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In-situ regeneration and sulfiding of catalysts in the refinery increase the emissions of harmful gases from refineries site. Oxidative regeneration of catalyst involves coke burn-off, thus generating CO, CO\textsubscript{2}, NO\textsubscript{x} and SO\textsubscript{x}, which accumulate in the reactor gas systems. Each of these gases must be treated in downstream process units in order to diminish refinery pollution.

In-situ sulfiding, or start-up of the unit with presulfurized catalysts, results in production of hydrogen sulfide in large excess. This dangerous gas, present in both gaseous and liquid streams during unit start-up, is a threat to the operations team; and also requires chemical treatment in downstream units.

Refiners committed to environment protection and safer operation will replace these in-situ catalyst treatments with ex-situ treatments, significantly reducing pollution of refinery air and water streams. By choosing both ex-situ regeneration and ex-situ pre-activation via patented technologies now commercially available in the European market, refiners nearly avoid generation and emission of these harmful pollutants. By moving these chemical treatments of the catalyst off-site, the refiner will also reduce the downtime of the units for regeneration and will shorten the start-up procedure.

In this paper, we evaluate the emissions during the in-situ regeneration of reforming catalyst and we define the benefits of ex-situ pre-activation of hydroprocessing catalyst by targeting environmental protection and reduced downtime.

INTRODUCTION

The refining industry recognizes its responsibilities in improving environmental performance. The task is not simple: Petroleum refining needs to stay competitive, while contributing to the global promise to make the planet a cleaner and better place to live.

If industrial practice in Europe remains unchanged, the 2012 target set by the Kyoto protocol to lower the overall emission of greenhouse gases to 7% below 1990 levels, will not be achieved. Refineries contribute 2.5 % of EU greenhouse emissions with
100 Mtons of CO$_2$ emitted. According to the Green Paper issued by the European Commission, petroleum refining belongs to the selected industries that can participate in EU-wide emission trading between industrial sectors. However, the problem of greenhouse emissions for refineries is not easy to solve. Refiners have been forced to produce fuels with tighter environmental specifications, which require new, energy-consuming processes, to produce these clean fuels.

How can refineries cope with the pressures coming from both sides, continue to be profitable, while keeping the environment clean? Perhaps looking outside the refinery fence can help.

Petroleum refining uses the crude oil as a raw material, and converts it into commercial products. However, the conversion level is not 100%. Some portion of the crude oil is used as an internal fuel to supply the heat for the processes, while a very small portion enters the waste stream. The refinery is under increasingly stringent regulations to ensure that this waste is processed in an environmentally sound manner to avoid pollution of the air, ground or water. In order to protect their workers and the environment, refiners employ numerous treatments to make these emissions and discharges streams less harmful before leaving the refinery. These treatments do not come cheap.

Post-treatments for pollution reduction at the refinery are not always the best answers for pollution reduction. In many cases, pre-treatment is the more complete answer to the problem of pollution. Pre-treatment works on prevention, rather than dealing with consequences. Some of pre-treatments are undertaken outside the refinery, at specialized locations. These facilities handle by-products, emissions and other kinds of waste routinely and efficiently, resulting in less pollution.

Catalysts are an essential part of dozens of refining processes. Manufactured at outside facilities, fresh catalysts are shipped to the refiner’s site without threat to the refinery’s environment. However, the changes that catalysts undergo during their use in petroleum processes require periodic chemical treatments to maintain or restore their ability to perform.

Hydroprocessing catalysts have been present in the industry since before World War II, with the objective of removing the sulfur and nitrogen species from fuels. The volumes of HDS catalysts employed at the refineries have been continually increasing, due to more stringent fuel specifications. Hydroprocessing catalysts lose their activity with time, and their relatively high costs drive refiners to use them in repeated cycles by intermittently restoring the major part of their activity.

Historically, catalyst activity was restored by in-situ regeneration and in-situ sulfiding. “In-situ” indicates that both chemical treatments were performed in the user’s reactor. Fuel oil or fuel gas was burned to supply the heat needed for both regeneration and sulfiding. Regeneration removes coke and reversible poisons like sulfur and nitrogen by oxidizing them into gaseous CO, CO$_2$, SO$_x$ and NO$_x$. Sulfiding converts the metal oxides impregnated onto the catalyst support into the corresponding metal sulfides, which is their active form. Sulfiding forms H$_2$S, which can enter the process water as a reaction by-product. Acidic gas streams, as well as water containing dissolved hydrogen sulfide, are removed from the reactor system during or after sulfiding. H$_2$S,
CO, SO\textsubscript{x} and NO\textsubscript{x} are hazardous materials and the quantities emitted into the air from the refinery are subjected to local regulation.

