Overview of FCC Gasoline Post-Treating Technologies

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ABSTRACT

Fluid catalytic cracking (FCC) of vacuum gas oil and atmospheric residue produces substantial amounts of naphtha and contributes largely to the gasoline pool. Significant reduction in gasoline sulfur is mandated by regulations with lower limits of 50 ppm or even 10 ppm. To achieve this corresponding FCC naphtha sulfur contents should be <90 / <20 ppm retrospectively. If FCC naphtha is hydrotreated using conventional catalysts, significant olefins saturation can also occur, which leads to a decrease of octane number. Consequently, it is essential to modify conventional hydrotreating catalysts in order to achieve deep desulfurization with minimum olefins saturation.

Major post-treating technologies can be divided into the following three generic types: (i) Selective hydrodesulfurization; (ii) Full desulfurization followed by octane recovery, and (iii) Sorption.

Moreover, several authors have modified the traditional Co-Mo/Alumina catalyst to improve the selectivity of hydrodesulfurization over olefins saturation. The configuration of the traditional catalyst is adjusted by introducing active metal oxides or alkaline earth. Researchers have also introduced material like HZSM-5, hydrotalcite and TiO\(_2\) to the alumina support.

This paper presents a prudent overview of available commercial processes as well as the trends in catalyst/process research in this area of growing importance.

1. INTRODUCTION

Fluid catalytic cracking (FCC) of vacuum gas oil and atmospheric residue produces substantial amounts of naphtha. Significant reduction in gasoline sulfur is mandated by regulations in many industrialized countries. The refiner’s objectives are to manufacture finished product gasoline within four to six years with 50 ppm sulfur, with a sensitivity case for future consideration, of a further sulfur reduction to 10 ppm. To achieve this corresponding FCC naphtha sulfur contents should be <90 / <20 ppm retrospectively. Refiners are currently looking at a variety of routes of controlling sulfur in FCC naphtha [Miller et al., 2001].

Studies have shown that sulfur compounds concentrate in the higher boiling portion of FCC naphtha, while olefins concentrate in the lower boiling portion as shown in Table 1 [Shorey et al., 1999]. Fractionation is therefore an attractive first step in many potential process configurations designed to reduce sulfur while maintaining olefins (and thus, octane). Applying conventional hydrotreating to the heavy FCC naphtha fraction is sufficient in many cases to achieve 100-150 ppm sulfur pool targets, with very little loss of octane. However,
where very low gasoline pool sulfur levels are required (in the <50 ppm sulfur range), removing sulfur from the intermediate, and in some cases even the light fraction will be necessary as well. If the end point of the light FCC naphtha stream is kept relatively low, a significant portion of the sulfur in this stream will be light mercaptans, which can be removed via caustic extraction or other emerging technologies. This avoids hydrotreating of the light naphtha, which would result in severe octane loss. Desulfurization of the intermediate FCC naphtha without serious octane loss is a much more technically challenging problem.

Table 1. Typical composition of FCC naphtha [Shorey et al., 1999].

<table>
<thead>
<tr>
<th>Property</th>
<th>IBP-75°C</th>
<th>75-125°C</th>
<th>125-150°C</th>
<th>150°C to FBP</th>
<th>Full range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fraction (wt %)</td>
<td>22</td>
<td>30</td>
<td>16</td>
<td>32</td>
<td>(100)</td>
</tr>
<tr>
<td>S, ppm</td>
<td>15</td>
<td>20</td>
<td>40</td>
<td>120</td>
<td>50</td>
</tr>
<tr>
<td>N, ppm</td>
<td>5</td>
<td>6</td>
<td>20</td>
<td>75</td>
<td>35</td>
</tr>
<tr>
<td>Br No., g/100 mL</td>
<td>100</td>
<td>75</td>
<td>45</td>
<td>25</td>
<td>70</td>
</tr>
<tr>
<td>PONA, wt %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P+N</td>
<td>33</td>
<td>38</td>
<td>30</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>O</td>
<td>65</td>
<td>50</td>
<td>30</td>
<td>20</td>
<td>45</td>
</tr>
<tr>
<td>A</td>
<td>2</td>
<td>12</td>
<td>40</td>
<td>60</td>
<td>25</td>
</tr>
<tr>
<td>RON</td>
<td>95</td>
<td>87</td>
<td>93</td>
<td>93</td>
<td>92</td>
</tr>
<tr>
<td>MON</td>
<td>81</td>
<td>77</td>
<td>81</td>
<td>82</td>
<td>80</td>
</tr>
</tbody>
</table>

