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White Paper

EnviroSOx enables full FCC operation through Turn Around

Applying BASF's EnviroSOx additive, the PKN ORLEN Płock refinery was able to maintain FCC flue gas SOx emissions below 800 mg/Nm^3 (@ 3 vol% O_2) during a planned hydrocracker turnaround, enabling the FCC to process non-hydrotreated feed without sacrificing throughput.

Introduction

PKN ORLEN operates the refineries in Płock (Poland), Kralupy (the Czech Republic) and Mazeikiu (Lithuania).

The Płock refinery has a Nelson complexity index of 9.5 and a capacity of 11.9 million tons per year of crude oil. PKN ORLEN's FCCU is an UOP "side-by-side" design plant of a nominal daily capacity of 4,578 tons per day.

During the planned turnaround of the hydrocracker, the FCC feed sulfur would increase from 0.5 wt% to 2.0 wt% requiring the need to control flue gas SOx emissions under 800 mg/Nm^3 @ 3 vol% O_2, the maximum allowed by the refinery.

EnviroSOx

BASF's EnviroSOx is the latest generation of environmental additives to control SOx emissions in FCC flue gas. By optimizing the combination of cerium oxide (CeO_2), magnesium oxide (MgO), and vanadium oxide (V_2O_5), BASF enhanced SOx pick up capacity in both full burn and partial burn regenerators while maintaining robust cycle stability and sulfur release. As a result, maximum SOx reduction is achieved with minimum dosage of additive.

EnviroSOx chemistry to pick up SOx and to regenerate MgO is depicted in *Figure 1*. It must be noted that only SO_3 will be picked up by MgO, therefore oxidation of SO_2 to SO_3 is one of the most important steps:

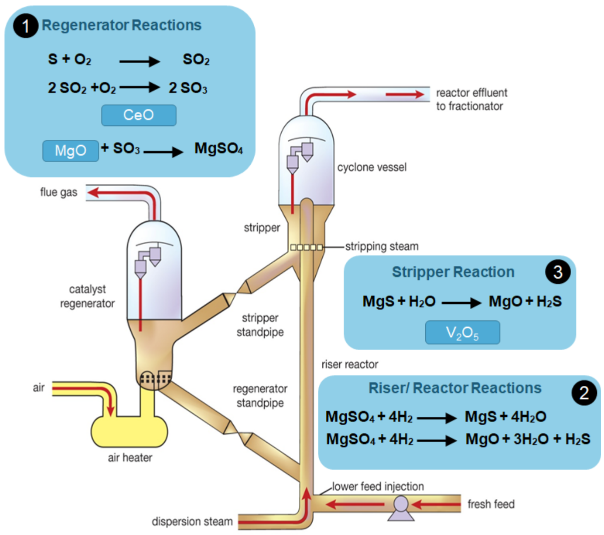

Fig.1 SOx pick up and MgO regeneration mechanism

Besides SO_2 oxidation and SO_3 pick up, the other important step is the MgO regeneration which, as shown in *Figure 1,* is accomplished in two sets of reactions: first in the riser reactor, and then in the stripper, where MgO regeneration is completed.

The performance of the additive to pick up SOx will depend on the operational conditions in the unit. It is influenced by the SOx partial pressure, catalyst circulation rate, regenerator temperature, stripper efficiency, and excess O_2. On the other hand, in partial burn operations, the CO_2/CO ratio will also be an important factor to drive the SOx removal effectiveness of the additive.

SOx Emissions control at Płock refinery

The base FCC Catalyst during the additive trial is BASF's Flex-Tech® Resid Catalyst. EnviroSOx additive was dosed separately into the FCC regenerator. Prior to the introduction there was no SOx reduction additive in the inventory.

To monitor the performance of the additive, a statistical model was calibrated using operation data collected three months prior to predict FCC SOx emissions. The model, developed with MINITAB (a statistical software package), demonstrated that refinery FCC SOx emissions correlate well with sulfur content in the feedstock, the feed rate, the regenerator temperature and O_2 content in flue gas. As there was no additive in use during the calibration period, the model output is considered as *uncontrolled SOx emissions* (*Figure 2*).

Emissions were regularly monitored by a flue gas analyzer, local refinery laboratory and by third party laboratory flue gas analysis. The online measurements were made locally (2-3 times/day) using a BASF supplied instrument corrected to a specified excess oxygen. Third party laboratory measurements were organized by refinery.

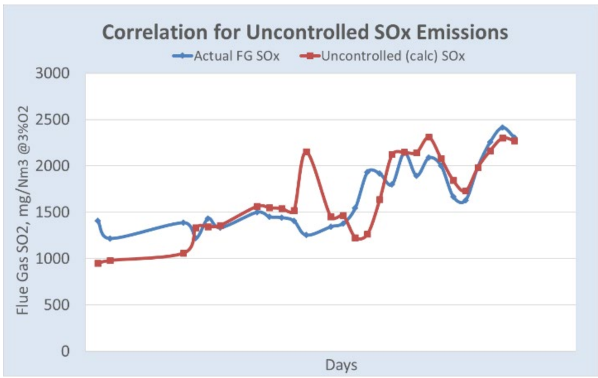

Fig.2 Comparison of statistical model and actual SOx emissions

Figure 3 illustrates the performance of EnviroSOx. Comparing the *actual* and *uncontrolled SOx* values, the Pick-Up-Factor (PUF) was calculated to be between 40 and 50 kg of SOx removed per kg of additive.