**CATALYST REGENERATION**

**In-situ method**

During the operating cycle, hydroprocessing catalyst accumulates coke. The coke is a condensed compound of carbon and hydrogen with carbon content much higher than in organic species originally present in crude oil. Sulfur and nitrogen compounds are also accumulated on catalyst surface in the coke. Eventually, the accumulation of these compounds results in intolerably high losses in catalyst activity. Coke, sulfur and nitrogen can be removed by oxidative regeneration, resulting in nearly complete activity recovery. At temperatures as high as 400°C, oxygen reacts with carbon, sulfur and nitrogen forming CO, CO\textsubscript{2}, SO\textsubscript{x}, NO\textsubscript{x}. These gases are either purged to the atmosphere or neutralized in close loop. Neutralization is a demanding and time-consuming process; requiring injection systems, trained operators and time. Years ago, it was an unspoken secret to perform regenerations at night, when the emissions were more difficult to notice.

The quantities of pollutants emitted are not difficult to estimate. Spent HDS catalysts have on average about 10 wt% carbon accumulated on the surface and in its pores. In-situ regeneration reduces the carbon level down to 2-3 wt%. A similar calculation can be applied to determine sulfur emissions. The average content on spent catalyst is typically around 6 wt%. If in-situ regeneration reduces sulfur to 2%, 80 tons of HDS catalyst will release 3.2 tons of sulfur upon regeneration. If we assume all of the sulfur is converted to SO\textsubscript{2}, then 6.4 tons of SO\textsubscript{2} are discharged.

Of course, catalysts quantities employed can be much higher, and so can the coke and sulfur content on the used catalyst. In fact, as fuel regulations become stricter, both the catalyst quantities employed and the contamination level on spent catalysts tend to increase.

In addition to the pollution concerns, unit downtime is a big concern during in-situ regeneration. In-situ regeneration is generally quite time-consuming and frequently becomes the rate-determining step for unit shutdown. In addition, the catalyst may need to be dumped after regeneration to perform reactor maintenance or to screen the catalyst to remove fines. However, in situ regeneration frequently gives poor activity recovery due to uneven gas flow. Often, portions of the bed go unregenerated, while others are exposed to excessive regeneration temperatures. For these reasons, refineries in most of the world (except for remote regions) have largely abandoned the practice of in-situ regeneration of hydroprocessing catalysts.

**Case study 1: Regeneration of standard noble metal reformer catalyst**

As just noted, in-situ regeneration of hydroprocessing catalysts has largely disappeared from modern refinery practices. However, refiners continue to regenerate reforming catalyst in-situ. While the emissions of oxides of sulfur and nitrogen are minimal during regeneration of these catalysts, many other issues associated with in-situ regeneration are illustrated in this case study.
In this example, the coke combustion phase of the regeneration of 50 tons of Pt/Re catalyst lasted for 6 days. Coke was oxidized into CO$_2$. Figure 1 shows the quantities of coke burned in the 3 reactors. Total coke burned from the catalyst was 7400 kg.

![Figure 1: Coke burnt in the reactors](image1)

Caustic soda was injected during regeneration primarily for neutralization of chlorides. Caustic will also partly neutralized acid gases like CO, CO$_2$ and SO$_2$. However, the long-term evaluation of the purge flows proved that only 10-20% of CO and CO$_2$ is neutralized by soda wash. HP separator outlet data showed levels of CO$_2$ present in the recycle gas (Figure 2).

![Figure 2: CO$_2$ in recycle gas](image2)

The difference between formed CO$_2$ and recycled and neutralized CO$_2$ is sent to fuel gas system or simply released to the atmosphere. The same is done with CO and SO$_x$ formed. As noted earlier, the amount of sulfur and nitrogen deposited on reforming catalyst is small due to pre-treatment catalyst employed. However, there
are cases when NHT catalyst does not trap all the sulfur from the feed and some quantity deposits on reformer catalyst, causing its quick deactivation. In this case, the quantities of NO$_x$ and SO$_x$ emitted can be substantial.