From the above discussion, it is clear that if FCC naphtha is hydrotreated using conventional catalysts, significant olefins saturation can occur during the HDS process, which leads to a decrease of octane number in the final product. Consequently, it is essential to modify conventional hydrotreating catalysts in order to achieve deep HDS with a minimum of olefins saturation.

2. ALTERNATIVE ROUTES

Two broad alternatives are available for meeting these sulfur standards namely, FCC Feed Pretreatment and FCC Naphtha Post-Treatment. The first step for a refinery will be to establish whether, on a generic basis either an FCC feed pretreatment approach or one of the FCC gasoline post treatment processes, had a clear technical and economic advantage [Wormsbecher et al., 1993; Nicholas, 2001; Sloley, A.W. (2001)].

2.1 Conventional FCC Feed Pre-treating

This is achieved by hydrotreating FCC feed, which results in reduced sulfur content, as well as nitrogen and metals content in FCC products. Hydrotreated FCC feed usually results in FCC yield benefits, usually with increased LPG and FCC gasoline yields at the expense of cycle oil and slurry. Isobutene yield in particular receive a yield boost, which can be of the order of 30%. Moreover, FCC gasoline octane losses are small to negligible. FCC pretreatment also significantly reduces FCC flue gas SO\textsubscript{x} emissions.

FCC feed pre-treatment had the highest Capital Expenditure requirements of all ‘viable’ process route selections. In part this is due to the high cost of the associated hydrogen generation and sulfur production costs. This option would require almost four times the amount of capital as the alternative solutions. This case also shows significantly higher operating costs, again in part due to the cost of hydrogen. For most cases the hydrogen demand was of the order of 150 Nm\textsuperscript{3}/m\textsuperscript{3} of FCC feed.
Furthermore the FCC pretreatment option could satisfy the base objective of 50-ppm gasoline production. However, to obtain 10 ppm gasoline sulfur further FCC gasoline post treatment would be required.

2.2 FCC Naphtha Post-treating

This is achieved by either hydrotreating or otherwise treat part or all of the FCC naphtha. Post-treating FCC naphtha is the minimum investment, least cost route for meeting the ultralow sulfur gasoline. Post-treating processes alone are sufficient for meeting these standards, and they entail lower investment and operating costs than the other approaches. Thus far, post-treating has been the approach of choice for most U.S. refineries.

3. POST-TREATMENT TECHNOLOGIES

Up to 1997, the only commercial technology for controlling the sulfur content of full-range FCC naphtha was what is now called “conventional hydrotreating”. A number of technology providers offered conventional hydrotreating processes for full-range FCC naphtha and other naphtha streams. Collectively, these processes had accumulated considerable commercial experience. They were reliable and well understood, and could accomplish the necessary degree of sulfur control.

Conventional FCC naphtha hydrotreating processes are expensive because they are non-selective. In the course of removing sulfur, most of the olefinic species present in the FCC naphtha are saturated. Olefin saturation leads to high-octane loss (> 10 numbers) and high hydrogen consumption, which account for the high cost of conventional hydrotreating. The average cost of achieving the 30 ppm gasoline sulfur standard with conventional hydrotreating was estimated to be in the range of 5 cents per gallon of complying gasoline (assuming that FCC naphtha constituted 30–40 vol% of the gasoline pool).

