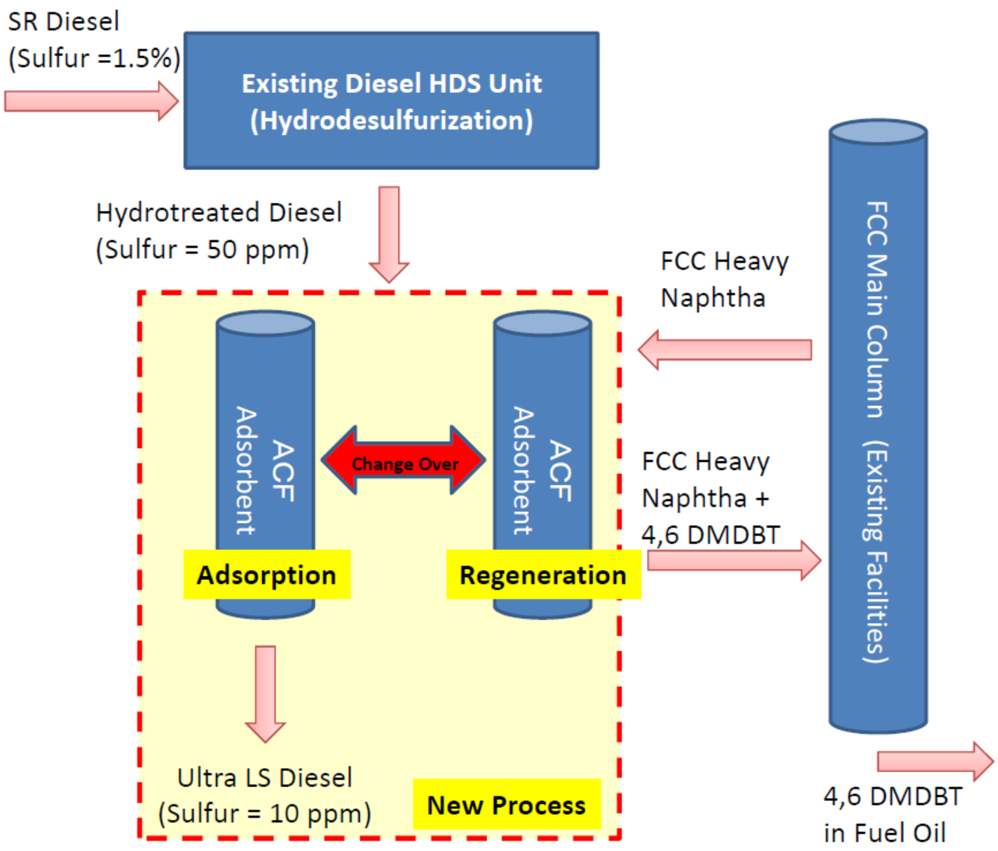

Fig. 5.2.1 Conceptual Flow Scheme for Ultra-deep Desulfurization Process

The spent Activated Carbon, which is saturated with adsorbed sulfur and nitrogen compounds, is processed in the regeneration step for reuse. An aromatic light distillate, such as heavy naphtha, from an FCC or RFCC unit, Coker naphtha from a Delayed 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 wt-ppm of sulfur content diesel.

5.2.2 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. 5.2.1, the existing Hydrodesulfurized unit is considered a pre-treatment section, removing the majority of sulfur compounds and producing 50 wt-ppm of sulfur content diesel. 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 Hydrodesulfurized unit. The additional facility for reducing the sulfur content from 50 wt-ppm to 10 wt-ppm is a post-treatment section, detailed in Fig. 5.2.2, where the remaining sulfur in Hydrodesulfurized 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.

