

## A Unique Way to Make Ultra Low Sulfur Diesel

Whasik Min\*

R&D Center, SK Corporation, 140-1, Wonchon-dong, Yusung-gu, Daejeon 305-712, Korea  
(Received 4 March 2002 • accepted 7 May 2002)

**Abstract**—SK Corporation has developed a new process, SK HDS Pretreatment process that enables the refiners to produce economically ultra-low-sulfur-diesel of below 10 ppm. This technology is based on the adsorptive removal of nitrogen containing compounds (NCC) from the feedstock to conventional hydrodesulfurization (HDS) units. The NCC is known to interfere with the activity of HDS catalysts. In the SK HDS Pretreatment Process, the feedstock to the HDS unit is pretreated, and 90% or more of NCC in the feedstock is removed, resulting in higher desulfurization in a conventional HDS unit. It was found that the degree of improvement in HDS is proportional to the degree of NCC removal. SK HDS Pretreatment Process is a cost-effective method for refineries to choose for 10 ppm ULSD production.

Key words: Ultra Low Sulfur Diesel (ULSD), Pretreatment, Hydrodesulfurization, Nitrogen Containing Compounds (NCC)

### INTRODUCTION

Refiners in most parts of the world are facing the situation where they have to produce automotive diesel fuels with very low sulfur levels in the foreseeable future. For example, the member states of EU plan to implement 50 ppm sulfur diesel regulation from 2005, while some of the states including Sweden, Finland, and Britain have already changed to ULSD of 50 ppm using tax benefit policies. Furthermore, European Commission recently finalized its proposal to require all 15 members to ensure the market availability of a 10 ppm ULSD from January 1, 2005. According to the proposal, Germany, Sweden, Finland must make a complete switch to 10 ppm ULSD before 2005. More member states are likely to adopt tax incentives to spur the introduction of 10 ppm ULSD in advance of the 2011 deadline for 100% conversion. In the US, the Environmental Protection Agency is in the process of setting the 10 ppm ULSD specification starting in June 2006. In Japan, it is most likely to introduce 50 ppm ULSD in metropolitan areas including Tokyo from early 2003, and to switch nationwide to 50 ppm sulfur regulation after 2004. In Korea, the regulation of sulfur content in automotive fuels is expected to be reduced significantly by 2005. Early introduction of ULSD with the sulfur content of 50 ppm or below in major cities is being discussed.

With these ever tightening regulations on the sulfur content of diesel fuel, refining industries all have difficulty in producing or determining how to produce the fuels that will satisfy the regulations. Producing the 50 ppm ULSD is already a big challenge for most of the refineries, an even bigger one would be to reduce the sulfur content of diesel fuel down to 10 ppm or below. It remains a hotly debated issue as to which technology to employ to produce 10 ppm ULSD and how to make the fuel available to the market in time.

At the moment, 10 ppm ULSD is available only in some coun-

tries in Europe and California of the United States. As long as the sulfur content of virgin Light Gas Oil (LGO) remains below 2,000-3,000 ppm, the conventional HDS processes can produce ULSD of 10-20 ppm, as is the case with BP's refineries in UK and California [Energy Information Administration, 2001]. Another example of producing ULSD would be to employ SynTechnology™ to treat kerosene or light cut LGO, as is done in a Swedish refinery [Energy Information Administration, 2001].

However, diesel fuel starting from low sulfur LGO or light feedstock alone can not meet the demand in the market, and most of the demand remains to be met with fuels from high sulfur LGO which usually contains the sulfur in the range of 10,000-15,000 ppm. This high sulfur LGO can not be treated in a single stage HDS unit to produce ULSD. Therefore, there still remains a strong demand for a process technology economically producing ULSD from high sulfur feedstock.

A single stage hydrodesulfurization (HDS) unit has been most commonly used to reduce sulfur content in diesel fuel into the current sulfur level of 500 ppm. However, enlarging the single stage reactor volume, may not be a realistic option to produce 10 ppm ULSD, because various contaminants, which inhibit the desulfurization reaction, are not properly removed. Therefore, the most practical method to produce 10 ppm ULSD is considered to be the two-stage deep desulfurization process [Energy Information Administration, 2001]. In this process, the sulfur levels are reduced down to around 250 ppm in the first stage and are further reduced down, after the hot gas that contains the inhibiting components are removed, to below 10 ppm in the second stage. In some cases, the first stage could be an existing HDS unit with moderate modifications.