Several non-conventional processes have now reached commercial and/or demonstration stage. All of these processes promised performance superior to conventional hydrotreating, with respect to octane loss, yield loss, hydrogen consumption, and investment and operating costs. With regard to costs, certain of the non-conventional processes offered average costs of achieving the 30 ppm gasoline sulfur standard in the range of 2.5 cents/gal of complying gasoline – about half that of conventional hydrotreating.

Several catalytic processes have been commercialized by licensors to help refiners to meet future stringent regulations on FCC gasoline. These include SCANfining® from ExxonMobil and Prime® G+ from Axens-IFP. Moreover, several authors have proposed new catalysts with reduced acidity of alumina carrier [Hillerova et al., 1994] or the use of less acidic or basic support such as TiO_2, SiO_2 or MgO. Recently it has been reported that the selectivity for HDS can be increased with CoMo catalysts supported on Mg-Al oxide supports [Klimova et al., 1998; Zhao et al., 2001]. The change in the size of MoS_2 crystallites corresponding to a decrease in number of MoS_2 edge-sites when the magnesium content is increased, leads to a decrease in the hydrogenation activity [Mey et al., 2002].

Six major licensed technologies were evaluated in the study. For comparative purposes these have been divided into the following three generic types.
3.1. Selective Hydrodesulfurization

Selective hydrodesulfurization achieved desulfurization with little olefins saturation. Hence, these processes exhibit a moderate loss of Research Octane and a low loss of Motor Octane. This can be minimized by FCC naphtha splitting and also by the incorporation of TAME technology on selective fractionated streams. $C_5$ yield loss is minimal or negligible and this offers a ‘low hydrogen consumption’ option. There is however a small reduction in olefin content of FCC naphtha should this prove to be a future gasoline product constraint. Reactor pressure is low to moderate.

The well-known processes in this category are IFP Prime G+, ExxonMobil SCANfining, and CD Tech CD Hydro / CDHDS+.

3.2. Full Desulfurisation plus Octane Recovery

Non-selective hydrotreating plus octane recovery achieves desulfurization with partial or total olefins saturation with accompanying olefin loss, but recovers most of the lost octane by secondary reactions such as isomerization. These processes employ medium pressure reactors, which promote both hydrocracking and isomerisation. $C_5$ yields are therefore debited by 3 to 5%. A small loss of FCC naphtha Research Octane results, but there is also a Motor Octane gain. These processes have the highest $H_2$ consumption; usually three times that of selective processes, with associated higher operating costs.

The processes under this category include UOP ISAL and ExxonMobil OCTgain.

3.3. Sorption

Sorption sequesters the sulfur in a solid sorbent medium and achieves desulfurization with little olefins saturation. This process exhibits a low loss of both Research Octane and Motor Octane. This can be minimized by FCC naphtha splitting and also by the incorporation of TAME technology on selective fractionated streams. $C_5$ yield loss is minimal or negligible and this offers a ‘low hydrogen consumption’ option. There is however a small reduction in olefin content of FCC naphtha should this prove to be a future gasoline product constraint. Reactor pressures are lowest of all options. One such process is S-Zorb process developed by Phillips Petroleum.

All of these processes could meet the basic and sensitivity case gasoline sulfur requirements. A generic comparison of processes is shown in Table 2.

Table 2. General comparison between different post-treating processes.