The records of kilograms of CO$_2$ purged per hour are showed in Figure 3.

**Figure 3**

![Figure 3](image)

In addition to the CO$_2$ formed by coke burn off from the reformer catalyst; the environment is polluted by CO$_2$ created by burning the fossil fuels in the unit heaters that are supplying heat for the reaction. In a time when the refining industry is trying to cut CO$_2$ emissions, in-situ regeneration is certainly a step in opposite direction. As with any combustion process, it is impossible to avoid CO$_2$ emissions. However, redirecting the combustion (in this case, catalyst regeneration) to a process unit specifically designed for efficient operation will certainly reduce the overall emissions.

**Ex-situ method**

Both hydrotreating and reforming catalyst can be regenerated by removing coke from the catalyst surface using TRICAT’s patented ebullated bed technology. During regeneration via the TRICAT Regeneration Process, the chlorines, SO$_x$ and NO$_x$ formed upon regeneration are neutralized by caustic treatment. Due to large air excess in the ebullated bed, complete combustion is achieved forming CO$_2$ and no hazardous carbon monoxide.

Among the additional beneficial results one can expect by choosing ex-situ regeneration are:

- Carbon and sulfur content are reduced to below 1 wt% ensuring that fully regenerated catalyst is delivered to the refiner for the subsequent cycle.
- No air pollution with acid gases.
- No discharge of neutralization products and caustic to the water stream.
• Increased time available for reactor inspection and maintenance.

**CATALYST SULFIDING**

*In-situ sulfiding and presulfurized catalyst*

Hydroprocessing catalysts are typically manufactured and delivered with active metal in oxidic form (e.g., MoO$_3$). The metals need to be converted into sulfides (e.g., MoS$_2$) prior to use. Sulfiding (or more generally, activation) can be performed at refiner’s site or at a specialized external location.

When in-situ sulfiding is performed, oxidic catalyst is loaded into reactor and hydrogen is introduced to the reactor system. Heat-up of the unit follows according to the process unit or catalyst licensor’s procedure. At a specified temperature, an external source of sulfur is injected into reactor. This compound (e.g., dimethyl disulfide or DMDS) can be injected directly or along with a straight run feed. As the reactor temperature increases, the sulfur compound decomposes and forms H$_2$S. Hydrogen and hydrogen sulfide react with catalyst metal to convert the oxide into the corresponding sulfide. Water is formed as sulfiding reaction by-product. The reactions are exothermic and two or three temperature holds are needed to allow the heat wave to pass through the catalyst bed. H$_2$S is formed in vast excess and after sulfiding is completed, the excess of H$_2$S needs to be treated before release. Water is also formed, equal to 5-10% of catalyst weight, and is saturated with hydrogen sulfide. The water must be drained frequently from the high or low pressure separator. This sour water is a threat to the safety of operating staff and requires neutralization before discharge as well.

Traditionally, catalyst sulfiding has been performed in-situ by adding a sulfur compound to the circulating gas, or by doping a refinery stream with a sulfur compound and circulating it through the catalyst bed. Many sulfiding chemicals are toxic and volatile with vapor pressures of up to few hundred millibars at 20°C. For that reason, it is critical to minimize leakage of these compounds to the atmosphere. The flash point of DMDS (the most widely employed sulfiding agent) is 16°C, which categorizes this chemical as flammable. It must be stored and handled with special care. DMDS also has a strong irritating odor, which is readily detected throughout the area if spilled. Other sulfiding agents, including polysulfides such as TNPS and TPS-54, have particular appeal due to their low vapor pressure at ambient temperature. However, polysulfides tend to leave carbon deposits on the catalyst via thermal decomposition. During decomposition, unsaturated hydrocarbons are formed. These unsaturates are very reactive, and have a tendency to polymerize leading to undesirable gum formation on the highly active fresh catalyst.