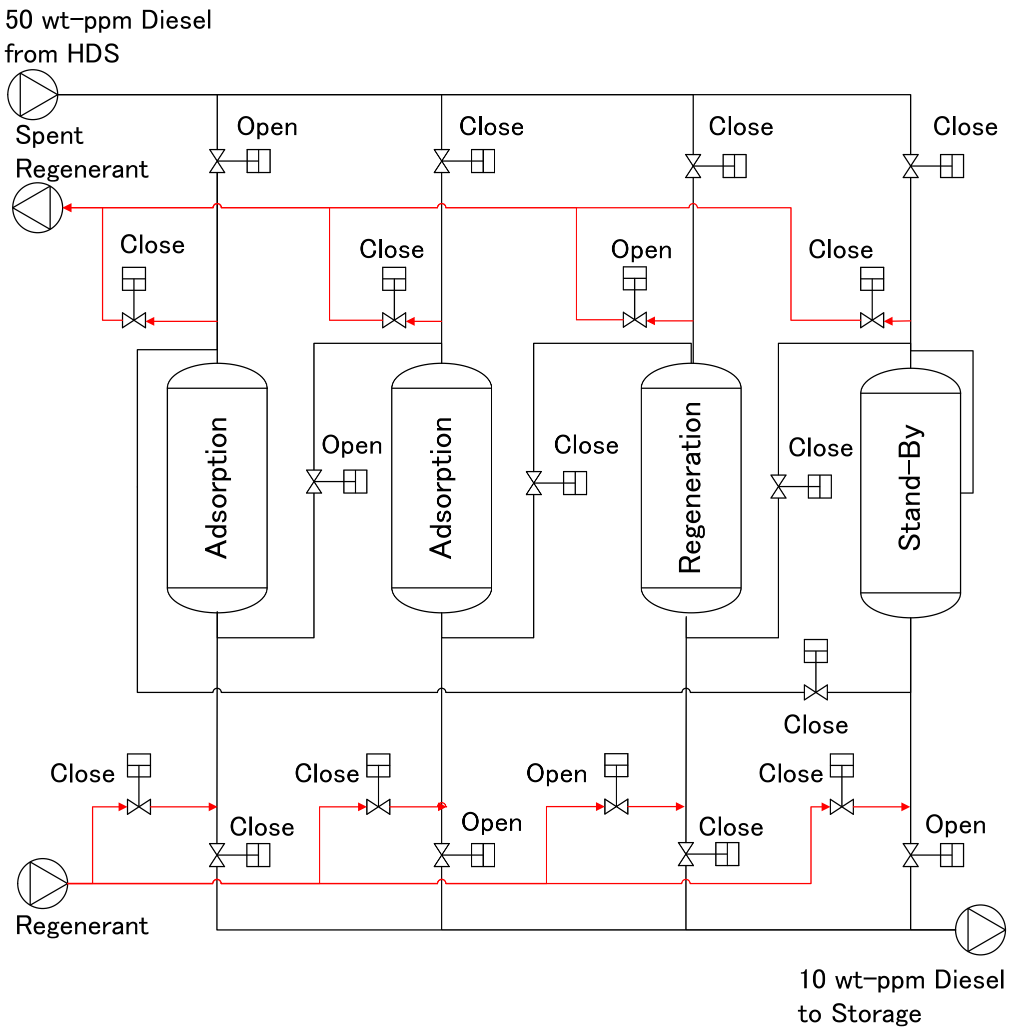

Fig. 5.2.2 Configuration of Absorbers for Adsorption and Regeneration

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

However, increased severity in the existing Hydrodesulfurized unit is required with the conventional process. The required operating conditions in the Hydrodesulfurization reactor for production of 50 wt-ppm of sulfur content diesel and 10 wt-ppm of sulfur content diesel are compared in Table 5.2.2.

Table 5.2.2 Comparison of New Process Scheme and Conventional Process

	New Process Scheme	Conventional Process
Sulfur in Reactor outlet	50 wt-ppm	10 wt-ppm
Catalyst Volume	**83 m^3**	**127 m^3**
Reactor Pressure Drop	2.0 kg/cm^2	3.1 kg/cm^2
Chemical H_2 Consumption	**300 SCFD/BBL**	**330 SCFD/BBL**
H_2 Partial Pressure	40 kg/cm^2	40 kg/cm^2

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 5.2.2, an additional 53% of catalyst is required to reduce the sulfur content from 50 wt-ppm to 10 wt-ppm 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 Hydrodesulfurized reaction are exponentially proportional to the bulk sulfur content 3). This additional catalyst volume increases the pressure drop in the reactor loop, affecting the required differential head and increasing energy required by the recycle compressor.