<table>
<thead>
<tr>
<th>General Type</th>
<th>Selective HDS</th>
<th>HDS plus Octane Recovery</th>
<th>Sorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>RON Change</td>
<td>Moderate loss</td>
<td>Small loss</td>
<td>Small loss</td>
</tr>
<tr>
<td>MON Change</td>
<td>Small loss</td>
<td>Gain</td>
<td>Small loss</td>
</tr>
<tr>
<td>$C_5$ Yield Loss, (vol%)</td>
<td>Minimal</td>
<td>Loss</td>
<td>Minimal</td>
</tr>
<tr>
<td>Olefin Reduction</td>
<td>Small/medium</td>
<td>Yes</td>
<td>Small</td>
</tr>
<tr>
<td>$H_2$ Consumption</td>
<td>Low</td>
<td>Moderate</td>
<td>Low</td>
</tr>
<tr>
<td>Pressure</td>
<td>Low/medium medium</td>
<td>Low</td>
<td>Low</td>
</tr>
</tbody>
</table>
4. DESCRIPTION OF MAJOR POST-TREATING PROCESSES

Table 3, based on publicly available information in March 2003, shows processes that the refining industry has selected to date for complying with the 30 ppm gasoline sulfur standard and the indicated number of installations for each [Rajguru et al., 2001].

4.1 Prime-G+ Process

Commercially proven Prime-G+ technology is the market leader for selective desulfurization of FCC naphtha. The process was developed by IFP/AXENS. The process is a modified version of the previously developed process known as PRIME G. Over 60 units have been licensed and eleven under commercial operation [Nicholas, 2001].

Table 3. Commercial processes for FCC naphtha desulfurization (reference)

<table>
<thead>
<tr>
<th>Process Licensor</th>
<th>Process</th>
<th>Technology</th>
<th>Number of Refineries</th>
</tr>
</thead>
<tbody>
<tr>
<td>IFP</td>
<td>Prime G+</td>
<td>Selective HDS</td>
<td>&gt; 60</td>
</tr>
<tr>
<td>ExxonMobil</td>
<td>SCANfining</td>
<td>Selective HDS</td>
<td>26</td>
</tr>
<tr>
<td>CD TECH</td>
<td>CD Hydro / CD HDS</td>
<td>Selective HDS</td>
<td>30</td>
</tr>
<tr>
<td>UOP</td>
<td>ISAL</td>
<td>HDS + Octane Recovery</td>
<td>5</td>
</tr>
<tr>
<td>ExxonMobil</td>
<td>OCTgain</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Phillips</td>
<td>S Zorb G</td>
<td>Sorption</td>
<td>10</td>
</tr>
</tbody>
</table>

Notes:
1. All process names are trademarked
2. HDS denotes Hydrodesulfurization
3. SuRCA™ is a sulfur-reducing FCC catalyst

The Prime-G+ process is designed to treat full range FCC gasoline by two stages. In the first stage the gasoline is treated in a fixed bed reactor to remove the diolefins and convert the light mercaptans and light sulfur compounds into heavier sulfur compounds. The effluent of the reactor is fractionated to produce olefin rich light naphtha (LN) stream and a sulfur rich heavy naphtha (HN) stream. The LN fraction is further treated in an etherification or alkylation units. The objective of the first stage is to remove all the diolefinc compounds which cause undesired high pressure drop and reduce the rate of circulation of the catalyst in the HDS section. The catalyst in the reactor of the first stage is tailored to maintain the octane number and minimize the consumption of hydrogen. In the second stage of the process the HN fraction is hydrotreated selectively using two proprietary catalysts. The first catalyst acts to remove most of the sulfur while minimizing the olefin saturation reactions. The second catalyst acts as a polisher of the remaining sulfur in the heavy naphtha stream without affecting the olefin content of the gasoline. The treated LN and HN streams are then blended and leave the process with extremely low sulfur content (less than 10 ppm) and virtually negligible octane losses. The Prime-G+ process is capable of treating FCC gasoline with sulfur level as high as 4000 ppm with a capacity over 100,000 BPSD.