However, to reduce the sulfur levels in the second stage to below 10 ppm, it requires much higher pressure, hydrogen to feed ratio, hydrogen purity and lower space velocity compared to the conditions used in most of the conventional HDS processes. If an existing single stage HDS unit were to be converted to a two-stage process, an additional reactor bed and a hot gas stripper have to be installed. The additional reactor requires higher mechanical strength to accommodate the much more severe reaction conditions than is

\*To whom correspondence should be addressed.

E-mail: wsmin@skcorp.com

<sup>†</sup>This paper is dedicated to Professor Wha Young Lee on the occasion of his retirement from Seoul National University.

required by the existing first stage reactor, which could increase the cost to refiners significantly. The severity of reaction conditions also increases as the feedstock contains more cracked material and has a higher endpoint, requiring an even heavier reactor, which further increases the capital investment. Higher hydrogen-to-feed ratio, coupled with the fact that the hydrogen consumption rises in a non-linear fashion at lower product sulfur levels, could in many cases mean a new hydrogen plant has to be built, which also contributes to increase significantly the capital investment and operational cost.

Many attempts have been made to address the issue of producing economically a 10 ppm ULSD. For example, S-zorb™ process, developed by Phillips to desulfurize FCC gasoline, has extended its application to ULSD production [Greenwood, 2001]. This process employs adsorption technology to reduce sulfur content without hydrogen consumption. Another example is biodesulfurization, which has been tested in the laboratories and pilot plants but has not shown its cost effectiveness in any commercial scale. Sulfur oxidation technology has been proposed as a method for producing 10 ppm ULSD. Sulfur in the organic sulfur compounds is converted in this technology to sulfone by peroxide added to the feedstock as an oxidant.

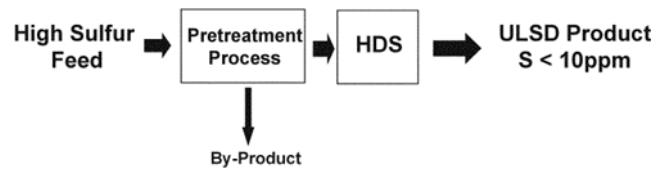
SK Corporation has developed over the past few years a unique technology, called SK HDS Pretreatment Process, to produce the 10 ppm ULSD. The technology is based on the adsorption technique, and is designed to remove NCC from the feedstock to the HDS process to improve the performance of conventional HDS units, by removing effectively the components that inhibit the desulfurization reaction in the HDS unit. The main advantages of this technology combined with the conventional HDS units, over two stage HDS process, for producing 10 ppm ULSD are lower capital cost to install the unit, requirement of lower pressure and temperature, and consumption of less hydrogen. This paper describes the details of the technical aspects of the process in the followings.

## 1. SK HDS Pretreatment Process

There are a variety of sulfur compounds in middle distillate streams including mercaptans, sulfides, disulfides, thiophenes, and benzothiophenes. The types of sulfur species present in the feedstock being processed, as well as the total sulfur have a large effect on the required severity and conditions for a desired product sulfur content. Analysis of hydrotreated straight run and cracked samples indicates that alkylated dibenzothiophenes (DBT), such as 4-methyl dibenzothiophene (4-MDBT) and 4,6-dimethyl dibenzothiophene (4,6-DMDBT), predominantly in the 330 to 380 °C boiling range, are the most difficult species to remove and make up most of the sulfur compounds [Knudsen et al., 2000].

There are two different reaction pathways for removal of the alkyl-substituted derivatives of dibenzothiophene: one is the direct sulfur extraction pathway, which is mainly inhibited by hydrogen sulfide, and the other being hydrogenation pathway, which is mainly inhibited by nitrogen-containing compounds (NCC). For non-refractive sulfur compounds, the intrinsic reactivity of sulfur removal via the direct extraction route is much higher than via the hydrogenation route. For most of the refractive sulfur compounds, the intrinsic reactivity is higher via the hydrogenation route than via the direct extraction route [Knudsen et al., 2000; Satterfield et al., 1975; Looif et al., 1998; Min et al., 1999].