Another major effect on energy consumption in Table 5.2.2 is an additional 10% in Hydrogen consumption. This is the result of Hydrogeneration of single ring aromatics, which partially occurs when the Hydrodesulfurization reactor is targeting 10 wt-ppm of sulfur content diesel production. This increases the operating costs owing to the additional Hydrogen production required.

5.2.3 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. 5.2.3a.

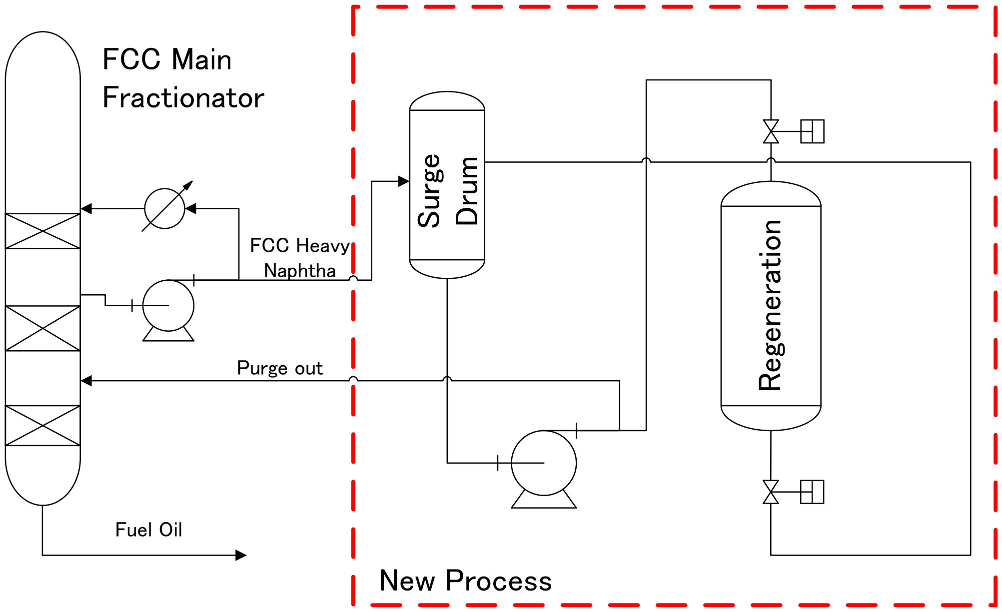

Fig. 5.2.3a Configuration of Regenerant Supply from and Return to Refinery

In the previous research 3), 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 Fig. 5.2.3b and Fig. 5.2.3c, is explained.