4.2. SCANfining Process

SCANfining (Selective Cat Naphtha hydrofining) is a selective catalytic hydrodesulfurization process developed by Exxon Research and Engineering. The process is based on a proprietary catalyst called RT-225, which was jointly developed by ExxonMobil and Akzo Nobel. Because of the importance of the support-metals interaction and the support design features, catalyst preparation procedures developed with Akzo Nobel are a key feature of the
RT-225 technology package. The process was put in operation in 1990. Many refineries worldwide are implementing SCANfining process to meet the requirement of low sulfur gasoline [Brignac et al., 2000].

Most of the sulfur content of FCC gasoline concentrates in the heavy portion of the naphtha. On the other hand the valuable olefins are concentrated in the intermediate and low portion of the naphtha. Hence, the FCC gasoline can be fractioned into three streams: the heavy high sulfur naphtha, intermediate naphtha and low cat naphtha. The sulfur content of the latter portion exist as mercaptans, sulfide and bisulfide species, which can be removed via traditional extraction techniques. The sulfur content of the intermediate and heavy portions of the gasoline can be hydrotreated by conventional hydrotreating techniques before the three portions are blended. The sulfur content of the FCC gasoline using this treating techniques ranges between 100 to 150 ppm with a loss of octane in the range of 2 to 6.

SCANfining process can be applied to the heavy and intermediate portion of the gasoline. The RT-225 catalyst is capable of selectively removing sulfur in the presence of hydrogen without affecting the octane number. Sulfur level as low as 10 ppm with a loss of octane less than 2 has been obtained in several commercial SCANfining units. A simplified process flow diagram of the SCANfining process is shown in Figure 1.

4.3. CDHYDRO/CDHDS Process

CDHYDRO (Catalytic Distillation Hydrogenation) and CDHDS (Catalytic Distillation HydroDeSulfurization) process is developed by the Catalytic Distillation Technologies, CDTECH. The start up of the first commercial CDHYDRO unit was successfully accomplished at New Brunswick refinery in 2001. A total of seven refineries are implementing this technology for the HDS of FCC gasoline [Gardener, 2001].

The FCC gasoline is first fractionated in a catalytic distillation tower in the presence of hydrogen into two streams. The top stream contains light cat naphtha (LCN) rich in olefins with almost zero sulfur content and the bottom stream contains medium and heavy cat naphtha (MCN and HCN, respectively). During the processing of the FCC gasoline, the LCN is separated to prevent olefin saturation and the light mercaptans and light sulfur compounds are converted to heavy sulfur compounds which joins the bottom MCN and HCN stream. The bottom product of the CDHYDRO tower is hydrotreated in the CDHDS unit to produce C7+ gasoline with low sulfur content as shown in Figures 2 and 3. The process does not require removal of diolefin from the feed and consumes lower quantities of hydrogen per barrel of FCC as compared to other commercial processes. In addition, the octane number remains unaffected.

5.4. ISAL Process

The process was developed by UOP and the research and development center of the Venezuelan government's PDVSA, INTEVEP [Houde, 2000]. The process utilizes proprietary fixed bed hydrosprocessing technology at low pressure to reduce the sulfur content of the gasoline and simultaneously preserve the octane number. The initial objective of the project was to investigate possible improvements in fixed-bed isomerization and alkylation technology. A great achievement of this project was the development of a new catalyst that has the ability to increase octane by an array of octane-enhancing reactions, including isomerization, dealkylation, conversion and molecular weight reduction. The catalyst
saturates most of the olefins present in the gasoline. However, it has the ability to increases
the ratio of isoparaffins to normal paraffins and produces lower molecular weight paraffinic
compounds, which has a positive impact on the octane number of the feed gasoline. This
feature of the new catalyst is not exhibited by traditional hydrotreating catalyst.

The UOP/INTEVEP researchers have carried out extensive laboratory and pilot plant tests in
what is known as ISAL second generation. Their objective has been to improve the catalyst
formulation by adjusting the metals function and zeolitic function aiming to increase the yield
of \( C_5^+ \) liquid product. In addition, the research has focused on modifying the configuration of
the ISAL process to lower the cost and improve operation.