Another important factor to consider during in-situ sulfiding is the possible reduction of the metal oxides to their base metal due to hydrogen exposure in the absence of H$_2$S at high temperature. This undesirable reaction irreversibly destroys the activity of the catalyst. As such, an excess of sulfur is injected to ensure that H$_2$S is not depleted from any portion of the reactor during sulfiding. However, poor distribution of the feed doped with sulfiding compound (or the direct addition of the sulfiding agent) can lead to partial deactivation of the catalyst bed.
In order to avoid the hazards of handling these sulfur compounds and to ensure that the sulfur gets well distributed throughout the catalyst bed, technology was developed over 30 years ago to avoid the need for sulfiding agents. This ex-situ technology is commonly called pre-sulfurizing. During ex-situ pre-sulfurizing, the catalyst is coated with a sulfur compound, avoiding the need for on-site sulfur injection. When loaded into reactor, during heat-up in hydrogen stream, \( \text{H}_2\text{S} \) is released from the pre-sulfurized catalyst by thermal decomposition of sulfur compound and then reacts with the catalyst metal oxides. However, the same chemical reactions occur in the user’s reactor as observed during in-situ sulfiding, and the same pollutants are formed. Again, \( \text{H}_2\text{S} \) is created in vast excess. Sour water is formed in the amount and needs to be drained with caution and neutralized.

**Ex-situ pre-activation**

A more recent technology is available that provides complete ex-situ catalyst sulfiding is catalyst ex-situ pre-activation. TRICAT’s patented method (called XpresS®) delivers catalyst to the user with the metals in their active form. Catalyst sulfiding reactions are performed at Tricat’s plant in Bitterfeld, Germany.

The benefits of employing XpresS® rather than in-situ sulfiding or pre-sulfurized catalysts include:

- Ex-situ pre-activated catalyst is homogeneously sulfided.
- Catalyst is stable and passivated so that it can be handled in air.
- The quantity of \( \text{H}_2\text{S} \) liberated from the catalyst when hydrogen is introduced is typically below 100 ppm in the reactor outlet stream.
- Negligible amounts of water are liberated from the catalyst upon start-up.
- Start-up of the unit is faster and vastly simplified.

The benefits of using pre-activated catalyst are illustrated further in the following examples.

**Case study 2: Diesel hydrotreater - In-situ sulfiding versus start-up with ex-situ pre-activated catalysts**

In this operation, a diesel hydrotreater typically performed liquid phase in-situ sulfiding of fresh catalysts with injection of DMDS to the liquid stream. Temperature records show three holds, following the procedure provided by the catalyst manufacturer (Figure 4). The first temperature hold allowed for the pre-wetting of catalyst bed. The second hold was maintained to allow thermal decomposition of DMDS and the initial sulfiding reactions. The third temperature hold was to finish sulfiding reactions. During the latter two holds, the pause in heating was needed to allow the temperature wave associated with the sulfiding reactions to pass through the reactor bed, and to avoid high temperature excursions in the catalyst bed.
By contrast, when the same unit was started with XpresS pre-activated catalyst, the temperature profile observed can be seen in Figure 5.

When compared to in-situ sulfiding, start-up with ex-situ pre-activated catalyst saved 20 hours. During in-situ sulfiding, 1520 liters of Dimethyl-disulfide (DMDS) were used to sulfide this small reactor filled with 8200 kg of catalyst. $\text{H}_2\text{S}$ produced by decomposition of DMDS was recycled, and bound to the catalyst. Approximately 600 liters of sour water was drained to waste water system for neutralization. $\text{H}_2\text{S}$ was produced in excess and when normal feed was introduced to the reactor, sour gas was released to the fuel gas system. This gas was burned in the process heaters or flair. As a result, 388 kg of $\text{SO}_2$ was emitted to the environment.
With pre-activated catalysts, the refinery enjoyed a much simpler, quicker and trouble-free start-up of their diesel unit. The operators completely avoided the use of sulfiding compounds. Because the catalyst was delivered in active sulfide form, catalyst metals were not in a danger of reduction at any point during start-up. Relative to the procedure supplied by the catalyst vendor for start-up with pre-sulfurized catalysts, 20 hours of temperature holds were saved by employing pre-activated catalyst.

In addition, hydrogen sulfide and acidic water formation were minimized, reducing impact on the environment.

**CASE STUDY 3: Mild Hydrocracker - Start-up with pre-sulfurized catalyst versus start-up with ex-situ pre-activated catalyst**

A mild hydrocracker (MHC) typically loaded ex-situ presulfurized catalyst into two reactors. The start-up timeline for this unit is presented in Figure 6.