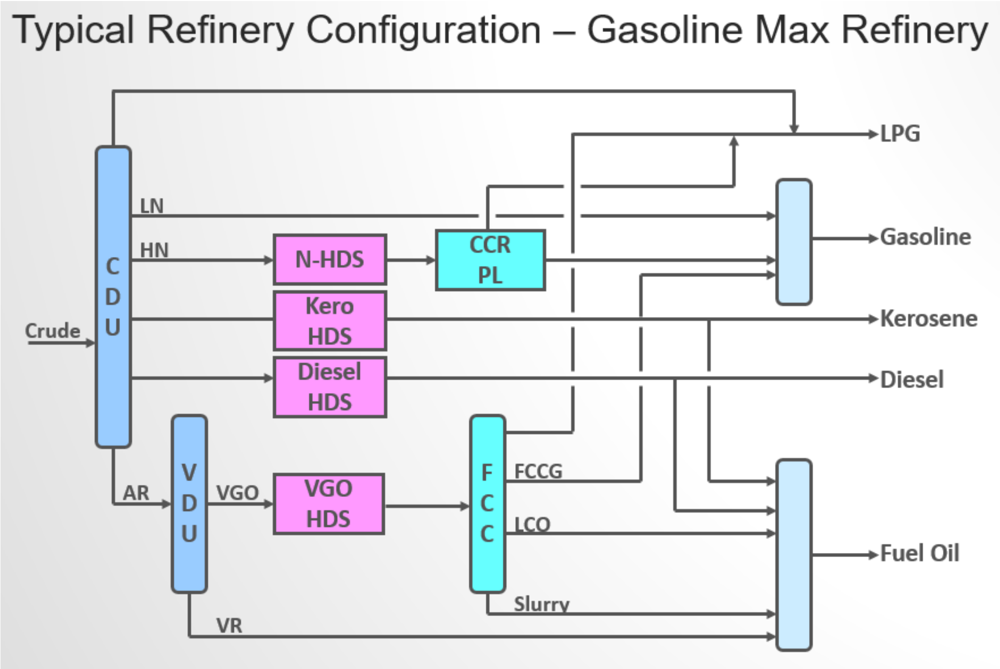

Fig. 5.2.3b Typical Refinery Configuration – Gasoline Max Refinery

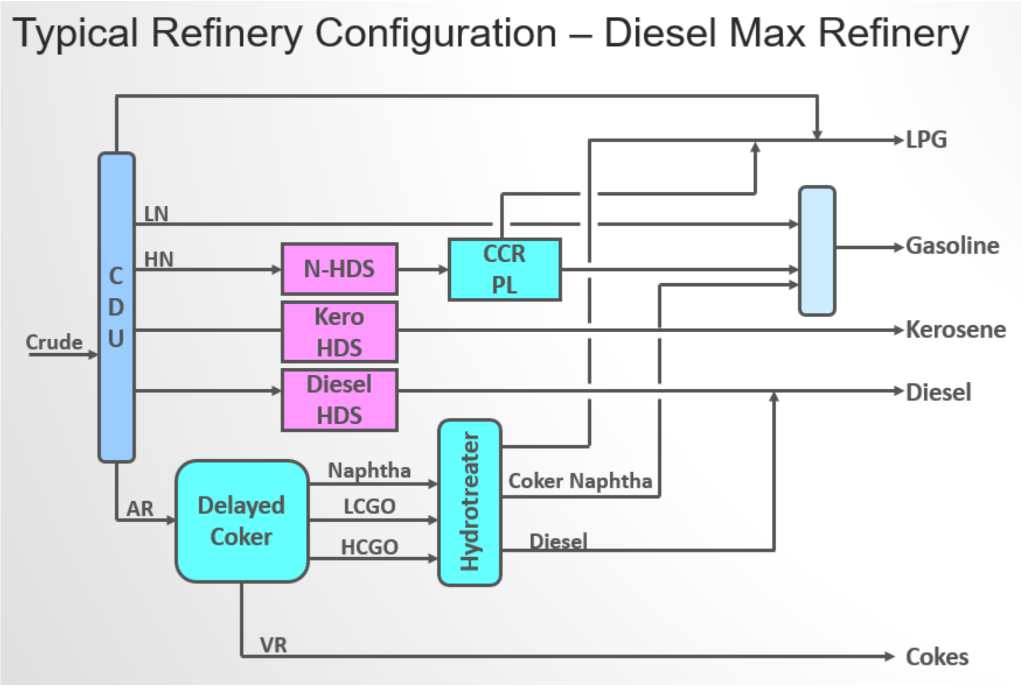

Fig. 5.2.3c Typical Refinery Configuration – Diesel Max Refinery

In the refinery configuration of Fig. 5.2.3b, the most suitable stream for regeneration of Activated Carbon is FCC heavy naphtha, considering its aromaticity and reprocessing path. The Coker naphtha from the Delayed Coker Unit in the refinery configuration in Fig. 5.2.3c 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 DMDBT or TMDBT of T.B.P = 366 – 380 degC +, 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 5.2.3).

Table 5.2.3 Comparison of FCC Main Fractionator Operating Conditions

	Original Operation	Proposed Scheme
Heavy Naphtha / LCO gap (*)	10.6 degC	9.6 degC
LCO / SLO gap (*)	25.3 degC	26.2 degC
LCO P/A Duty	20.1 MW	20.1 MW
HCO P/A Duty	45.3 MW	44.1 MW

(*) ASTM D86 Gap between 95% distillate of light stream and 5% distillate of heavy stream

The present data given from the process simulator is on the follow basis:

FCC Unit Capacity:	65,000 BPSD
Regenerant Supply Return:	300 BPSD

The results shown in Table 5.2.3 indicate that this proposed new scheme does not significantly affect the FCC unit operation and refinery energy balance.

The final step is the drying of the adsorption bed using nitrogen under vacuum conditions to remove the hydrocarbons captured in the adsorption bed.