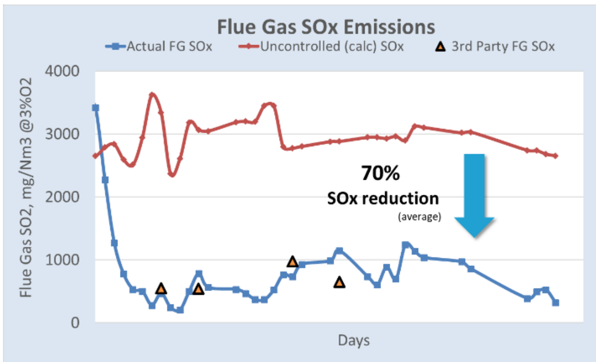

Fig.3 SOx emissions monitoring during EnviroSOx trial

The additive proved to be very effective in reducing PKN ORLEN Płock FCC Flue Gas SOx emissions below the target of 800 mg/Nm³ @ 3% O_2. Effectively reducing SOx emissions by 70 wt% enabled the refinery to operate within the emissions limit without having to interrupt the FCC operation.

Throughout the application of EnviroSOx FCC feed sulfur exceeded the anticipated concertation. In typical operations, without the additive, the refinery would respond by decreasing feed rate or switching feed sources (*Figure 4*).

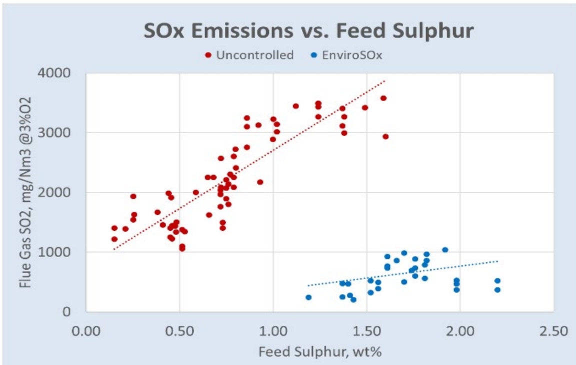

Fig.4 SOx emissions vs. Feed sulfur

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EnviroSOx demonstrated good retention

Another important property for SOx additives is the attrition resistance after multiple cycles of absorption and desorption. During the FCC process, MgO in the additive interacts with sulfur containing species to form magnesium sulfate ($MgSO_4$). This chemical interaction imparts physical stress on the additive particle. In subsequent steps, MgO is regenerated, continuing the stress profile. Repetitive cycles as such can cause additive particle fracture and degrade the attrition resistance over time. Excessive degradation can cause severe loss of SOx additive from the circulating catalyst inventory and reduced SOx control performance. [1]

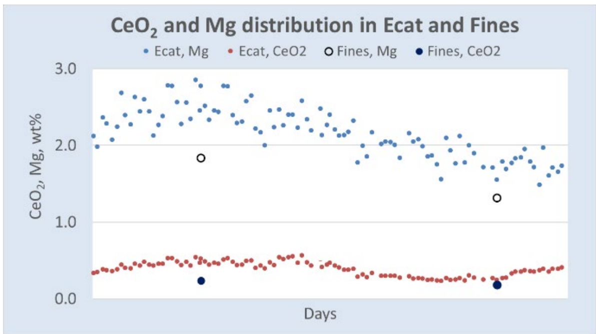

Fig.5 Distribution of CeO_2 and Mg

A key improvement offered by EnviroSOx is its stability. The optimization of components delivers a higher attrition resistance of EnviroSOx resulting in minimum losses. In *Figure 5*, the composition of Ecat and Fines are compared. Both, CeO_2 and Mg, were measured in Ecat and fines samples. The fines showed values that are below the Ecat ones, demonstrating there is no preferential loss of additive in the unit.

Conclusions

EnviroSOx delivered premium performance in controlling FCC SOx emissions at PKN Orlen Płock Refinery. The additive exhibited a PUF between 40-50 offering over 70 wt% SOx reduction compared to operation without the additive in the inventory.

By using BASF additive, PKN ORLEN Płock refinery was able to maintain FCC flue gas SOx emissions below 800 mg/Nm^3 (@ 3 vol% O_2) during a planned hydrocracker turnaround, allowing a continuous, safe and environmentally complaint operation.

References

[1] *Nanoporous materials forge a path forward to enable sustainable growth: Technology advancements in fluid catalytic cracking.* **M.Clough, J. C. Pope, L. TanXin Lin, V. Komvokis, S.Pan, B. Yilmaz.** December 2017, Microporous and Mesoporous Materials, Vol. 254, pp. 45-58.

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BASF-10654 Rev.10/19