Although refractory types take up only small part of total sulfur



**Fig. 1. Relationship of SK HDS pretreatment process to existing HDS unit.**

compounds, they are most difficult to be converted by hydrogenation because they have to compete with NCC for active sites of catalysts for hydrogenation and the NCC has generally higher adsorptivity compared to refractory compounds. As a result, refractory compounds are deprived of the chance to take up the active sites to be hydrogenated. Furthermore, denitration reaction is slower than desulfurization reaction, thus the NCC resides on the active sites longer than the sulfur compounds, which also make the refractory sulfur compounds difficult to convert.

Based on this observation, SK Corporation has focussed on developing technologies to remove the NCC from feedstock to HDS unit and found a proprietary adsorbent works well for this purpose. The SK HDS Pretreatment Process is a unique adsorption process to remove the NCC from the feed to HDS unit by making it, together with several kinds of polar compounds, adsorbed on a proprietary adsorbent and removed in the later stage from the adsorbent in a liquid-phase desorption step. As such, SK HDS Pretreatment Process is intended to be employed as a supplementary unit for the existing HDS unit, as shown in Fig. 1. As most of the NCC and some of the undesirable polar compounds are removed, the conversion is much improved in HDS unit. The improvement is enough to make 10 ppm ULSD if a catalyst with reasonably high activity is used in HDS unit.

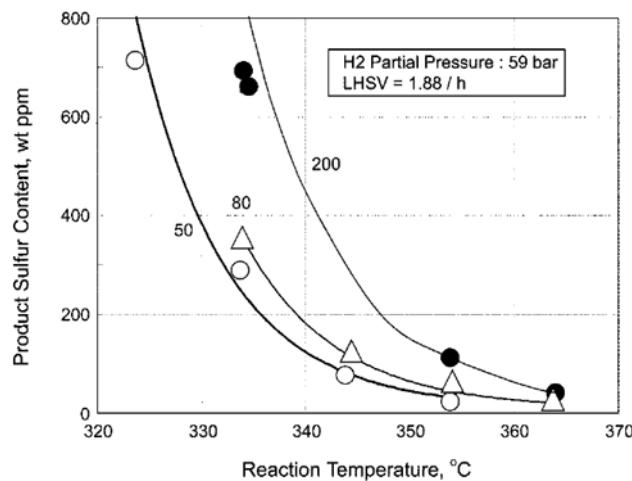
The by-product of SK HDS Pretreatment Process typically with a yield of 2%, comprises a large quantity of polar compounds having such functional groups as -COOH (naphthenic acids), -OH (phenols), -N (pyridines) and -NH (pyrroles), higher benzologue sulfur compounds than dibenzothiophenes, plus saturated hydrocarbons and aromatic compounds. Depending on the kinds of feedstock and yield, this by-product has different physical properties and chemical composition.

The composition of by-product, rejected from straight run LGO, has been investigated by employing various analysis techniques, including FT-IR and FD-MS. The result shows that the NCC is indeed heavily accumulated in the by-product which consists of about 8% of total NCC, out of which 4.3% is basic NCC such as quinoline and the rest being non-basic NCC, such as indoles and carbazoles. It also contains 3.4% of naphthenic acids, with the balance being feedstock, LGO, in the higher boiling range [Min et al., 2001]. Thus by-product can conveniently be blended into high-sulfur diesel fuels or heavy fuel oils.