5.3 Result

5.3.1 Additional Equipment & Their Size

Based on the experiment, the average amount of Activated Carbon required to reduce the sulfur content from 50 wt-ppm to 10 wt-ppm was 1 g of Activated Carbon per 120 ml of treated oil, as shown in Fig. 5.3.1.b.

Thus, for 25,000 BPSD of diesel production, 22 m^3 of Activated Carbon is required as an adsorbent, with an adsorber change out period of 12 hr. As shown in Fig. 5.2.2, 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 as follows:

Absorbers & Vessels

Service	Number	Inside Día.	Tangential Length
Absorbers	4	2,500 mm	6,000 mm
Surge Drum	1	1,500 mm	4,000 mm

Pumps

Service	Number	Capacity	Diff. Head
Regeneration Pump	2	150 m^3/hr	90 meters

Others

Absorbent:	100 m3
Ejectors:	2
Analyzers:	3

As an order of magnitude estimate, the provision of these new facilities requires less than 20 Million USD for engineering, procurement and construction.

5.3.2 Required Modification in Existing Facilities for Conventional Process

As indicated in Table 5.2.3, an additional 53% of catalyst is required for the Hydrodesulfurization reactor reduce the sulfur content of diesel produced from 50 wt-ppm of sulfur content to 10 wt-ppm, 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 wt-ppm of sulfur content specification for diesel requires the following major modifications:

- Replacement or modification of the reactor

- Modification of the Hydrogen supply facilities to increase the Hydrogen 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 Hydrodesulfurized unit for 10 wt-ppm of sulfur content and build a new diesel Hydrodesulfurized unit to compensate for the reduced throughput. This approach costs only a few million USD, depending on the size of the new unit.

5.4 Discussion

As noted in Section 5.3 of this paper, the conventional process–achieving the lower sulfur content in diesel by increasing the severity of Hydrodesulfurization 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. The proposed new scheme of post treatment for Hydrodesulfurization of Straight Run Diesel using the adsorptive process, is technically and economically justified for ultra-low sulfur diesel production. In the real world, the present author experienced the termination, postpone or major changes in Front End Engineering Design for revamp project due to constraints of existing facility, which are explained in Section 5.1. With proposed new scheme, however, does not conflict with those constraint and thus the best solutions. Although the use of this technology in revamp project was studied in this Chapter, application in newly built units are expected to be feasible since catalyst volume, reactor pressure drops, required Hydrogen partial pressure can be reduced by increasing the reactivity in Hydrodesulfurization with pre-treatment and target reduction of target sulfur content in reactor outlet by replying on the post treatment.

There might be further utilization of this technology for residue hydrotreating process and hydrocracking process. In the normal design of those unit, the reactor contains the desulfurization catalyst for the purpose to produce the diesel product of 10 wt-ppm sulfur. By using this technology, catalyst bed for Hydrodesulfurization can be eliminated, which reduce the size of reactor, reactor pressure drops and required Hydrogen partial pressure. Another benefit for application of this process is to extend the life of catalyst. As the severity of reactor is drastically lowered, the life catalyst will be longer, and interval of turnaround maintenance can be prolonged, which provides the financial benefit.

One of the remarkable finding in this Chapter is the discovery of Regenerant for Activated Carbons. As explained in the Chapter 4, it was proven that the Aromatic Solution, such as toluene, 1-methyl naphthalene and tetralin, can be used as desorbent of adsorbed sulfur and nitrogen compounds for regeneration. Although dedicated distillation process was proposed for separation of sulfur / nitrogen compounds from desorbent in Chapter 4, utilization of FCC Gasoline, Coker Naphtha and Reformate from CCR Platformer shall have economic benefit from operation cost and capital cost.

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

5.5 Conclusion

The proposed adsorptive sulfur removal process produces the 10 wt-ppm of sulfur content diesel with minimal effect on the existing refinery operation, as shown in Section 5.2. 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.

5.6 References

[1] Y. Sano, K.-H. Choi, Y. Korai, I. Mochida, Applied Catalysis B 49 (2004) 219.

[2] Y. Sano, K.-H. Choi, Y. Korai, I. Mochida, Energy Fuels 18 (2004) 644.