A typical ISAL process flow scheme is shown in Figure 4. The ISAL catalyst is divided into
multiple beds. Quench gas is introduced between catalyst beds to provide a fair distribution
of the heat of reaction. This procedure provides better control of the reactor temperature,
which eventually leads to a longer catalyst life. The ISAL process is similar to a
conventional hydrotreating unit. Hence with little cost it can easily replace an existing
hydrotreating unit.

5.5. OCTGAIN Process

The OCTGAIN process is developed by ExxonMobil Research and Engineering. The first
commercial implementation of OCTGAIN was in 1991 (Shih, 1999). The process uses
proprietary catalyst known as OCT-100 in the early version of the process. The OCT-100
catalyst was further improved in the second and third generation. The commercial names of
the second and third generation catalysts are OCT-125 and OCT 230 respectively. The
OCTGAIN process is designed to desulfurize heavy sulfur compounds, such as thiophenic
compounds, while maintaining or enhancing the octane number of the gasoline.

A simplified OCTGAIN process flow diagram is shown in Figure 5. The heart of the
reaction section is a fixed multi-bed reactor with intermediate cooling system operating at
relatively low pressure. The catalyst in the multi-bed reactor hydrodesulfuizes the sulfur
compounds and saturates most of the olefins and then builds the octane of the processed fluid
by increasing the \( C_5^+ \) yield. The separate catalyst beds and the intermediate cooling system
provide good flexibility and control of the severity of the desulfurization process. The
OCTGAIN process is designed to handle both heavy cat naphtha (HCN) and intermediate cat
naphtha (ICN). 98 % desulfurization of FCC gasoline with 2% increase in the octane number
has been reported by some refineries implementing OCTGAIN process.

5.6. OATS Process

OATS process (Olefin Alkylation of Thiophenic Sulfur) is developed jointly by British
Petroleum and Axens. The process complements Prime G+ process for HDS of FCC
gasoline. The process is now in full operation in three refineries. Two process options are
available for commercial treatment of FCC gasoline. In the first option the intermediate and
heavy cat naphtha is treated in the OATS reactor and then hydrotreated to produce low-level
sulfur naphtha to be blended with other gasoline streams. In the second option the full range
FCC gasoline is treated in the OATS reactor and then fractionated into light low sulfur
naphtha and a heavy naphtha streams. The heavy naphtha stream is hydrotreated before it is
blended with other gasoline streams. Two main classes of reaction occur over the proprietary
catalyst in the reaction section: Sulfur Shift Reactions and Olefin Shift Reactions. In the first
class of reactions the light sulfur species and the heavy thiophenic compounds react with olefins (alkylation) to produce sulfur compound with high boiling point. Hence, the light portion of the naphtha becomes essentially sulfur free. In the second class of reactions the light olefins are oligomized and then isomerized yielding products having high-octane value and low Reid vapor pressure. This essentially leads to lower hydrogen consumption in the hydrotreating section. PrimeG+ process can be implemented in the hydrotreating section for extremely low sulfur level.

5.7. S-Zorb Process

The process was developed by Phillips Petroleum to lower the sulfur level of gasoline without affecting the octane number. The first commercial S-Zorb Gasoline unit was put in operation in 2001 at Texas, USA refinery. The process is based on a proprietary catalyst that adsorbs the sulfur atoms from the hydrocarbon molecules containing sulfur and releases the hydrocarbon portion of the molecules. The process is designed to prevent hydrogen sulfide from escaping into the product stream aiming to cease the reverse reaction of hydrogen sulfide with olefins, which produces mercaptans.