## 2. Advantages and Characteristics

### 2-1. NCC Removal Versus HDS Improvement

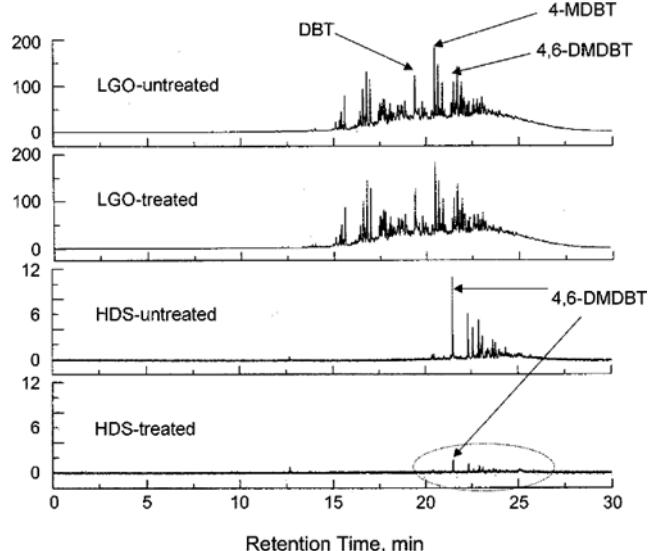
To determine the benefit of removal of NCC from the feedstock for HDS performance, tests have been carried out with a pilot scale HDS unit. Feed is a high sulfur LGO containing 1.34% of sulfur and total nitrogen content is 200 ppm. The pilot unit has been operated at the conditions representative of those of ordinary HDS unit.



**Fig. 2. The effect of feed nitrogen content on HDS efficiency (Figures in the graph refer to nitrogen content in the feed, in wt. ppm).**

Fig. 2 shows the effect of both reaction temperature and feed nitrogen content on product sulfur levels. It shows that the desulfurization is significantly improved at all reaction temperatures as the feed nitrogen content decreases. For example, at the same reaction temperature of around 354 °C, the product sulfur content is reduced from around 120 ppm to below 20 ppm, as the feed nitrogen content is reduced from the original value of 200 to 50 ppm.

Fig. 3 shows the chromatograms of four streams; LGO as a base feedstock, LGO treated for NCC removal, HDS product of untreated LGO, and HDS product of treated LGO. This figure explains how SK HDS Pretreatment Process works to assist HDS units dramatically improve its conversion efficiency. Comparison of the top two chromatograms tells as that pretreatment of base LGO, or the removal of polar compounds alone, brings about no appreciable change in total sulfur content and distribution of the sulfur containing compounds. Third chromatogram represents the typical change in total



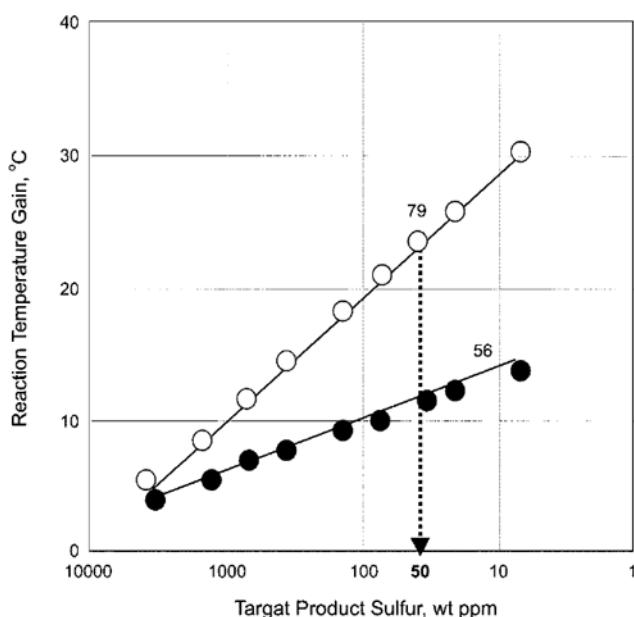
**Fig. 3. Sulfur Species Analysis by GC-AED.**

amount and distribution of sulfurous species when the feed is treated in HDS process. Total amount of sulfur has been drastically reduced and the distribution of sulfurous species has also been changed as a result of HDS reaction. However, the refractory sulfur, typically 4,6-DMDBT, still remains in significant amount. The fourth chromatogram shows that most of the sulfurous species, including 4,6-DMDBT, has been almost completely converted, indicating the potential benefit of the NCC removal technology adopted in SK HDS Pretreatment Process for improved performance of existing HDS unit.