[3] Y. Sano, K.-H. Choi, Y. Korai, I. Mochida, American Chemical Society Division of Fuel Chemistry 48 (1) (2003) 138.

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CHAPTER 6
CONCLUSIONS

6.1 Summary of Research

The sulfur free fuel is desired to reduce the emission of pollutant to reduce the environmental issues. As of 2018, developed country such as western Europe, North America and Japan, and Refinery purposed for exporting to those country have completed the renewal of existing refinery to produce the sulfur free fuel, which meets the regulation. This trend is now in approach to developing country, such as South East Asia, South America, etc…

The government of those countries, however, hesitates to apply this new regulation considering the status of existing domestic refineries, who are not capable of producing such high-quality fuel. Due to growing environmental concerns, those refineries are planning to modernize their facilities to meet new regulation. However, there are several challenges for refineries in developing country to meet the new severer regulation. The examples are as follows:

- More catalyst is required for existing refinery since reaction kinetics is extremely lower in the region of 50 wt-ppm of sulfur content and less.
- The nitrogen compound in diesel inhibit the desulfurization reaction
- The reactivity increases in higher temperature, but hydrocarbon will be decomposed when temperature getting higher than 380 degC
- Severer reaction condition results in more Hydrogen consumption, which affects the Hydrogen network in refinery.
- As refinery repeated the revamp on existing facility, the available design margin on major equipment is no longer available

The series of researches have evident that the Activated Carbon has the unique characteristics – adsorbing the refractory sulfur compounds and nitrogen compound in Straight Run Diesel with high selectivity. Also, the series of research discovered that the adsorptive treatment of Straight Run Diesel with Activated Carbon provides the remarkable improvement for Hydrodesulfurization Reaction due to reduced amount of nitrogen compounds. Likewise, adsorptive treatment for Hydrotreated Straight Run Gas Oil (Referred as H-Straight Run Diesel, hereafter.) produced the “zero sulfur Gas Oil”, which is desired from oil market.

Adsorptive treatment is, by nature, highly energy efficient process and thus always preferred in the industry. Through the series of researches and experience in actual refinery construction project, authors found that the adsorptive treatment for Gas Oil with Activated Carbon will be the final piece of Gas Oil Desulfurization Process, integrated with current technology in commercial plant.

Chapter 1

In this Chapter as a first step, the relationship between sulfur compounds remained in automotive fuel and environmental pollution is described to support the background of this Doctoral dissertation. As a reference, the history of sulfur regulation for diesel and gasoline in product Japan was introduced.

Then, reality of refinery business and application of sulfur regulation for gasoline and diesel in the world was described as well as typical flow scheme of Diesel Hydrodesulfurization Facility is explained to identify the constraint for refiners. The facts described in this Chapter emphasis the strong needs for new process of high capital and energy efficiency.

Chapter 2

This chapter shows the results of experimental adsorptive treatment for petroleum product / biproduct, where diesel, gasoline and kerosene were processed by laboratory-scaled adsorption bed with Activated Carbon and see how much sulfur / nitrogen compounds are removed. This experimental was taken place under various operating temperature and various type of Activated Carbon for reviewing those relationship.

The results indicated that the Straight Run Diesel treated with Activated Carbon shows the lesser nitrogen content than those in Straight Run Diesel, which expects the higher reaction kinetics in downstream Hydrodesulfurization Reaction. In this experimental for Straight Run Diesel, MAXSORB-II of highest surface area, pore volume and oxygen content showed highest nitrogen removal capability among the various other Activated Carbons. Also, another experimental showed that the further activation of Activated Carbon with certain acid solvent improves the capability of nitrogen removal from Straight Run Diesel. This effect is further analyzed in Chapter 3.

Similarly, Activated Carbon shows its adsorptive capability for removal of sulfur compounds in Straight Run Diesel as well as Kerosene and LCO. However, no sulfur removal was found in FCC Gasoline, which is the most interested stream in industry. The experimental results indicated that the adsorption of sulfur compounds is related to the properties of bulk materials, which is further studies in Chapter 4.

Chapter 3

This chapter shows the further study on relationship between Reaction Kinetics of Hydrodesulfurization and Nitrogen / Refractory Sulfur Compounds in feedstock for Hydrodesulfurization Reaction.