Records of $\text{H}_2\text{S}$ formation during start-up were not kept; however, more than 10 tons of sour water containing $\text{H}_2\text{S}$ was drained from HP separator during heat-up. The water had to be drained frequently and carefully with safety precautions taken. The sour water was directed to wastewater system for neutralization.

During the most recent turnaround, the unit employed pre-activated catalyst. In this case less than 200 liters of sour water was drained (a 98% reduction!), and only few ppm $\text{H}_2\text{S}$ were detected in recycle gas. The refinery reported that about 20 hours were saved on unit start-up. The start-up temperature profile is shown in Figure 7. With economic uplift of 20 EUR/ton for this unit, and a daily throughput of 1600 tons, the direct savings due to the shorter start-up were 30,000 EUR.
In addition, the unit operators were spared from the necessity to treat 9800 liters of sour water. Although it is difficult to quantify this benefit, it is clear that it is of substantial value to the refinery in reducing the risk of pollution and injury.

**Figure 7**

![Graph showing catalyst bed temperature over time](image)

**CASE STUDY 4: Naphtha hydrotreater - Start-up with pre-sulfurized catalysts; records of acid gas purge and sour water drained**

In this case, a hydrotreating reactor was loaded with pre-sulfurized catalyst. Thermal decomposition of the sulfur compound impregnated onto the catalyst should have provided enough H₂S for conversion of catalyst metal oxides into corresponding sulfides.

Upon heat-up, negligible quantities of H₂S were detected in the recycle gas system, at the expected decomposition temperature. The refinery opted to introduce feed with high sulfur content to serve as a supplemental sulfur source for catalyst sulfiding. To achieve desulfurization, more hydrogen was needed. As make-up hydrogen was introduced, sour gas was released. Figure 8 shows the quantities of sour gas leaving the reactor system.
As per the requirements for pre-sulfurized catalysts, the amine scrubber was not put into service. As a result, this sour stream had to be purged without scrubbing. We can assume that H$_2$S was burned and released into environment in the form of SO$_2$.

In the meantime, substantial quantities of sour water containing dissolved H$_2$S were drained from the reactor system, as shown in Figure 9.

Start-up of this NHT unit with pre-sulfurized catalyst did not go by the book. Unexpectedly, the absence of H$_2$S, which was supposed to come off the presulfurized catalyst, led the refiner to decide to introduce feed sooner than expected. Fortunately, refiner had available straight run, high sulfur feed, which they
used as a sulfur source and they introduced it quick enough to avoid the risk of metals reduction. As noted earlier, reduction of catalyst metals can occur when at elevated temperature there is no H$_2$S present. Reduction can form lower valence metal oxide or metal itself and by that cause the irreversible damage on the catalyst.

In order to avoid any risk of damaging catalyst, ex-situ pre-activation will be chosen for the subsequent start-up of this unit. XpresS® technology will deliver stable, ready to use catalyst. No special care will be required for activation, as it is already done prior to delivery.

Due to the delay at NHT catalyst sulfiding, refiner also delayed production of reformate, high-octane component for gasoline blending. The use of pre-activated catalyst for the consequent cycle will shorten the NHT unit start-up and enable quicker restart of the highly profitable reforming unit.

**CONCLUSION**

In the modern refining world, the safety and environmental impact of a proposed change in operation is often at least as important as the financial impact of the action.

As refiners search for techniques to reduce emissions, it is clear that selecting ex-situ catalyst treatments is a big step in the right direction. This action provides environmental and safety benefits, along with a favorable return on investment. Catalysts sent for external regeneration and pre-activation are returned to the refinery as homogeneously treated and chemically stable materials with the guaranteed levels of pre-activated metals.

Concerns about emissions, water neutralization, unit operations and maintenance, as well as waste disposal are either eliminated or removed from the refinery site. In addition, while catalysts are away for treatment, vessels are available for inspection and maintenance. Time savings are obtained by reduced unit downtime and streamlined start-ups.

The refining industry has experienced significant changes in the past decade. Nowadays, refining projects tend to focus increasingly on safety, environmental protection, and energy consumption. Profitable operations must be targeted at the same time, as refiners strive to increase yields and efficiency. Under such demanding conditions, refiners are increasingly relying on catalyst treatments at off-site facilities, expressly designed to meet these objectives.

**References**

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