The benefit of removal of NCC can also be assessed in terms of reaction temperature gain, which is defined as the degree of reduction in reaction temperature achieved with the removal of NCC in getting the same sulfur content level in the product with the same untreated base feedstock. Fig. 4 shows how reaction temperature gain changes according to the change in feed nitrogen content as well as targeted product sulfur level. As the target sulfur level decreases, the reaction temperature gain increases logarithmically. Also shown in this graph is that the reaction temperature gain increases significantly as the nitrogen removal ratio (NRR) increases. For example, with the target sulfur level of 50 ppm, the reaction temperature gain could be as much as 24 °C, when about 80% of nitrogen is removed from the feed. If the demand becomes stronger to reduce the sulfur content in the fuel further, for example to 10 ppm, the reaction temperature gain is even higher, about 30 °C. This graph clearly demonstrates that as the regulation on sulfur content becomes more stringent, SK HDS Pretreatment Process would become ever more effective tool for refiners to choose from to comply with the regulation.

The relationship between NCC removal and HDS gain, as defined below, is presented in Fig. 5.

$$\text{HDS gain} = 1 - \frac{\text{product sulfur for pretreated feed}}{\text{product sulfur for base feed}}$$



**Fig. 4. Effect of NRR on reaction temperature gain at various product sulfur levels (Figures in the graph refer to NRR, %).**

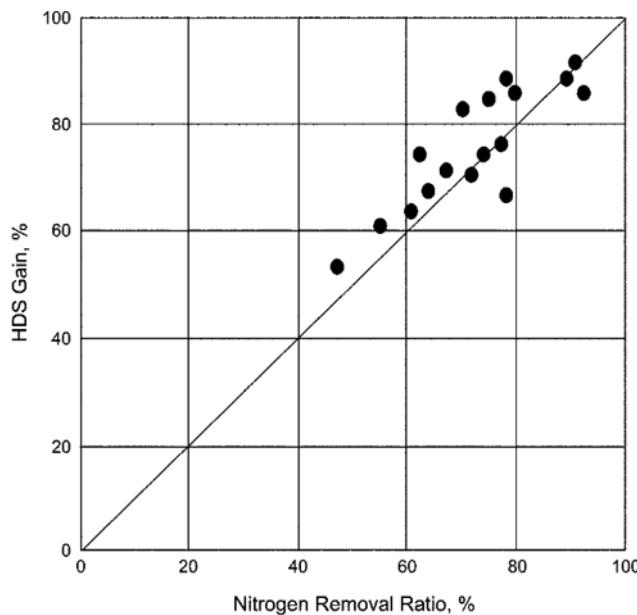


Fig. 5. Effect of NRR on HDS gain.

Tests have been conducted with CoMo type HDS catalysts at bed average temperature of 360 °C and the HDS gain is found to be linearly correlated with NRR. The linear relationship appears to be not affected too much by the kinds of straight-run LGO and change in operating conditions of pressure and temperature.

#### 2-2. Cases SK HDS Pretreatment Process Can Best Serve

Many of the existing low pressure HDS units operating in the range of 40 bar or below can be revamped to produce the product that meets the low sulfur diesel regulation at around 500 ppm, by increasing the severity of operation conditions. However, producing ULSD of 10 ppm sulfur levels by revamping these units is not a realistic option. All the current available technologies require op-

eration pressures significantly higher than the designed maximum allowable pressure of the existing units to produce 10 ppm ULSD. SK HDS Pretreatment process could be a good solution in this situation where the refiners can not increase the operation pressure significantly in their HDS units. SK's Process allows low pressure operation to produce 10 ppm ULSD. Fig. 6 shows the potential of SK's Process to produce 10 ppm ULSD even at low pressure HDS unit. If NRR is more than 90%, which is not a challenge at all for SK HDS Pretreatment Process, 10 ppm ULSD can be readily produced from LGO's with the endpoint of 360 °C at the hydrogen partial pressure of as low as 30 bar, equivalent to total pressure of about 40 bar. It only requires the advanced catalysts in HDS units, operated at reaction temperature of about 360 °C and LHSV of 2 per hour.