The feed to the process is FCC gasoline combined with a small hydrogen stream. The stream is heated until all the gasoline is vaporized. The vaporized gasoline is then injected into a fluid bed reactor where the sulfur from the feed is adsorbed on the catalyst. The reactor is designed to include a disengaging zone to remove all suspended catalyst particles from the effluent stream. The product stream, which exits the reactor as a vapor, with low sulfur content is then condensed before leaving the process. The sulfur captured in the sorbent (catalyst) is treated with oxygen in a continuous regeneration process. The cleaned catalyst is reconditioned before it is returned to the reactor. The reactor operates at 650-775 F and 100-350 psig depending on the nature of the feed. The S Zorb process can operate with hydrogen purities as low as seventy percent. A sulfur level as low as 10 ppm can be achieved by controlling the rate of circulation of the catalyst. The octane loss accompanying the desulfurization process is less than 1 and more than 99% the feed volumetric rate is recovered in the product stream.

6. REVIEW OF FCC POSTREATING CATALYST

As stated earlier the key to the HDS technology is the catalyst. The traditional HDS catalyst is either cobalt–molybdenum mixed oxide or nickel–molybdenum mixed oxides supported on alumina. The reactor operating conditions are usually set at pressure of 20 bar, temperature of 350 ºC, H<sub>2</sub> to feed ratio of 300, and liquid hourly space velocity of 3 hr<sup>-1</sup>. Under these conditions the rate of saturation of olefinic compounds is appreciable. Researchers have studied the effect of different catalyst configuration on the rate of the HDS and olefin saturation to come up with a better alternative which meet the requirement of low sulfur level and low octane losses. The strategy is to tune the acidity of the active sites by introducing less or more acidic metals on different catalyst supports and then test the performance of the catalyst at various operating temperature, pressure, H<sub>2</sub> to feed ratio and space velocity. Rossini [Rossini, 1994] conducted an excellent review of the impact of catalytic materials on fuel reformulation. In the following paragraphs we present the main ideas and the important results published in the area of FCC catalyst posttretating.

One of the feasible idea is to perform the HDS process on the traditional catalyst and then substitute the loss in octane resulted from the hydrogenation of olefins by isomerising the effluent [Anabtawi et al., 1994]. Another idea was to expose the FCC gasoline to less
reactive or spent catalyst [Zhao et al., 2002]. That will reduce the severity of the HDS process but improve the selectivity.

Mey et. al. [Mey et al., 2002] studied the reactivity of a synthetic feed over a sulfided CoMo/Al₂O₃ traditional catalyst. The synthetic feed contains model molecules 2-methylthiophene (species 1) and 2,3-dimethylbut-2-ene (species 2) dissolved in orthoxylene and heptane. Species 1 represents a sulfur containing molecules while species 2 represents a typical olefin that can be found in a typical FCC gasoline. The aim of the study was to understand the mechanism by which the sulfur containing species and olefinic species react at different pressures (1 and 20 bar) and different sulfur level of the feed (1000 and 10000 ppm). They realized that at high pressure, there is competitive adsorption on the active sites which is in favor of the olefinic species especially at low sulfur level. The HDS of species 1 was also more significant at low sulfur level. This indicates that the HDS/Olefin hydrogenation selectivity decreases with the increase of the sulfur level in the feed. They also detected thiols resulted from the combination of H₂S with the olefins or incomplete HDS of the sulfur containing product. The presence of thiols was observed only at high pressures. The authors recommended using the test to evaluate the activity and selectivity performance of various catalysts.