The experimental result shows that the remaining sulfur content in Hydrotreated Straight Run Diesel is remarkably lowered when the feedstock is treated with Activated Carbon. Based on the experimental with various nitrogen and sulfur content in feedstock, it was found that the reaction kinetics can be explained by Langmuir–Hinshelwood type equation and Hydrodesulfurized is inhibited by the nitrogen compounds in 0.75 order and refractory sulfur compounds in first order. This result indicated that the removal of Nitrogen Compound from the feed stock for Hydrodesulfurized Reaction is beneficial for certain extend but less effective if targeting the product sulfur content of less than 10 wt-ppm. This is because the bottleneck of Hydrodesulfurization reaction such extremely low range is due to the very low content of sulfur compound itself.

The study results in this Chapter provided an idea for limitation of pretreatment for Hydrodesulfurization, using Activated Carbon as adsorbent.

Chapter 4

In this chapter, the integrated process for diesel desulfurization was proposed by using study results discovered in Chapter 2 & 3.

The experimental results in this chapter showed that the diesel product of less than 10 wt-ppm sulfur content can be produced from Hydrodesulfurized Straight Run Diesel, by adsorptive treatment with Activated Carbon. In order to apply this technology in commercial plant, however, it is essential to establish the regeneration process of spent Activated Carbon since cost of Activated Carbon is expensive, comparing with refinery margin for diesel desulfurization.

Through a series of experimental in this chapter, it was found that the Toluene and other aromatic fluid works as the desorbent for adsorbed Nitrogen / Sulfur Compounds on Activated Carbon and regenerated Activated Carbon shows the almost exact same adsorption capability as fresh Activated Carbon. As such, it was technically proven for proposed integrated process consisted of Pre-Treatment (Adsorptive removal of Nitrogen Compounds for improvement of Hydrodesulfurization Reaction), Hydrodesulfurization (removal of Bulk sulfur species) and Post-Treatment (Removal of remaining sulfur compounds)

Chapter 5

The feasibility study on actual application of process proposed in Chapter 4 has been presented in this Chapter. Based on the reality happened in the Refinery Industry, the proposed process scheme for low sulfur Gas Oil Production gives several favors on the actual implementation, especially for revamp on existing Hydrodesulfurized unit. In the study, the economic study has been conducted based on the current market data and it shows the high feasibility by integrated with current technology in commercial plant.

6.2 Conclusion and Further Work

The series of researches discovered that the new Gas Oil Desulfurization Process, using the Activated Carbon as Adsorbent, contributes the refinery industry for improvement of product quality with lower capital cost.

In addition, following benefit for adopting this process is expected:

(1) Reduced Fuel Consumption / CO_2 Emission since severity of Hydrodesulfurized Reaction (= Hydrogen recycle Rate & Reactor Inlet Temperature)

(2) Longer Hydrodesulfurized catalyst life due to lower severity. This may be connected to longer Turnaround Cycle, minimizing the non-operating losses in Refinery.

Considering the future application of Carbon Tax (In effect on 2019 by Singapore Government) and recent tight Refinery margin, reduction of fuel consumption in operating units gives huge advantage to Refiners.

In order to apply this new technology to commercial plant, however, additional efforts below are required:

I. Scale-up and long-term operation Study

II. Detailed Design of Equipment and adsorbent bed

III. Optimization of Activated Carbon Characteristic and operating condition

All the studies and experimental were conducted and succeeded in the laboratory scale, which uses only 0.3 gram of Activated Carbon in 7 mm-ID / 30 mm-length piping and several cycle lengths is examined. On the other hand, inventory of adsorbers in commercial plant is expected to be a few tons of Activated Carbon and the period of several months by going through the adsorption – regeneration cycle. Therefore, scale up study by using pilot plant is mandatory required before actual implementation. Technical challenges may often be hidden in the process and economical solution has to be explored by detail engineering.

There may be additional room for optimization of Activated Carbon Property and Operating Condition. Not only for improving the adsorption capability, the optimization of shape for easy handling, loading density against pressure drop and minimization of channeling problem are another challenge. Also, the waste treatment process after usage shall be established to avoid the environmental issues.

Although there are several further steps for commercial application, I believe that this cost effective / environmentally friendly technology is very promising process for commercial applications.