The effectiveness of employing SK HDS Pretreatment Process in improving the HDS performance is not limited to the above mentioned quality of LGO's. It can be easily applied for LGO with higher endpoint of 390 °C with the modern HDS units designed to operate at higher pressure of about 50 bar. Fig. 7 shows that, when nitrogen in the feed is removed by 75% or more, 10 ppm ULSD can be produced from LGO with the endpoint of 394 °C without the need to increase the reaction temperature above 380 °C, the temperature where the thermal cracking starts to be significant. In fact, 10 ppm has been achieved at much lower temperature of 360 °C in this case. It requires the similar operation conditions and catalyst, just except the higher pressure than is required for LGO's with the endpoint of 360 °C.

#### 2-3. Poly-Aromatics Reduction

Besides sulfur, it has long been disputed whether the aromatics content should be a part of the quality standards of diesel fuel. Nevertheless, automotive diesel fuels with low aromatic content are already manufactured and sold regionally in the United States and Northern Europe.

It has been observed that the removal of NCC also affects on polyaromatics content of HDS product. Fig. 8 shows there is no difference in total aromatics contents between the products from base

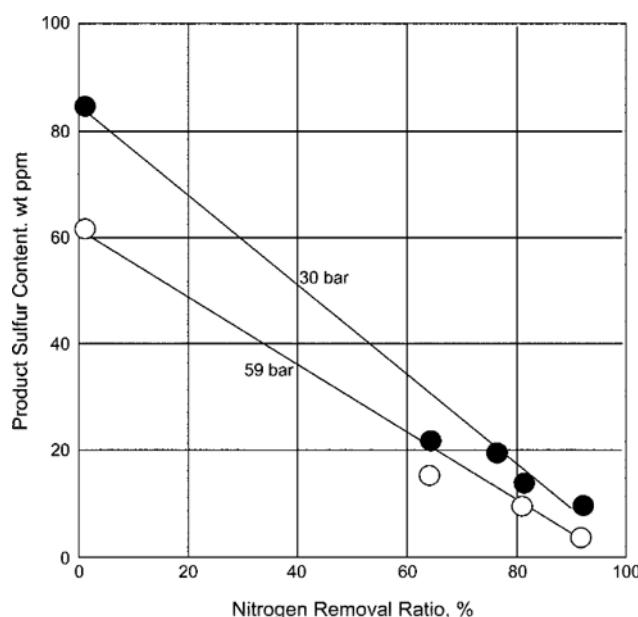


Fig. 6. Effect of pressure on product sulfur content at different NRR (Endpoint=364 °C; S=1.11 wt%; N=200 wt. ppm).

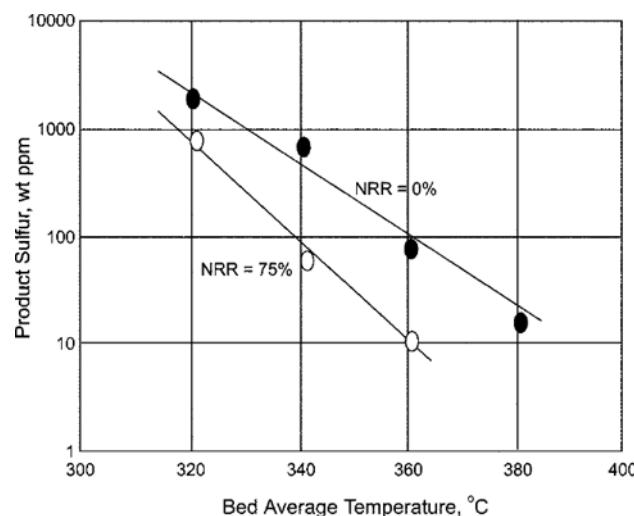


Fig. 7. Effect of temperature on product sulfur level at the different NRR ( $H_2$  partial pressure=52 bar; LHSV=1.88/hr;  $H_2$ /Oil=170  $Nm^3/kl$ ).