Zhao et al. [Zhao et al., 2002] modified the traditional HDS catalyst by introducing alkaline earth and VIII, IB metal oxide. They also used modified alumina support in the forms of HZSM-5/γ-Al₂O₃ and HZSM-5/γ-Al₂O₃-TiO₂. Their study aimed at evaluating the effect of catalyst additives and catalyst supports on the HDS ratio and octane number of the treated FCC gasoline. The catalysts were prepared by the incipient wetness techniques. The additives were incorporated by impregnating the catalyst with aqueous solutions of metal and alkaline earth nitrate. The catalyst supports were prepared by impregnating commercial alumina with an isopropanol solution of tetra-i-buty-titanate. The catalysts in the sulfided forms were exposed to traditional FCC gasoline feed at operating conditions close to the industrial values. The researchers observed that the research octane number of the treated gasoline increases with the increase of mass percent of HZSM-5 while the HDS activity decreases. They attributed this behavior to the increase of hydroisomirization activity with the increase of mass percent of HZSM-5. They further noticed that the presence TiO₂ in the support has a positive effect on the HDS activity. They postulated that the TiO₂ changes the interaction between the active metal sites and the support by facilitating the conversion of MoO₃ to MoS₂. The experimental data indicated that the activity of HDS is highest for the support HZSM-5/γ-Al₂O₃-TiO₂ among all supports. The additives have also appreciable influence on the rate of HDS. The results showed that the addition of alkaline earth and VIII, IB metal oxide reduced the HDS and RON while the addition of Ba increased the HDS and RON.

Yin et al. [Yin et al., 2002] used the method of monolayer dispersion to prepare several supported solid base catalysts. They compared the HDS/Olefin hydrogenation selectivity at identical operating conditions for three catalyst: traditional CoMo/Al₂O₃, CoMo on oxide from hydrotalcite-like compounds, and CoMo prepared by monolayer dispersion. They found that the HDS/Olefin hydrogenation selectivity of the catalyst prepared using the monolayer dispersion method is the greatest. However, it appear from their results that there is slight drop in the % HDS of the FCC feed.

Zhao et al. [Zhao et al., 2003] studied the effect of catalyst support particularly the hydrotalcite on the HDS and olefin hydrogenation of FCC gasoline. They synthesized
Magnesium–aluminum, copper–aluminum, zinc–aluminum hydrotalcite compounds using the co-precipitation method. Their experimental data revealed that the catalyst support has an appreciable impact on the rate of olefin hydrogenation, hydrodesulfurization yield and consequently the octane level of the treated gasoline. They concluded that the HDS/Olefin hydrogenation selectivity of the hydrotalcite support is better than the traditional $\gamma$-Al$_2$O$_3$ support. They classified the activity of the metal supports as follows:

Hydrodesulfurization activity order:

$\gamma$-Al$_2$O$_3$ > $\gamma$-Al$_2$O$_3$+Mg–Al hydrotalcite > $\gamma$-Al$_2$O$_3$+Cu–Al hydrotalcite > $\gamma$-Al$_2$O$_3$+Zn–Al hydrotalcite

Olefin hydrogenation activity order:

$\gamma$-Al$_2$O$_3$ > $\gamma$-Al$_2$O$_3$+Mg–Al hydrotalcite > $\gamma$-Al$_2$O$_3$+Cu–Al hydrotalcite > $\gamma$-Al$_2$O$_3$+Zn–Al hydrotalcite

7. CONCLUDING REMARKS

Post-treating FCC naphtha is the minimum investment, least cost route for meeting the ultra-low sulfur gasoline specification. Processes that have been commercialized involve (i) Selective hydrodesulfurization; (ii) Full desulfurization followed by octane recovery; or (iii) Sorption. Selection of a particular process to meet future stringent regulations on FCC gasoline at a particular refinery, however, will involve a compromise between the best available technology and economic solution. Furthermore, new and advanced processes are likely to be available in the near future as research is very active in this area.

Catalysts for selective hydrodesulfurization are getting increased attention. The selectivity of HDS over hydrogenation can be improved by modifying the configuration of the catalyst’s active sites and support. Further studies in this area are required to elucidate the nature and distribution of active studies leading to design of tailor-made catalysts.

8. ACKNOWLEDGEMENT

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9. REFERENCES


Figure 1. Simplified process diagram of SCANfining.

Figure 2. Simplified flow diagram of CDHYDRO process.
Figure 3.  Simplified flow diagram of CDHDS process

Figure 4.  ISAL Process flow scheme
Figure 5. Simplified OCTGAIN process flow diagram.