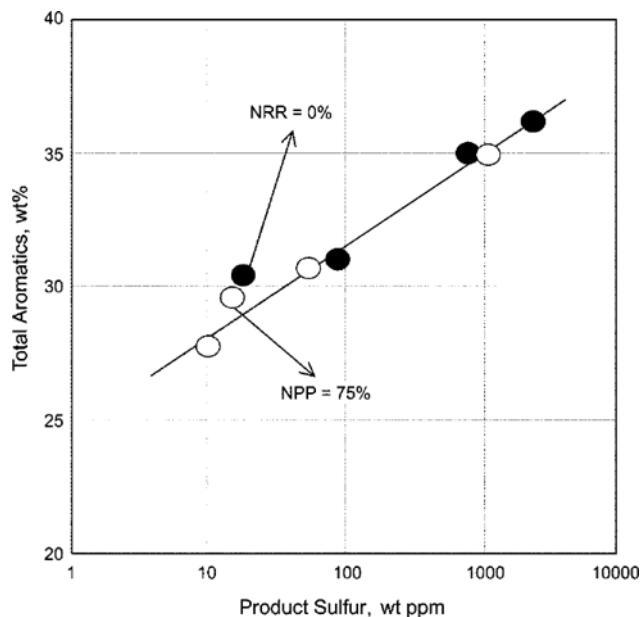


Fig. 8. Reduction of total aromatics content.

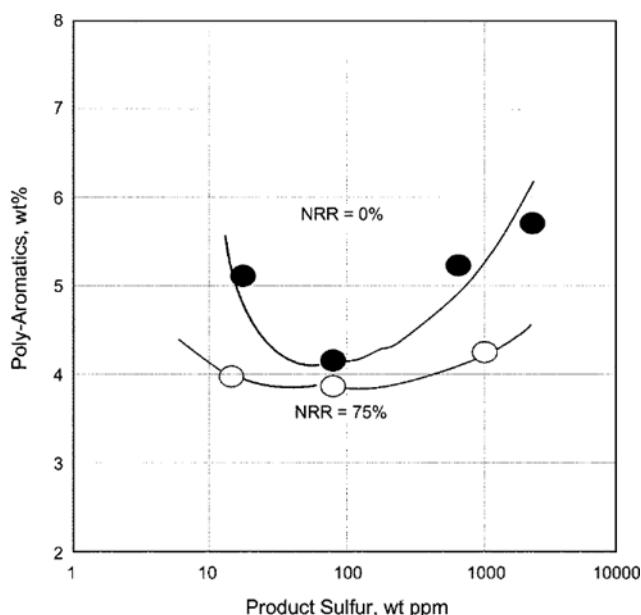


Fig. 9. Reduction of poly-aromatics content.

feedstock and feedstock pretreated to remove NCC. However, an appreciable difference in poly-aromatics contents is observed, as shown in Fig. 9, between the products from treated and untreated feedstocks. With treated feedstock of 75% NRR, the poly-aromatics content remains unchanged at different product sulfur levels and lower than that of untreated feedstock. With untreated feedstock, as the reaction temperature increases, as reflected in the decrease in the product sulfur level, the poly-aromatics are saturated and its content drops. However, as the reaction temperature increases further as to give rise to product sulfur level of around 100 ppm, the poly-aromatics content stops to decrease and at the reaction temperature corresponding to 10 ppm sulfur, the content increases, sug-

gesting the condensation reaction becomes significant.

#### 2-4. Characteristics of SK HDS Pretreatment Process

The other features of the SK HDS Pretreatment Process are listed as follows:

- No or minimum modification to the existing HDS unit
- No restriction for SK process location within the refinery
- No or minimum downtime required for the existing HDS unit
- Mild operating conditions: ambient temperature and low pressure is required
- Lower hydrogen consumption rate than for the case of HDS catalyst volume increase at the same sulfur level, because other hydrogen consuming compounds such as poly-aromatics, oxygen-containing compounds are removed together with NCC from the feed to HDS unit.
- Lighter product color and better color stability

#### 3. Economics

Basic engineering design package of SK HDS Pretreatment Process for commercial unit of 10,000 barrels per day capacity has been completed and the demonstration plant is being built in one of SK's refineries, scheduled to be operational from July 2002. This design package includes the units for steam stripping and fired heater for solvent recovery.

Total investment cost of SK process is estimated US\$18.2MM as of first quarter of year 2001, based on the capacity of 30,000 barrels per stream day, US Gulf Coast. Only minor modifications are required for the existing HDS unit to install SK Pretreatment Process upstream of HDS unit. Approximate cost of modification is estimated about \$1.5MM for a 30,000 barrels per stream day unit.

The total utility consumption of SK's Process for the case of steam stripping for solvent recovery is shown in Table 1.

The adsorbent is expected to last two years with little or no losses. The predicted adsorbent cost is \$0.10 per barrel of charge regardless of unit capacity. Solvent losses are in the range of about \$0.02 per barrel of feed.

#### CONCLUSION

SK Corporation has developed a new process, SK HDS Pretreatment Process, to address the issue of producing in a cost-effective manner the diesel fuels that meet the severe regulations on sulfur content. Cost effective production of 10 ppm ULSD is expected by using this pretreatment process installed upstream of an existing HDS unit. Main advantages of coupling the SK HDS Pretreatment Process with the existing HDS units to produce 10 ppm ULSD are listed as follows:

1. Allows the operation of HDS unit at lower temperature by more than 20 °C for the same level of product sulfur content.
2. Allows the operation of HDS unit at lower pressure and accepts

Table 1. Utility consumption (Steam Stripping Case, per Barrel of Feed)

Steam	0.03 Ton
Cooling water	1.8 Ton
Electricity	0.5 kW

heavier distillation range of feedstock than conventional HDS approach.

3. Requires no or minimum modification of existing HDS units.
4. Causes virtually no downtime for HDS unit.
5. Requires reduced hydrogen consumption by about 10%, compared to simple reactor volume increase for the same product sulfur level of 50 ppm.
6. Reduces poly-aromatics content by up to 1% point.
7. Improves color and storage stability of HDS product.

## REFERENCES

Energy Information Administration, Report No. SR/OIAF/2001-01, May (2001).

Greenwood, G., Clean Fuel Conference 2001, San Antonio, USA, Jan. 30-Feb. 1 (2001).

Kim, K. L. and Choi, K. S., "Kinetics of Hydrodesulfurization of Dibenzothiophene over  $\text{NiO}-\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$  Catalyst," *Korean J. Chem. Eng.*, **5**, 177 (1988).

Kim, M. C. and Kim, K. L., "A Role of Molybdenum and Shape Selectivity of Catalysts in Simultaneous Reactions of Hydrocracking and Hydrodesulfurization," *Korean J. Chem. Eng.*, **13**, 1 (1996).

Knudsen, K. G., Whitehurst, D. D. and Zeuthen, P., AIChE 2000 Spring National Meeting, Atlanta, GA, March 5-9 (2000).

Kwak, C. and Moon, S. H., "Effect of the Fluorine-Addition Order on the Hydrodesulfurization Activity of Fluorinated  $\text{NiW}/\text{Al}_2\text{O}_3$  Catalysts," *Korean J. Chem. Eng.*, **16**, 608 (1999).

van Looij, F., van der Laan, P., Stork, W. H. J., Dicamillo, D. J. and Swain, "Key Parameters in Deep Hydrodesulfurization of Diesel Fuel," *J. Appl. Catal. A : General*, **170**(1), 1 (1998).

Min, W. S., Clean Fuel 2001 Conference, San Antonio, USA, Jan. 28-Feb. 1 (2001).

Min, W. S., Khang, S. Y., Min, D. S., Ryu, J. W., You, K. S., Kim, N. J., Kogan, V. M. and Choi, K. I., The 4th European Congress on Catalysis, Rimini, Italy, September 5-10 (1999).

Park, H. K., Kim, D. S. and Kim, K. L., "Hydrodesulfurization of Dibenzothiophene over Supported and Unsupported Molybdenum Carbide Catalysts," *Korean J. Chem. Eng.*, **15**, 625 (1998).

Satterfield, C. N., Modell, M. and Mayer, J. F., "Interactions between Catalytic Hydrodesulfurization of Thiophene and Hydrodenitration of Pyridine," *AIChE J.*, **21**, 1100 (1975).